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CONFIGURATION INTERACTION IN THE RARE EARTHS AND ITS EFFECT ON THE STARK LEVELS OF $PrCl_3$ AND $GdCl_3 \cdot 6H_2O$

Berkeley, California

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Katheryn Edmonds Rajnak

(Ph. D. Thesis)

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ABSTRACT

The techniques of Racah have been used to obtain expressions for the matrix elements of the Coulomb interaction between the configuration $4f^2$ and the excited configurations 4f6p and 4f5f, and between $4f^7$ and $4f^6 6p$. Approximate SCF radial wave functions were computed for Pr^{+3} and Tm^{+3} and used to calculate the necessary radial integrals. A second-order crystal field interaction between the configurations $4f^2$ and 4f5d was also considered. While these mechanisms lead to rather large shifts in some of the Stark levels of Pr^{+3} in $PrCl_3$, no one mechanism gives shifts large enough to explain the observed discrepancy between the experimental levels of the $^1D_2$ and those calculated by Margolis. The interaction of $4f^7$ with $4f^6 6p$ is not large enough to explain the splitting of the $^1P_{7/2}$ and $^6P_{5/2}$ levels of $GdCl_3 \cdot 6H_2O$ observed by Dieke and Leopold.

I. INTRODUCTION

Analysis of the optical spectra of rare earth ions has thus far been based on the assumption that the ground electronic configurations are pure $4f^n5s^25p^6$ and that the spectra arise from transitions within these configurations. While many people have recognized the limitations of such an approximation,[1-3] few attempts have been made to actually compute the perturbing effects of higher configurations. By including configuration interaction, Racah was able to fit the levels of nine configurations of Th III quite satisfactorily.[4] Judd has employed the interaction of $4f^65s^25p^6$ with $4f^65s^25p^56p$ to explain the anomalous quadrupole coupling in europium ethylsulfate.[5] Judd also found configuration interaction to be important in determining the optical absorption intensities of $NdCl_3$ and $ErCl_3$ solutions.[6] Wong has found that by considering the interaction of $4f^2$ with $5d^2$ the fit of the $PrCl_3$ spectra could be improved.[7] Lacroix concluded that interaction of $4f^7$ with $4f^66p$ or $4f^65f$ is too small to explain the observed splitting of the ^8S ground state of Gd^{+3} in cubic crystals,[8] but he gives no detailed calculations. The present work was undertaken to investigate the effect of configuration interaction on the crystal field levels of rare earth ions, with particular application to the $^1D_2$ level of $PrCl_3$ and the ^6P term of $GdCl_3 \cdot 6H_2O$.

The usual approximation is to consider that the rare earth ion is situated in a static electric field whose effect can be represented by several crystal field parameters $A_k^m\langle r^k\rangle$ that depend on the symmetry of the crystal and are determined to give the best fit to the experimental

spectrum.[9,10] With the exception of the $^1D_2$ level, Judd[11] found that this theory, with the inclusion of deviations from LS coupling, fitted the data of Sayre et al.[12] for $PrCl_3$ very well with the four parameters necessary for C_{3h} symmetry. The more recent calculation of Margolis, which includes in addition spin-spin and orbit-orbit interactions[2], fits about 40 levels of Sayre et al., and Dieke and Sarup,[3] except the $^1D_2$, with surprisingly little change in the crystal field parameters, and a standard deviation of 4 cm^{-1}. But the $^1D_2$ level exhibits a standard deviation of about 17 cm^{-1}. Since the calculations of Margolis include all possible effects within the configuration $4f^2$, some form of configuration interaction remains as the most likely explanation for this large discrepancy. The only other effect that has not been considered is the possibility of actual covalent bonding between the Pr^{+3} ion and other ions in the crystal. But it is difficult to explain why this should affect one level so much more strongly than the others.

In the case of $GdCl_3 \cdot 6H_2O$, a relatively large splitting is observed in the $^6P_{7/2}$ and $^6P_{5/2}$ levels.[14] But the crystal field matrix elements are zero for the sextet states of f^7 and there should be no first-order splitting. Judd has shown that the splitting cannot be explained by a combination of spin-orbit and the crystal field acting linearly.[15] Thus, part of the splitting must arise from second-order crystal field interactions between levels and/or from configuration interaction. The latter possibility is considered here.

The general matrix elements of the Coulomb interactions $Q = e^2/r_{ij}$ are derived in Sec. II. Sec. IV is devoted to obtaining the

necessary eigenfunctions for Pr^{+3} and Tm^{+3}. The remaining sections deal with specific applications to the Pr^{+3} and Gd^{+3} problems outlined above.

Higher configurations may be mixed into f^n by the Coulomb interaction between electrons, $Q = \sum_{i<j} e^2/r_{ij}$, where the sum runs over all electrons outside closed shells. Since S^2 and L^2 commute with Q, it connects only states of the same S and L in different configurations, and its matrix elements are independent of J. As a result of this interaction the state $|f^n\alpha SL\rangle$ becomes

$$|f^n\alpha SL\rangle - \sum_{\ell',\beta} \frac{(f^{n-1}\ell'\beta SL|Q|f^n\alpha SL)}{\Delta E} |f^{n-1}\ell'\beta SL\rangle . \quad (1)$$

This produces a shift in the crystal field levels which is different for different terms. Since Q also commutes with the parity operator, there will be interaction only between configurations of the same parity. In this case, a 4f electron may only be promoted to another state of odd parity, i.e., to a 6p or 5f (or some higher p or f) orbital. A two-electron excitation, an interaction between the configurations $4f^2$ and $5d^2$ for example, has been shown to be important in determining the positions of the centers of gravity of the multiplets[7]. However, since the one-electron crystal field operator has no nonzero matrix elements between such configurations, the effect on the crystal field levels would be second order in configuration interaction.

If the separation between configuration is much greater than the separation between terms within a configuration, ΔE is, to a first approximation, constant for all terms. For the same $|f^nSL\rangle$, if it may be assumed that ΔE and the radial integrals involved are only slightly altered in going from one crystal to another, the

Coulomb interaction should be nearly the same for all crystals. The shifts it causes in corresponding crystal field levels would then vary only as the crystal field parameters vary when the liqand is changed.

Alternatively, there may be a second-order crystal field interaction between terms of the configuration f^n and those of some higher configuration $f^{n-1}\ell'$. Such interactions produce a second-order depression in the crystal field levels of the form

$$\sum_{\ell'\beta} \frac{(f^n\alpha SLJJ_z|V|f^{n-1}\ell'\beta SLJJ_z)(f^{n-1}\ell'\beta SLJJ_z|V|f^n\alpha SLJJ_z)}{\Delta E},$$

where V is the crystal field potential, and ΔE is the energy separation between the interacting levels.

In Sec. II-B, general expressions for the matrix elements of Q between configurations f^n and $f^{n-1}\ell'$ will be considered. A full discussion of the crystal field interaction is deferred until Sec. III-C.

II. CONFIGURATION INTERACTION

A. Tensor Operators and Classification of States

1. Tensor Operators

The states of f^n may be specified by linear combinations of Slater determinants, and matrix elements between them calculated in a straightforward manner according to the methods given by Condon and Shortley.[16] However, this becomes extremely tedious for more than two or three f electrons. For such cases the tensor operator techniques introduced by Racah (hereafter referred to as II, III, and IV) can simplify the calculations a great deal.[17-19] The following is a brief survey of those results most frequently used in the calculations to follow.

An irreducible tensor operator of rank k is defined by Racah (II) as an operator $T^{(k)}$ whose 2k + 1 components $T^{(k)}_q (q = -k, -k+1, \ldots, k)$ satisfy the same commutation relations with the total angular momentum J as the spherical harmonics:

$$\left[(J_x \pm iJ_y),\ T^{(k)}_q\right] = \left[(k \mp q)(k \pm q + 1)\right]^{1/2} T^{(k)}_{q\pm 1}$$

and

$$\left[J_z,\ T^{(k)}_q\right] = qT^{(k)}_q .$$

For k = 1 we have

$$T^{(1)}_{\pm 1} = \frac{1}{\sqrt{2}}\ (T_x \pm iT_y), \qquad T^{(1)}_0 = T_z .$$

Thus it is easily seen that J is a tensor operator of rank 1 with components $J_\pm$, J_z. Another tensor operator that will appear often in the following sections is $C^{(k)}$ defined by

$$C_q^{(k)} = \left(\frac{4\pi}{2k+1}\right)^{\frac{1}{2}} Y_{kq} \,, \qquad (2)$$

where Y_{kq} is the usual spherical harmonic. In terms of tensor operators the Wigner-Eckart theorem becomes (II):

$$\left(\alpha jm \left| T_q^{(k)} \right| \alpha' j' m'\right) = (-1)^{j+m} \left(\alpha j \left\| T^{(k)} \right\| \alpha' j'\right) V(jj'k;-mm'q) \qquad (3)$$

where V is a form of the vector coupling coefficient. This relation determines the phases.

The scalar product of two irreducible tensor operators of the same rank is defined (II) as

$$\left(T^{(k)} \cdot U^{(k)}\right) = \sum_q (-1)^q T_q^{(k)} U_{-q}^{(k)} \,.$$

Matrix elements of the scalar product of two commuting tensor operators are given by

$$\left(\gamma j_1 j_2 jm \left| T^{(k)} \cdot U^{(k)} \right| \gamma' j_1' j_2' jm\right) = (-1)^{j_1+j_2'-j} \sum_{\gamma''} \left(\gamma j_1 \left\| T^{(k)} \right\| \gamma'' j_1'\right)$$

$$\times \left(\gamma'' j_2 \left\| U^{(k)} \right\| \gamma' j_2'\right) W\left(j_1 j_2 j_1'; jk\right) \,, \qquad (4)$$

where Racah's W coefficient is a summation over products of vector coupling coefficients.

2. <u>3-j and 6-j Symbols</u>

In the calculations that follow, the V and W coefficients above are always used in terms of the related 3-j and 6-j symbols of Wigner. The 3-j symbol is defined by[20]

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} \left(2j_3+1\right)^{-\frac{1}{2}} \left(j_1 m_1 j_2 m_2 \middle| j_1 j_2 j_3 -m_3\right),$$

where $\left(j_1 m_1 j_2 m_2 \middle| j_1 j_2 j_3 -m_3\right)$ is the usual Clebsch-Gordon coefficient.

Racah's V coefficient becomes[21]

$$V\left(j_1 j_2 j_3; m_1 m_2 m_3\right) = (-1)^{j_3+j_2-j_1} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} .$$

The symmetry properties of the 3-j symbol are given by Edmonds.[20] For the symbol to be nonzero, j_1, j_2, and j_3 must be able to form the sides of a triangle and $m_1 + m_2 + m_3$ must equal zero. Changing the signs of all the m's introduces the phase $(-1)^{j_1+j_2+j_3}$.

The 6-j symbol is given by[22]

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix} = (-1)^{j_1+j_2+\ell_1+\ell_2} W\left(j_1 j_2 j_3; \ell_1 \ell_2 \ell_3\right) .$$

Equations (3) and (4) may be written in terms of these quantities for future reference.[23,24]

$$\left(\gamma' j' m' \left| T^{(k)}_q \right| \gamma j m\right) = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \left(\gamma' j' \left\| T^{(k)} \right\| \gamma j\right) \qquad (5)$$

$$\left(\gamma' j_1' j_2' J' M' \left| T^{(k)} \cdot U^{(k)} \right| \gamma j_1 j_2 J M\right) = (-1)^{j_1+j_2'+J} \delta(J,J'),\ \delta(M,M') \begin{Bmatrix} J & j_2' & j_1' \\ k & j_1 & j_2 \end{Bmatrix}$$

$$\times \sum_{\gamma''} \left(\gamma' j_1' \left\| T(k) \right\| \gamma'' j_1\right) \left(\gamma'' j_2' \left\| U^{(k)} \right\| \gamma j_2\right) . \qquad (6)$$

It can also be shown that for a tensor operator operating only on part one of a coupled system,[24]

$$\left(\gamma' j_1' j_2 J' \left\| T^{(k)} \right\| \gamma j_1 j_2 J\right) = (-1)^{j_1'+j_2+J+k} \left[(2J+1)(2J'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} j_1' & J' & j_2 \\ J & j_1 & k \end{Bmatrix} \left(\gamma' j_1' \left\| T^{(k)} \right\| \gamma j_1\right) . \qquad (7)$$

Similarly, for a tensor operator operating only on part two of a coupled system[24]

$$\left(\gamma' j_1 j_2' J' \left\| U^{(k)} \right\| \gamma j_1 j_2 J\right) = (-1)^{j_1+j_2+J'+k} \left[(2J+1)(2J'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} j_2' & J' & j_1 \\ J & j_2 & k \end{Bmatrix} \left(\gamma' j_2' \| U^{(k)} \| \gamma j_2\right). \qquad (8)$$

Reduced matrix elements of $C^{(k)}$ may be written as[25]

$$\left(\ell' \| C^{(k)} \| \ell\right) = (-1)^{\ell'} \left[(2\ell+1)(2\ell'+1)\right]^{\frac{1}{2}} \begin{pmatrix} \ell' & k & \ell \\ 0 & 0 & 0 \end{pmatrix}. \qquad (9)$$

3. Classification of states of f^n

In the approximation of LS coupling, the states of the configuration f^n may be labled by the quantum numbers SLJ. For many terms of f^n, however, S and L do not unambiguously determine the state, i.e., there may be several distinct states with the same values of S and L. The simplest example[26] occurs in the configuration $s\ell\ell'$. For $\ell\ell'$=pd the s and p electrons may be coupled to ^3P or ^1P, both of which may then be coupled with a d electron to give two ^2D terms, sp(^3P)d ^2D and sp(^1P)d ^2D, which have different energies. However, for configurations f^n the number of different terms with the same S and L may be quite large. To deal with such situations, Racah (IV) considered a group theoretical classification of the states of f^n.

By considering the transformation properties of the states of f^n under the operations of R_7, the $(2\ell+1)$ dimensional rotation group for $\ell=3$, and one of its subgroups G_2, Racah defined two new quantum numbers, W and U. W labels the irreducible representations of R_7, and U the irreducible representations of G_2. W is a set of 3 integers, $W = (w_1 w_2 w_3)$, where $w_1 \geq w_2 \geq w_3 \geq 0$, and U is a set of two integers, $U = (u_1 u_2)$, with $u_1 \geq u_2 \geq 0$. The seniority number ν introduced earlier by Racah (III) is related to W. The quantum numbers $|f^n WUSL\rangle$

are sufficient to designate all the states of f^2, f^3, and f^4, and all terms of highest and next-to-highest multiplicity for higher configurations.[27]

A state $|\ell^n WUSL\rangle$ may be expanded in terms of products of states of the first n-1 particles with states of the nth particle (III)

$$\psi(f^n WUSL) = \sum_{\substack{W'U' \\ S'L'}} \psi\left(f^{n-1}(W'U'S'L')fSL\right)\left(f^{n-1}(W'U'S'L')fSL \Big\} f^n WUSL\right),$$

where $\left(f^{n-1}(W'U'S'L')\ fSL\Big\} f^n WUSL\right)$ is a coefficient of fractional parentage (c.f.p.). The properties of the c.f.p. have been discussed in detail by Racah (IV). They may be written as the product of three factors:

$$\left(f^{n-1}(W'U'\nu'S'L')\ fSL\Big\} f^n WU\nu SL\right)$$

$$= (UL + f\,|UL)(WU + f\,|WU)\left(f^{n-1}\nu'S' + f\Big\} f^n \nu S\right) \qquad (10)$$

The first two quantities are tablulated by Racah (IV) and formulae are given for computing the third.

B. <u>Matrix Elements $(f^n WUSL|Q|f^{n-1}(W'U'S'L')\ell'SL)$</u>

In atomic units where $e^2 = 1$, the electrostatic interaction between electrons is $Q = \sum_{i<j} 1/r_{ij}$. This may be expanded[28] to give

$$Q = \sum_{i<j} \sum_k \frac{r_<^k}{r_>^{k+1}} P_k(\cos \omega_{ij}),$$

where ω_{ij} is the angle between the radius vectors to the two electrons. But $P_k(\cos \omega_{ij})$ may be rewritten as (II):

$$P_k(\cos \omega_{ij}) = C_i^{(k)} \cdot C_j^{(k)} ,$$

where the $C_i^{(k)}$ are the operators defined in Eq. (2). The matrix

element to be evaluated then becomes

$$\left(f^n WUSL \middle| Q \middle| f^{n-1}(W'U'S'L')\ell' SL\right)$$

$$= \sum_k \left(f^n WUSL \middle| \sum_{i<j} \frac{r_<^k}{r_>^{k+1}} C_i^{(k)} \cdot C_j^{(k)} \middle| f^{n-1}(W'U'S'L')\ell' SL\right). \quad (11)$$

Due to the orthogonality of the f and ℓ' functions, the matrix element is zero whenever i and j are both among the first n-1 electrons. Thus the only nonzero terms will be those where either i or j is the nth electron. In this case the radial part of the integral becomes

$$\iint P(4f;r_i)\, P(4f;r_j)\, \frac{r_<^k}{r_>^{k+1}}\, P(4f;r_i)\, P(n'\ell';r_j)\, dr_i dr_j = R^k(4f4f,4fn'\ell'),$$

as defined by Condon and Shortley.[29]

The methods of Racah (III) may be used to evaluate the angular part of the matrix element,

$$\left(f^n WUSL \middle| \sum_{i<j} C_i^{(k)} \cdot C_j^{(k)} \middle| f^{n-1}(W'U'S'L')\, pSL\right).$$

The sum is

$$\sum_{i<j} C_i^{(k)} \cdot C_j^{(k)} = C_1^{(k)} \cdot C_2^{(k)} + C_1^{(k)} \cdot C_3^{(k)} + C_2^{(k)} \cdot C_3^{(k)}$$

$$+ C_1^{(k)} \cdot C_4^{(k)} + \ldots,$$

but

$$\left[\Sigma_i C_i^{(k)}\right]^2 = C_1^{(k)} \cdot C_1^{(k)} + C_1^{(k)} \cdot C_2^{(k)} + C_2^{(k)} \cdot C_1^{(k)} + C_2^{(k)} + C_2^{(k)} + \ldots;$$

thus,

$$\frac{1}{2}\left[\Sigma_i C_i^{(k)}\right]^2 - \Sigma_i C_i^{(k)2} = \sum_{i<j} C_i^{(k)} \cdot C_j^{(k)}.$$

Since $\left(C_i^{(k)}\right)^2$ is a scalar, its matrix elements will always be zero due to the orthogonality of the angular parts of f and ℓ', and

$$\left(f^n WUSL \middle| \sum_{i<j} C_i^{(k)} \cdot C_j^{(k)} \middle| f^{n-1}(W'U'S'L')\ell' SL\right)$$

$$= \frac{1}{2}\left(f^n WUSL \middle| \left[\sum_i C_i^{(k)}\right]^2 \middle| f^{n-1}(W'U'S'L')\ell' SL\right). \qquad (12)$$

But for $\ell' = 5f$ the angular parts are not orthogonal, and this method cannot be used without some modification. Consequently, from this point the derivation only holds for $\ell' = p$.

For the case of $n'\ell' = n'\ell$ the matrix elements of $\sum_i C_i^{(k)} \cdot C_i^{(k)}$ must be subtracted. The formulas given below hold for $\ell = \ell'$ if

$$\left(\ell^n WUSL \middle| \sum_i C_i^{(k)} \cdot C_i^{(k)} \middle| \ell^{n-1}(W'U'S'L')\ell' SL\right)$$

$$= \sqrt{2}\left(\ell^n WUSL \left\{ \middle| \ell^{n-1}(W'U'S'L') + \ell\right)\left(\ell \| C^{(k)} \| \ell'\right)^2 \frac{\delta(\ell,\ell')}{(2\ell+1)}$$

is subtracted from right-hand side of Eq. (12).

Using Racah's (33)II, we obtain

$$\left(f^n\ WUSL \middle| \sum_{i<j} \left(C_i^{(k)} \cdot C_j^{(k)}\right) \middle| f^{n-1}(W'U'S'L')p\ SL\right)$$

$$= \frac{1}{2(2L+1)} \sum_{\psi''} (-1)^{L-L''} \left(f^n WUSL \middle\| \sum_i C_i^{(k)} \middle\| f^n\ W''U''SL''\right)$$

$$\times \left(f^n\ W''U''SL'' \middle\| \sum_i C_i^{(k)} \middle\| f^{n-1}(W'U'S'L')p\ SL\right) + \sum_{\psi''} \sum_{L'''} (-1)^{L-L'''}$$

$$\times \left(f^n WUSL \middle\| \sum_i C_i^{(k)} \middle\| f^{n-1}(W''U''S''L'')\ pSL'''\right)$$

$$\times \left(f^{n-1}(W''U''S''L'')p\ SL''' \middle\| \sum_i C_i^{(k)} \middle\| f^{n-1}(W'U'S'L')p\ SL\right),$$

where ψ'' denotes the quantum numbers $W''U''S''L''$.

Putting

$$\left(f^n WUSL \left\| \sum_i C_i^{(k)} \right\| f^n W''U''SL''\right) = A,$$

$$\left(f^n W''U''SL'' \left\| \sum_i C_i^{(k)} \right\| f^{n-1}(W'U'S'L')\ pSL\right) = B,$$

$$\left(f^n WUSL \left\| \sum_i C_i^{(k)} \right\| f^{n-1}(W''U''S''L'')\ pSL'''\right) = C,$$

$$\left(f^{n-1}(W''U''S''L'')p\ SL''' \left\| \sum_i C_i^{(k)} \right\| f^{n-1}(W'U'S'L')pSL\right) = D$$

gives

$$\left(f^n WUSL \left| \sum_{i<j} C_i^{(k)} \cdot C_j^{(k)} \right| f^{n-1}(W'U'S'L')pSL\right)$$

$$= \frac{1}{2(2L+1)} \left[\sum_{\psi''} (-1)^{L-L''} A \cdot B + \sum_{\psi''} \sum_{L'''} (-1)^{L-L'''} C \cdot D \right] . \quad (13)$$

These matrix elements will be considered one at a time.

To evaluate A, first note (23)III of Racah where, for $F = \Sigma_i f_i$,

$$\left(\ell^n \alpha SLM_S M_L \middle| F \middle| \ell^n \alpha' S'L'M'_S M'_L\right) = n \sum_{\alpha_1 S_1 L_1} \left(\ell^n \alpha SL \left\{ \middle| \ell^{n-1}(\alpha_1 S_1 L_1)\ell SL\right)\right.$$

$$\times \left(S_1 L_1 \ell_n SLM_S M_L \middle| f_n \middle| S_1 L_1 \ell_n SL'M'_S M'_L\right) \left.\left(\ell^{n-1}(\alpha_1 S_1 L_1)\ell S'L' \middle| \right\} \ell^n \alpha' S'L'\right) .$$

This merely states that if the first (n-1) electrons are recoupled to the same $|\ell^{n-1}(\alpha_1 S_1 L_1)\rangle$, the matrix element of the sum is just n times the matrix element for the nth electron. Thus we obtain

$$A = \left(f^n WUSL \| \Sigma_i C_i^{(k)} \| f^n W''U''S''L''\right) = n\Sigma_{\psi_1}\left(f^n WUSL \{ | f^{n-1}(\psi_1) fSL\right)$$

$$\times \left(S_1L_1fSL \| C_n^{(k)} \| S_1L_1fSL''\right)\left(f^n W''U''S''L'' \{ | f^{n-1}(\psi_1) fS''L''\right). \quad (14)$$

$C_n^{(k)}$ is now a tensor operator of rank k operating on the second part of a coupled system. Applying (8) with

$$j_1 = L_1 \qquad j_2'' = j_2 = f \qquad J = L'' \qquad J' = L,$$

we have

$$\left(S_1L_1fSL \| C_n^{(k)} \| S_1L_1fSL''\right)$$

$$= (-1)^{L_1+3+L+k}\left[(2L+1)(2L''+1)\right]^{\frac{1}{2}}\begin{Bmatrix} 3 & L & L_1 \\ L'' & 3 & k \end{Bmatrix}\left(f \| C^{(k)} \| f\right). \quad (15)$$

Using Eq. (9), one obtains

$$\left(f \| C^{(k)} \| f\right) = 7(-1)^3 \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} . \qquad (16)$$

Combining Eqs. (14), (15), and (16), one has

$$A = \left(f^n WUSL \| \Sigma_i C_i^{(k)} \| f^n W''U''S''L''\right) = 7n\, \Sigma_{\psi_1}\left(f^n WUSL \{ | f^{n-1}(\psi_1)\, fSL\right)$$

$$\times \left(f^n W''U''S''L'' \{ | f^{n-1}(\psi_1) fS''L''\right)(-1)^{L_1+L+k}\left[(2L+1)(2L''+1)\right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} 3 & L & L_1 \\ L'' & 3 & k \end{Bmatrix} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \delta(S,S''). \qquad (17)$$

Now $B = \left(f^n W''U''S''L'' \| \Sigma_i C_i^{(k)} \| f^{n-1}(W'U'S'L')pSL\right)$. In an analogous manner, using (27)III, the first (n-1) electrons on the left may be recoupled indentically with those on the right, giving

$$B = \left(f^n W''U''S''L'' \| C^{(k)} \| f^{n-1}(W'U'S'L')pSL\right)$$

$$= \sqrt{2ln}\left(f^n W''U''S''L'' \{ | f^{n-1}(W'U'S'L')fS''L''\right)$$

$$x(-1)^{L'+L''+k}[(2L''+1)(2L+1)]^{\frac{1}{2}}\begin{Bmatrix} 3 & L'' & L' \\ L & 1 & k \end{Bmatrix}\begin{pmatrix} 3 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}. \quad (18)$$

Similarly, one has

$$C = \left(f^n WUSL \| C^{(k)} \| f^{n-1}(W''U''S''L'')pSL'''\right)$$
$$= \sqrt{2ln}\left(f^n WUSL \left\{ | f^{n-1}(W''U''S''L'')fSL \right)\right.$$
$$x(-1)^{L''+L+k}\sqrt{(2L+1)(2L'''+1)} \begin{Bmatrix} 3 & L & L'' \\ L''' & 1 & k \end{Bmatrix}\begin{pmatrix} 3 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}. \quad (19)$$

$$D = \left(f^{n-1}(W''U''S''L'')pSL'''\| \sum_i C_i^{(k)} \| f^{n-1}(W'U'S'L')pSL\right).$$

Here the sum on i may be divided into two parts, that acting only on the first (n-1) electrons and that acting on the nth. This gives

$$D = \left(f^{n-1}(W''U''S''L'')pSL'''\| \sum_{i=1}^{n-1} C_i^{(k)} \| f^{n-1}(W'U'S'L')pSL\right)$$
$$+ \left(f^{n-1}(W''U''S''L'')pSL'''\| C_n^{(k)} \| f^{n-1}(W'U'S'L')pSL\right)$$

The first term involves an operator operating only on part one of a coupled system and the second term one operating only on part two. Applying Eq. (7) and Eq. (8), one obtains

$$D = (-1)^{L''+1+L+k}[(2L+1)(2L'''+1)]^{\frac{1}{2}}\begin{Bmatrix} L'' & L''' & 1 \\ L & L' & k \end{Bmatrix}$$
$$x\left(f^{n-1}W''U''S''L''\| \sum_i C_i^{(k)} \| f^{n-1}W'U'S'L'\right)$$
$$+ \delta(\psi'',\psi')(-1)^{L'+1+L'''+k}[(2L'''+1)(2L+1)]^{\frac{1}{2}}\begin{Bmatrix} 1 & L''' & L \\ L & 1 & k \end{Bmatrix}(p\| C^{(k)} \| p). \quad (20)$$

The reduced matrix element in the first term can now be evaluated in the same manner as A, giving

$$D = \left(f^{n-1}(W''U''S''L'')pSL'''\Big\| \sum_i C_i^{(k)} \Big\| f^{n-1}(W'U'S'L')pSL\right)$$

$$= (n-1)^{L+3}\, 7[(2L+1)(2L'+1)(2L''+1)(2L'''+1)]^{\frac{1}{2}} \begin{Bmatrix} L'' & L''' & 1 \\ L & L' & k \end{Bmatrix}$$

$$\times \sum_{\psi_1} \left(f^{n-1}(\psi'')\Big\{\Big| f^{n-2}(\psi_1)fS''L''\right)\left(f^{n-1}(\psi')\Big\{\Big| f^{n-2}(\psi_1)fS'L'\right)$$

$$\times (-1)^{L_1} \begin{Bmatrix} 3 & L'' & L_1 \\ L' & 3 & k \end{Bmatrix} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}$$

$$+ \delta(\psi',\psi'')(-1)^{L'+L'''}\, 3[(2L'''+1)(2L+1)]^{\frac{1}{2}} \begin{Bmatrix} 1 & L''' & L' \\ L & 1 & k \end{Bmatrix} \begin{pmatrix} 1 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}. \quad (21)$$

All the matrix elements involve 3-j symbols of the form $\begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}$, where ℓ and ℓ' are both odd. The symmetry relations then allow only even values of k. The triangular conditions of $\begin{pmatrix} 3 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}$ allow only $k = 2$ and $k = 4$.

Even with only two allowed values of k, the summations involved in the above formulae may be quite tedious. Fortunately for f^2 and f^7, the cases to be considered, the formulae may be somewhat simplified. The specialized formulae for these configurations are considered in sections II-C and VI.

C. The Configuration $f^2(Pr^{+3})$

Two 4f electrons may be coupled to form ^1S, ^3P, ^1D, ^3F, ^1G, ^3H, and ^1I terms. The configuration fp, however, contains ^3G, ^3F, ^3D, ^1G, and ^1D. Since Q mixes only states of the same S and L in different configurations, the Coulomb interaction will be nonzero only for the ^1D, ^1G, and ^3F terms which are common to the two configurations. The configuration 4f5f, however, contains all the terms of $4f^2$ plus additional ones which are forbidden in $4f^2$ by the Pauli exclusion

principle. Thus configuration interaction between $4f^2$ and 4f5f will affect all of the terms of $4f^2$.

1. Special Formulae for f^2

After calculating the matrix elements of Q between $4f^2$ and 4f6p for several terms of f^2 it became apparent that the two summations in Eq. (13) were equal, i.e., for n = 2,

$$\sum_{\psi''}(-1)^{L-L''}\left(f^2SL\|C^{(k)}\|f^2S''L''\right)\left(f^2S''L''\|C^{(k)}\|f(S'L')pSL\right)$$
$$=\sum_{\psi'',\psi'''}(-1)^{L-L''}\left(f^2SL\|C^{(k)}\|f(S'''L''')pSL''\right)$$
$$\times\left(f(S'''L''')pSL''\|C^{(k)}\|f(S'L')pSL\right) .$$

It can be shown that this is generally true for interactions of the configuration ℓ^2 with $\ell\ell'$, and that the resulting expression for the matrix elements of Q is identical with that which would be obtained by using Eq. (6) (see Appendix A). Thus with either Eq. (11) and Eq. (6), or the results of Appendix A we obtain

$$\left(\ell^2SL|Q|\ell\ell'SL\right)=\Sigma_k\,(-1)^L\sqrt{2}\left(\ell\|C^{(k)}\|\ell'\right)\left(\ell\|C^{(k)}\|\ell\right)$$
$$\begin{Bmatrix}\ell' & L & \ell\\ \ell & k & \ell\end{Bmatrix}R^k(\ell\ell,\ell\ell'). \qquad (22)$$

The factor of $\sqrt{2}$ arises from the fact that the state $|\ell\ell'>$ must be written as $(1/\sqrt{2})(|\ell\ell'>+|\ell'\ell>)$, which gives two identical matrix elements or a factor of $2/\sqrt{2}=\sqrt{2}$ times the result computed from Eq. (6). The use of Racah's equations in Appendix A builds in this result automatically.

2. Calculation of $(f^2SL|Q|fpSL)$ and $(4f^2SL|Q|4f5fSL)$

If we put ℓ = f and ℓ' = p into Eq. (22), and make use of Eq. (9), the matrix elements become

$$\left(f^2SL|Q|fpSL\right) = \sum_k (-1)^L\, 7[2\cdot 3\cdot 7]^{\frac{1}{2}} \begin{pmatrix} 3 & k & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & L & 3 \\ 3 & k & 3 \end{Bmatrix}$$

$$\times\, R^k(4f4f;4f6p), \qquad (23)$$

where the allowed values of k are 2 and 4. With the values of the 3-j and 6-j symbols obtained from the tables of Rotenberg et al,[30] the matrix elements of Q were calculated for SL = ^1D, ^1G, and ^3F. The results are given in Table IA.

For ℓ = 4f and ℓ' = 5f, Eq. (22) becomes

$$\left(4f^2SL|Q|4f5fSL\right) = \sum_k (-1)^L\, 49\sqrt{2} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} 3 & L & 3 \\ 3 & k & 3 \end{Bmatrix} R^k(4f4f;4f5f). \qquad (24)$$

This expression was used to obtain the matrix elements given in Table IB for all terms of f^2. In this case there are nonzero terms for K = 6 as well as for k = 2 and k = 4.

The matrix elements in Table I all involve parameters $R^k(4f4f;4fnl)$. Unfortunately, one has no criteria for making even an educated guess as to their values. These could be left as parameters, and determined to give the best fit to the observed spectra; but, since adding more parameters usually improves the fit, such a method would not really determine whether either of these mechanisms is important in Pr^{+3} spectra. If, however, a "reasonable" estimate of the radial integrals can be obtained, it may allow determination of which mechanism, if any, is important. A least-squares fit to determine the best values of the relevent parameters could then be carried out. It was with this in mind that the calculation of 5f and 6p wave functions for Pr^{+3} was undertaken. The method of obtaining the wave functions is discussed

Table I. Matrix elements between f^2 and $f\ell'$.

A. $(f^2SL|Q|fp\ SL)$

Term	$(f^2SL\|Q\|fp\ SL)$
^1D	$\frac{-4\sqrt{6}}{25\sqrt{7}} R^2(4f4f;4f6p) - \frac{2\sqrt{6}}{9\sqrt{7}} R^4(4f4f;4f6p)$
^3F	$\frac{-6}{5\sqrt{21}} R^2(4f4f;4f6p) + \frac{2}{3\sqrt{21}} R^4(4f4f;4f6p)$
^1G	$\frac{-22}{5\sqrt{11\cdot 21}} R^2(4f4f;4f6p) - \frac{2}{3\sqrt{11\cdot 21}} R^4(4f4f;4f6p)$

B. $(4f^2SL|Q|4f5f\ SL)$

Term	$(4f^2SL\|Q\|4f5f\ SL)$
^3P	$\frac{\sqrt{2}}{5} R^2(4f4f;4f5f) + \frac{\sqrt{2}}{33} R^2(4f4f;4f5f) - \frac{25\sqrt{2}}{11\cdot 13} R^6(4f4f;4f5f)$
^1D	$\frac{19\sqrt{2}}{9\cdot 25} R^2(4f4f;4f5f) - \frac{\sqrt{2}}{11} R^4(4f4f;4f5f) + \frac{125\sqrt{2}}{99\cdot 13} R^6(4f4f;4f5f)$
^3F	$-\frac{2\sqrt{2}}{45} R^2(4f4f;4f5f) - \frac{\sqrt{2}}{33} R^4(4f4f;4f5f) - \frac{50\sqrt{2}}{99\cdot 13} R^6(4f4f;4f5f)$
^1G	$-\frac{2\sqrt{2}}{15} R^2(4f4f;4f5f) + \frac{97\sqrt{2}}{9\cdot 121} R^4(4f4f;4f5f) + \frac{50\sqrt{2}}{39\cdot 121} R^6(4f4f;4f5f)$
^3H	$-\frac{\sqrt{2}}{9} R^2(4f4f;4f5f) - \frac{17\sqrt{2}}{3\cdot 121} R^4(4f4f;4f5f) - \frac{25\sqrt{2}}{9\cdot 121\cdot 13} R^6(4f4f;4f5f)$
^1I	$\frac{\sqrt{2}}{9} R^2(4f4f;4f5f) + \frac{\sqrt{2}}{121} R^4(4f4f;4f5f) + \frac{25\sqrt{2}}{9\cdot 121\cdot 169} R^6(4f4f;4f5f)$

in detail in Sec. IV. In Sec. V the integrals obtained are combined with the present results.

III. THE CRYSTAL FIELD

A. Crystal Field Matrix Elements

1. Crystal Field Potential

When a rare-earth ion is placed in a crystal, the electrostatic field due to the anions removes some of the degeneracy of the free-ion J levels and causes them to be split. The extent of this splitting depends on the strength and the symmetry of the electric field. If a simple electrostatic model is used, the potential at the rare earth ion due to the crystal field may be expanded in a sum of spherical harmonics. For C_{3h} symmetry, where the cation is surrounded by 9 charges at distances ρ_1 and ρ_2 (see Fig. 1), the crystal field potential has been given by Stevens.[9]

$$V = A_2^0\, \Sigma(3z^2 - r^2) + A_4^0\, \Sigma(35z^4 - 30z^2r^2 + 3r^4)$$
$$+ A_6^0\, \Sigma(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6)$$
$$+ A_6^6\, \Sigma(x^6 - 15x^4y^2 + 15x^2y^4 - y^6),$$

where the summations are over the coordinates of all the electrons. The A_k^m are functions of the lattice, and in matrix elements of V they always appear multiplied by $< r^k >$ for a single f electron. The products $A_k^m < r^k >$ are known as crystal field parameters and are usually empirically determined to give the best fit to the observed spectrum. This use of empirical values of the crystal field parameters to some extent makes up for the fact that the point charge model is not correct. In rare earth crystal, $A_2^0 < r^2 >$ is usually much less than expected.[1,31] For $PrCl_3$, the $A_2^0 < r^2 >$ calculated by Wong[32] differs from

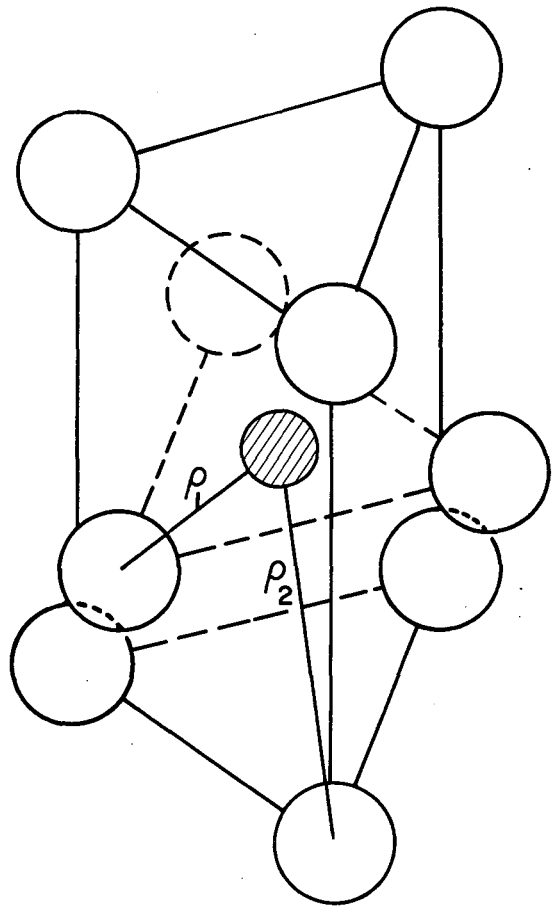

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Fig. 1. Structure of $PrCl_3$.

that determined empirically by Margolis[2] by a factor of 19:

	Wong (cm^{-1})	Margolis (cm^{-1})
$A_2^0 < r^2 >$	903	47.26
$A_4^0 < r^4 >$	-10.7	-40.58
$A_6^0 < r^6 >$	-120	-39.62*
$A_6^6 < r^6 >$	-107	402.72*

[* The crystal field parameters quoted in reference 2 (Margolis) are based on a different normalization than that used in this work. The sign of $A_6^0 < r^6 >$ has therefore been changed and $A_6^6 < r^6 >$ multiplied by 15.1 to account for Margolis' use of unnormalized vector coupling coefficients. See Reference 33.] This large discrepancy between the values of $A_2^0 < r^2 >$ arises from a screening of the 4f electrons by the outer shells of the Pr^{+3} ion, preventing them from feeling the full effect of the crystal field. This screening has been attributed[5] to the virtual cancellation of such matrix elements as $\left(4f^2\psi|V|4f^2\psi'\right)$ by second-order terms of the type

$$-\left(4f^2\psi|V|T\psi''\right)\left(T\psi''|Q|4f^2\psi'\right)/\Delta E_T ,$$

where T is an excited configuration.

2. Operator Equivalents

Stevens has shown that within a manifold of given J there is a simple relationship between the matrix elements of the crystal field potential and their operator equivalents which are functions of J and J_z

that transform according to the same irreducible representation of the rotation group. For example, the operator equivalent of $\Sigma(3z^2 - r^2)$ is $\left[3J_z^2 - J(J+1)\right]$, and the matrix elements of V_2^0 are connected to those of $\left[3J_z^2 - J(J+1)\right]$ by a proportionality constant α that must be determined for each $|f^n SLJ\rangle$ but which is independent of J_z within that manifold. Thus

$$(\psi_{JJ_z}|\Sigma(3z^2 - r^2)|\psi'_{JJ_z}) = \alpha < r^2 > \left[3J_z^2 - J(J+1)\right] \equiv \alpha < r^2 > f_1(J,J_z),$$

$$(\psi_{JJ_z}|\Sigma(35z^4 - 30r^2z^2 + 3r^4)|\psi'_{JJ_z}) = \beta < r^4 > \left[35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2\right] \equiv \beta < r^4 > f_2(J,J_z),$$

$$(\psi_{JJ_z}\Sigma(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6)|\psi'_{JJ_z}) = \gamma < r^6 > \left[231J_z^2 - 315J(J+1)J_z^4 + 735J_z^4 + 105J^2(J+1)^2J_z^2 - 525J(J+1)J_z^2 + 294J_z^2 - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1)\right] \equiv \gamma < r^6 > f_3(J,J_z),$$

and

$$(\psi_{JJ_z}|\Sigma(x^6 - 15x^4y^2 + 15x^2y^4 - y^6)|\psi'_{JJ'_z}) = \gamma < r^6 > \frac{1}{2}\left[J_+^6 + J_-^6\right] \equiv \gamma < r^6 > f_4(J,J_z),$$

where the operator-equivalent factors are related to reduced matrix elements of $C^{(k)}$ and are considered in greater detail in the next section. For the $^3H_4$, $^1G_4$, $^3F_4$, $^3F_3$, $^1D_2$, $^3P_2$ and $^3P_1$ states of Pr^{+3} they have been tabulated by Judd.[11] In the following sections, the operator equivalents will be used in the form $f_1(J,J_z)$, etc., simplify the notation. They have been tabulated for various values of J and J_z by Stevens[9] and Elliott and Stevens[34].

B. The Effect of Configuration Interaction on the Crystal Field Levels

1. Corrections to α, β, and γ

In the approximation of pure $4f^2$ configuration the matrix elements of V_2^0, the second-degree term in the crystal field potential, may be written as

$$\left(4f^2SLJJ_z\middle|V_2^0\middle|4f^2SLJJ_z\right) = \alpha A_2^0 < r^2 > f_1\left(J,J_z\right). \qquad (25)$$

If, however, there is configuration mixing between $4f^2$ and $4f\ell'$, the state $|f^2SLJJ_z>$ becomes

$$|SLJJ_z> = |4f^2SLJJ_z> - \frac{(4f\ell'SL|Q|4f^2SL)}{\Delta E}\,|4f\ell'SLJJ_z>$$

$$= |4f^2SLJJ_z> - a|4f\ell'SLJJ_z> .$$

In this case, Eq. (25) becomes

$$\left(SLJJ_z\middle|V_2^0\middle|SLJJ_z\right) = \left(4f^2SLJJ_z\middle|V_2^0\middle|4f^2SLJJ_z\right)$$

$$- 2a\left(4f^2SLJJ_z\middle|V_2^0\middle|4f\ell'SLJJ_z\right) + a^2\left(4f\ell'SLJJ_z\middle|V_2^0\middle|4f\ell'SLJJ_z\right). \qquad (26)$$

Neglecting the term in a^2 which is second-order in ΔE, we may write

$$\left(SLJJ_z\middle|V_2^0\middle|SLJJ_z\right) = \alpha_{ff}A_2^0 < r_{ff}^2 > f_1(J,J_z) - 2a\alpha_{f\ell'}\,A_2^0 < r_{f\ell'}^2 > f_1(J,J_z). \qquad (27)$$

The a^2 terms are considered in Appendix B. They involve integrals of the form $< r_{f'f'}^k >$ or $< r_{pp}^k >$ which are highly dependent on the exact form of the wave function used. If the free-ion 5f and 6p functions obtained in Sec. IV are assumed to hold in the chloride crystal, their maxima are very near the chloride nucleus. Thus, they cannot be expected to give reliable values of $< r_{f'f'}^k >$ or $< r_{pp}^k >$ in the crystal. If these 4f and 6p functions are used, however, the contributions from the a^2 terms are less than 10% of those from the terms that are first order in a, and their neglect is justified.

The matrix elements of V_2^0 in Eq. (27) may be arbitrarily set equal to $\alpha A_2^0 < r^2 > f_1(J,J_z)$, as in Eq. (25), and α reinterpreted in such a way that it takes into account the effects of configuration interaction. Thus α will no longer be α_{ff} but some weighted average of $\alpha_{f\ell'}$. If this is done and the A_2^0's are all assumed to be the same, we find

$$\alpha < r^2 > = \alpha_{ff} < r_{ff}^2 > - 2a\alpha_{f\ell'} < r_{f\ell'}^2 > .$$

Dividing by $\alpha_{ff} < r_{ff}^2 >$ gives

$$\frac{\alpha}{\alpha_{ff}} = 1-2a \frac{\alpha_{f\ell'}}{\alpha_{ff}} \frac{< r_{f\ell'}^2 >}{< r_{ff}^2 >} . \qquad (28)$$

If the ratio $< r_{f\ell'}^2 >/< r_{ff}^2 >$ can be determined, α/α_{ff} becomes a numerical factor such that if α_{ff} is multiplied by α/α_{ff} the experimental spectrum should be reproduced if the matrix elements of V_2^0 are written as

$$\left(SLJJ_z \middle| V_2^0 \middle| SLJJ_z\right) = \left(\frac{\alpha}{\alpha_{ff}}\right) \alpha_{ff} A_2^0 < r^2 > f_1(J,J_z),$$

where $A_2^0 < r^2 >$ is the usual crystal field parameter. In a similar manner the effects of configuration interaction on the fourth- and sixth-degree terms in V may be incorporated as corrections to β and γ.

The same method has been used by Judd to take into account deviations from LS coupling.[11] In that case, however, there are no approximations involved. The A_2^0's are all the same and $< r^2 >$ is always $< r_{ff}^2 >$. Since A_2^0 is a measure of the degree to which the electron involved is shielded from the crystal field (small A_2^0 gives a small splitting and therefore large shielding), the A_2^0 that measures the shielding of an inner 4f electron is not likely to be the same as that for an outer 5f or 6p electron. Thus, one would not be surprised if the results obtained from such as approximation were in the right direction, but too small, perhaps even by the factor of

19 discussed above, to explain the discrepancies between observed and calculated spectra. While such simple considerations hold for the effect on a single term in V, the actual situation is more complicated. V is a sum of four terms whose relative signs and magnitudes vary a great deal from one Stark level to another. Thus the effect of such as assumption must be considered separately for each level. This is taken up in detail when actual numerical results are obtained in Sec. V.

2. Calculation of Operator Equivalent Factors

As an example, consider the calculation of α_{fp}:

$$\left(f^2SLJJ_z\middle|V_2^0\middle|fpSLJJ_z\right) = \alpha_{fp}\, A_2^0 < r_{fp}^2 > f_1(J,J_z); \qquad (29)$$

but

$$V_2^0 = A_2^0 \sum_i \left(3z_i^2 - r_i^2\right),$$

and

$$\sum_i \left(3z_i^2 - r_i^2\right) = 2\sum_i r_i^2\, C_i^{(2)} . \qquad (30)$$

If we use Eq. (30) and the Wigner-Eckart theorem (5), Eq. (29) becomes

$$\left(f^2SLJJ_z\middle|V_2^0\middle|fpSLJJ_z\right) = 2\, A_2^0\, (-1)^{J-J_z}\begin{pmatrix} J & 2 & J \\ -J_z & 0 & J_z \end{pmatrix}\left(f^2SLJ\middle\|\sum_i C_i^{(2)}\middle\|fpSLJ\right). \qquad (31)$$

If part one of the coupled system is S, and part two is L, then $\Sigma_i C_i^{(2)}$ is an operator only on part two and Eq. (8) applies, leaving a reduced matrix element of the form $\left(f^2SL\middle\|\sum_i C_i^{(2)}\middle\|fpSL\right)$. For i = 1, this is zero due to the orthogononality of the f and p functions. For i = 2, Eq. (8) may be applied again, along with Eq. (9), giving

$$\left(f^2SLJJ_z\middle|V_2^0\middle|fpSLJJ_z\right) = 2\sqrt{2}\, A_2^0 < r_{fp}^2 > (-1)^{S-J_z+2J}$$

$$(2L+1)(2J+1)\begin{pmatrix} J & 2 & J \\ -J_z & 0 & J_z \end{pmatrix} \begin{Bmatrix} L & J & S \\ J & L & 2 \end{Bmatrix} \begin{Bmatrix} 3 & L & 3 \\ L & 1 & 2 \end{Bmatrix} \begin{pmatrix} 3 & 2 & 1 \\ 0 & 0 & 0 \end{pmatrix} . \qquad (32)$$

$\begin{pmatrix} J & 2 & J \\ -J_z & 0 & J_z \end{pmatrix}$ may be evaluated from the tables of Edmonds:[35]

$$\begin{pmatrix} J & 2 & J \\ -J_z & 0 & J_z \end{pmatrix} = 2(-1)^{J-J_z} \left[\frac{(2J-2)!}{(2J+3)!}\right]^{\frac{1}{2}} f_1(J,J_z) \qquad (33)$$

If Eq. (33) is substituted into Eq. (32), and the resulting expression set equal to $\alpha_{fp} A_2^0 < r_{fp}^2 > f_1(J,J_z)$, we obtain

$$\alpha_{fp} = 12\sqrt{\frac{2}{5}}\ (2L+1)(2J+1)(-1)^{S-J} \left[\frac{(2J-2)!}{(2J+3)!}\right]^{\frac{1}{2}} \begin{Bmatrix} L & J & S \\ J & L & 3 \end{Bmatrix} \begin{Bmatrix} 3 & L & 3 \\ L & 1 & 2 \end{Bmatrix} , \qquad (34)$$

where the 3-j symbol $\begin{pmatrix} 3 & 2 & 1 \\ 0 & 0 & 0 \end{pmatrix}$ has been evaluated. Similarly,

$$\beta_{fp} = \frac{32}{3}\sqrt{6}\ (2L+1)(2J+1)(-1)^{S+3-J} \left[\frac{(2J-4)!}{(2J+5)!}\right]^{\frac{1}{2}} \begin{Bmatrix} L & J & S \\ J & L & 4 \end{Bmatrix} \begin{Bmatrix} 3 & L & 3 \\ L & 1 & 4 \end{Bmatrix} , \qquad (35)$$

and γ_{fp} is zero.

In a similar manner, expressions for $\alpha_{ff'}$, $\beta_{ff'}$, $\gamma_{ff'}$ were derived:

$$\alpha_{ff'} = \frac{56\sqrt{2}}{\sqrt{7\cdot 15}}\ (2L+1)(2J+1)(-1)^{S+3+3J} \left[\frac{(2J-2)!}{(2J+3)!}\right] \begin{Bmatrix} L & J & S \\ J & L & 2 \end{Bmatrix} \begin{Bmatrix} 3 & L & 3 \\ L & 3 & 2 \end{Bmatrix} ,$$

$$\beta_{ff'} = \frac{16\cdot 14}{\sqrt{77}}\ (2L+1)(2J+1)(-1)^{S+3J} \left[\frac{(2J-4)!}{(2J+5)!}\right]^{\frac{1}{2}} \begin{Bmatrix} L & J & S \\ J & L & 4 \end{Bmatrix} \begin{Bmatrix} 3 & L & 3 \\ L & 3 & 4 \end{Bmatrix} , \qquad (36)$$

and

$$\gamma_{ff'} = \frac{16\cdot 280\sqrt{2}}{\sqrt{39\cdot 77}}\ (2L+1)(2J+1)(-1)^{S+3J+3} \left[\frac{(2J-6)!}{(2J+7)!}\right] \begin{Bmatrix} L & J & S \\ J & L & 6 \end{Bmatrix} \begin{Bmatrix} 3 & L & 3 \\ L & 3 & 6 \end{Bmatrix} .$$

The operator-equivalent factors calculated from the above expressions are given in Tables IIA and IIB. The $\alpha_{ff'}$, $\beta_{ff'}$, and γ_{ff} not given by Judd[11] were calculated in a similar manner.

Table IIA: Operator Equivalent Factors for $4f^2 \rightarrow 4f6p$

Level	α_{ff} [a]	α_{fp}	β_{ff} [a]	β_{fp}	γ_{ff} [a]	γ_{fp}
$^1D_2$	$\frac{22}{15 \cdot 21}$	$\frac{12\sqrt{2}}{35\sqrt{21}}$	$\frac{4}{7 \cdot 27}$	$\frac{2\sqrt{2}}{27 \cdot 7\sqrt{21}}$	0	0
$^3F_4$	$\frac{1}{126}$	$\frac{3}{28\sqrt{21}}$	$\frac{-1}{45 \cdot 77}$	$\frac{1}{7 \cdot 45\sqrt{21}}$	$\frac{1}{13 \cdot 63 \cdot 99}$	0
$^3F_3$	$\frac{1}{90}$	$\frac{3}{20\sqrt{21}}$	$\frac{-1}{45 \cdot 99}$	$\frac{1}{81 \cdot 5\sqrt{21}}$	$\frac{-1}{39 \cdot 99}$	0
$^3F_2$	$\frac{8}{21 \cdot 15}$	$\frac{12}{35\sqrt{21}}$	$\frac{-2}{7 \cdot 81}$	$\frac{22}{27 \cdot 21\sqrt{21}}$	0	0
$^1G_4$	$\frac{-2}{11 \cdot 35}$	$\frac{9}{35\sqrt{21 \cdot 11}}$	$\frac{-46}{11 \cdot 45 \cdot 77}$	$\frac{-2}{15 \cdot 7\sqrt{21 \cdot 11}}$	$\frac{-4}{13 \cdot 33 \cdot 77}$	0

[a] Except for $^3F_2$, these factors are from Judd (See reference 11).

Table IIB. Operator Equivalent Factors for $4f^2 \rightarrow 4f5f$

SLJ	α_{ff} [a]	$\alpha_{ff'}$	β_{ff} [a]	$\beta_{ff'}$	γ_{ff} [a]	$\gamma_{ff'}$
$^3P_2$	$\frac{1}{15}$	$\frac{1}{15\sqrt{2}}$	0	0	0	0
$^3P_1$	$\frac{-1}{5}$	$\frac{-1}{5\sqrt{2}}$	0	0	0	0
$^1D_2$	$\frac{22}{15\cdot 21}$	$\frac{22}{15\cdot 21\sqrt{2}}$	$\frac{4}{7\cdot 27}$	$\frac{4}{7\cdot 27\sqrt{2}}$	0	0
$^3F_4$	$\frac{1}{126}$	$\frac{1}{126\sqrt{2}}$	$\frac{-1}{45\cdot 77}$	$\frac{-1}{45\cdot 77\sqrt{2}}$	$\frac{1}{13\cdot 63\cdot 99}$	$\frac{1}{13\cdot 63\cdot 99\sqrt{2}}$
$^3F_3$	$\frac{1}{90}$	$\frac{1}{90\sqrt{2}}$	$\frac{-1}{45\cdot 99}$	$\frac{-1}{45\cdot 99\sqrt{2}}$	$\frac{-1}{39\cdot 99}$	$\frac{-1}{39\cdot 99\sqrt{2}}$
$^3F_2$	$\frac{8}{21\cdot 15}$	$\frac{8}{21\cdot 15\sqrt{2}}$	$\frac{-2}{7\cdot 81}$	$\frac{-2}{7\cdot 81\sqrt{2}}$	0	0
$^1G_4$	$\frac{-2}{11\cdot 35}$	$\frac{-2}{11\cdot 35\sqrt{2}}$	$\frac{-46}{11\cdot 45\cdot 77}$	$\frac{-46}{11\cdot 45\cdot 77\sqrt{2}}$	$\frac{-4}{13\cdot 33\cdot 77}$	$\frac{-4}{13\cdot 33\cdot 77\sqrt{2}}$
$^3H_6$	$\frac{-1}{99}$	$\frac{-1}{99\sqrt{2}}$	$\frac{-8}{45\cdot 9\cdot 121}$	$\frac{-8}{45\cdot 9\cdot 121\sqrt{2}}$	$\frac{5}{21\cdot 99\cdot 13\cdot 33}$	$\frac{5}{21\cdot 99\cdot 13\cdot 33\sqrt{2}}$
$^3H_5$	$\frac{-1}{75}$	$\frac{-1}{75\sqrt{2}}$	$\frac{-8}{63\cdot 15\cdot 33}$	$\frac{-8}{63\cdot 15\cdot 33\sqrt{2}}$	$\frac{1}{9\cdot 13\cdot 35\cdot 33}$	$\frac{1}{9\cdot 13\cdot 35\cdot 33\sqrt{2}}$
$^3H_4$	$\frac{-52}{25\cdot 99}$	$\frac{-52}{25\cdot 99\sqrt{2}}$	$\frac{-4}{55\cdot 99}$	$\frac{-4}{55\cdot 99\sqrt{2}}$	$\frac{16\cdot 17}{9\cdot 55\cdot 91\cdot 99}$	$\frac{16\cdot 17}{9\cdot 55\cdot 91\cdot 99\sqrt{2}}$
$^1I_6$	$\frac{-2}{99}$	$\frac{-2}{99\sqrt{2}}$	$\frac{4}{15\cdot 33\cdot 33}$	$\frac{4}{15\cdot 33\cdot 33\sqrt{2}}$	$\frac{-2}{63\cdot 99\cdot 11\cdot 13}$	$\frac{-2}{63\cdot 99\cdot 11\cdot 13\sqrt{2}}$

[a] Except for $^3F_2$, $^3H_3$, $^3H_6$, and $^1I_6$ these are taken from Judd (See reference 11).

C. Configuration Interaction Due to the Crystal Field

The Stark levels of the configuration $4f^2$ may also be shifted by a second-order crystal field interaction between $4f^2$ and some higher configuration. In this case, the excited configuration need no longer be of even parity and interaction with the lowest excited configuration 4f5d is possible. Because of the smaller energy denominator, this might be expected to be the largest of such interactions. The depression of the crystal field levels of $^1D_2$ due to such a mechanism is

$$\sum_{LJJ_z} \frac{\left(f^2\ {}^1D_2 J'_z \,|\, V \,|\, fd\,{}^1LJJ_z\right)^2}{\Delta E} \qquad (37)$$

Unfortunately, such a mechanism is not specific to the $^1D_2$. A similar interaction is also possible for all of the other states of f^2.

Since the coupling of an f to a d electron with a tensor operator of rank k always involves the 3-j symbol

$$\begin{pmatrix} 3 & k & 2 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{3+k+2} \begin{pmatrix} 3 & k & 2 \\ 0 & 0 & 0 \end{pmatrix} ,$$

k must be odd, i.e., only terms in V which have zero matrix elements in the configuration f^2 will contribute here. The symmetry of the crystal requires that $k \leqslant 6$. Since it involves $< r_{fd}^5 >$, V_5^3 is expected to make the largest contribution. A fifth-rank tensor will couple the $^1D_2$ of f^2 only to the $^1F_3$, $^1G_4$, and $^1H_5$ of fd, but it will couple the $^1G_4$ of f^2 with all of the singlets of fd. The triplet levels of f^2 may interact with many different levels of fd, 14 for the $^3H_4$. Due to the fact that the energy differences must be estimated the results are only approximate, and it was not felt that carrying out these computations would add anything to the general conclusions obtained from consideration

of the $^1D_2$ and $^1G_4$ levels. The effect of $|fd^3F>$, the lowest triplet in fd, on the levels of $^3H_4$ was computed, however. The resulting shifts in all components were less than 1 cm^{-1}.

The configuration fd has not yet been analyzed for Pr^{+3} but data are available for LaII[36] and CeIII[37]. In both cases the lowest term is ^1G. This may be coupled to both the $^1D_2$ and $^1G_4$ of f^2 by V_5^3 term in the crystal field potential. The other singlets in LaII are ^1D lying 2300 cm^{-1} above the ^1G, ^1F at 7900 cm^{-1}, ^1P at 11000 cm^{-1}, and ^1H at 12000 cm^{-1}. In the case of CeIII, the ^1P and ^1H terms are reversed and the total width of the configuration is about 3000 cm^{-1} larger. The LaII data was used in the following calculations. Taking the energy levels from the CeIII spectrum would change the results by less than 0.1 cm^{-1}.

The graph of Dieke et al. shows that the centers of gravity of the f^2 and fd configurations differ by about 55,000 cm^{-1}.[38] The energy difference between the 4f and 5d functions calculated in Sec. IV is 42,000 cm^{-1}. From their work on the free ion, Dieke et al. conclude that it is probable that the crystal field spectra of the configurations $4f^2$ can be observed to 50,000 cm^{-1}. Therefore, the energy difference of 55,000 cm^{-1} from Dieke was taken as the energy difference between the ground terms of the two configurations. The effect of a smaller ΔE is to increase the shifts arising from interaction with the lower levels of fd more than it does those arising from interaction with the higher levels. If ΔE is 45,000 cm^{-1}, the shifts calculated here are multiplied by factors of 1.4 to 1.2.

With these energy estimates, the crystal field interaction between the configurations f^2 and fd can now be computed, if the crystal field parameter $A_5^3 < r_{fd}^5 >$ is known. It is usual to determine this parameter

from the experimental spectrum. Here, however, in order to determine the importance of such a mechanism, we must obtain theoretically at least an estimate of its value. This is considered in the next section. In Section 2 below the angular part of the crystal field matrix elements necessary to describe this interaction is obtained.

1. Calculation of A_5^3

The potential seen by an electron of Pr^{+3} due to its surroundings may be written as

$$V = \sum_{i<j} q_j e^2 / r_{ij} .$$

Expanding $1/r_{ij}$, making the usual assumption that the magnitude of the electron radius vector $\vec{r}_i$, is always less than that of the radius vector to the external charge $\vec{\rho}_j$, and using the spherical harmonic addition theorem, this becomes

$$V = \sum_{ikm} q_j e^2 \frac{r_i^{\,k}}{\rho_j^{\,k+1}} \quad \frac{4\pi}{2k+1} \; Y^*_{km}(\alpha_j, \beta_j) \cdot Y_{km}(\theta_i, \Phi) .$$

In order to obtain a real potential the km^{th} term, V_k^m may be written as

$$V_k^m = \sum_i r_i^{\,k} A_k^m (Y_{km} + Y^*_{km}),$$

where

$$A_k^m = \left[a_{km}^2 + b_{km}^2 \right]^{\frac{1}{2}} ,$$

$$a_{km} = \left[\frac{(k-m)!}{(k+m)!} \right]^{\frac{1}{2}} \Sigma_j \frac{q_j e^2}{\rho_j^{\,k+1}} \quad P_k^m (\cos \alpha_j) \cos m\beta_j ,$$

and

$$b_{km} = \left[\frac{(k-m)!}{(k+m)!} \right]^{\frac{1}{2}} \Sigma_j \frac{q_j e^2}{\rho_j^{\,k+1}} \quad P_k^m (\cos \alpha_j) \sin m\beta_j .$$

Changing the Y_{km} to tensor operators, we get

$$V_5^3 = \Sigma_i \; r_i^5 \; A_5^3 \left(C_3^{(5)} + C_{-3}^{(5)} \right).$$

From the data given by Zachariasen[39] the structure of $PrCl_3$ may be calculated (see Fig. 1). If ρ_1 is the distance to the Cl^- ions in the central plane, and ρ_2 the distance to those above and below, and the corresponding angles with the vertical axis are α_1 and α_2,

$$\rho_1 = 2.966 \text{ Å} = 5.605 \text{ a.u.} \qquad \alpha_1 = 90^\circ,$$

and

$$\rho_2 = 2.989 \text{ Å} = 5.648 \text{ a.u.} \qquad \alpha_2 = 43^\circ 3' .$$

The distances agree with those given by Hutchison and Wong.[40] The upper and lower triangles are rotated from that in the plane by $57^\circ 39'$. This was rounded off to 60° in the following calculation. All the $q_j = -1$ and $e^2 = 1$ in a.u. Using these numbers, A_5^3 may be calculated:

$$A_5^3 = 0.1185 \times 10^{-3}.$$

Using the 4f and 5d eigenfunctions in Sec. IV, $< r_{fd}^5 >$ has been calculated by Judd:[6]

$$< r_{fd}^5 > = 50.5 \text{ a.u.}$$

This gives

$$A_5^3 < r_{fd}^5 > = 5.98 \times 10^{-3} \text{ a.u.} = 1310 \text{ cm}^{-1}. \qquad (38)$$

The matrix elements of V_5^3 now become

$$\left(f^2 SL'J'J_z' \middle| V_5^3 \middle| fdSLJJ_z \right) = 1310 \left(f^2 SL'J'J_z' \middle| C_3^{(5)} + C_{-3}^{(5)} \middle| fdSLJJ_z \right) . \qquad (39)$$

2. <u>Angular matrix elements of V_5^3</u>

Using Eq. (5), the matrix elements of V_5^3 become

$$\left(f^2 SL'J'J_z' \middle| V_5^3 \middle| fdSLJJ_z \right) = 1310 \, (-1)^{J' - J_z'} \left[\begin{pmatrix} J' & 5 & J \\ -J_z' & 3 & J_z \end{pmatrix} \right] + \left[\begin{pmatrix} J' & 5 & J \\ -J_z' & -3 & J_z \end{pmatrix} \right]$$
$$\times \left(f^2 SL'J' \| C^{(5)} \| fdSLJ \right).$$

By applying Eq. (8) twice and Eq. (9), we obtain

$$(f^2SL'J'\|C^{(5)}\|fdSLJ) = (-1)^{J'+L'+L}\left[2\cdot 35(2J+1)(2L+1)(2J'+1)(2L'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} L' & J' & S \\ J & L & 5 \end{Bmatrix} \begin{Bmatrix} 3 & L' & 3 \\ L & 2 & 5 \end{Bmatrix} \begin{pmatrix} 3 & 5 & 2 \\ 0 & 0 & 0 \end{pmatrix}.$$

This gives

$$(f^2SL'J'J'_z|V_5^3|fdLJJ_z) = 1310(-1)^{L'+L-J'_z}\left[(70(2J+1)(2L+1)(2J'+1)(2L'+1)\right]^{\frac{1}{2}}$$

$$\times \begin{Bmatrix} L' & J' & S \\ J & L & 5 \end{Bmatrix} \begin{Bmatrix} 3 & L' & 3 \\ L & 2 & 5 \end{Bmatrix} \begin{pmatrix} 3 & 5 & 2 \\ 0 & 0 & 0 \end{pmatrix} \left[\begin{pmatrix} J' & 5 & J \\ -J'_z & 3 & J_z \end{pmatrix}\right] + \left[\begin{pmatrix} J' & 5 & J \\ -J'_z & -3 & J_z \end{pmatrix}\right].$$

The matrix elements of $\left(C_3^{(5)} + C_{-3}^{(5)}\right)$ for all possible interactions of $^1D_2$ and $^1G_4$ with states of fd are given in Tables IIIA-H.

Table IV shows the shifts (without adjustment of the center of gravity) in the Stark levels of $^1D_2$ and $^1G_4$ arising from these various interactions. Figure 2 shows the levels computed by Margolis[2] without configuration interaction along with the present results, after adjustment of the center of gravity to agree with that of the experimental levels. The numbers in parentheses are the shifts necessary to bring the theory into agreement with experiment. The levels are labeled by Hellwege's crystal quantum numbers μ; $J_z = \mu (\mathrm{mod}\ 6)$. Due to the breakdown of LS coupling, none of the states are pure and the $^1G_4$ is highly mixed with the other $J = 4$ states. Using the intermediate coupling functions of Margolis (see Sec. V), the impurity of the $^1G_4$ has been taken into account (neglecting the effects due to the $^3H_4$ and $^3F_4$).

From the figure it can be seen that even if they were larger, the shifts of the $^1D_2$ levels are not in the right ratio to explain the observed discrepancy. In order to reproduce the observed spectrum the ± 1 levels must be pushed upwards while the 0 level is depressed. The total

Table IIIA. $(f^2\ {}^1D_2 J_z' \mid C_3^{(5)} + C_{-3}^{(5)} \mid fd\ {}^1G_4 J_z)$

J_z' \ J_z	∓ 1	∓ 2	± 3	± 4
0			$\frac{\pm 5\sqrt{2}}{11\sqrt{21}}$	
± 1		0		$\frac{\mp 5\sqrt{2}}{33\sqrt{7}}$
± 2	$\pm \frac{5}{33}$			

Table IIIB. $(f^2\ {}^1D_2 J_z' \mid C_3^{(5)} + C_{-3}^{(5)} \mid fd\ {}^1F_3 J_z)$

J_z' \ J_z	∓ 1	∓ 2	± 3
0			$\frac{\mp 5\sqrt{2}}{99\sqrt{7}}$
± 1		$\frac{\mp 10\sqrt{2}}{99\sqrt{7}}$	
± 2	$\frac{\pm 5\sqrt{5}}{99\sqrt{7}}$		

Table IIIC. $(f^2\ {}^1D_2\ J'_z \mid C_3^{(5)} + C_{-3}^{(5)} \mid fd\ {}^1H_5 J_z)$

J'_z \ J_z	∓ 1	∓ 2	± 3	± 4	± 5
0			$\frac{\pm 5}{99\sqrt{7}}$		
± 1		$\frac{\pm 50}{99\sqrt{7}}$		$\frac{\pm 35}{33\sqrt{21}}$	
± 2	$\frac{\pm 20}{99}$				$\frac{\mp 5\sqrt{10}}{33\sqrt{21}}$

Table III D. $(f^2\ {}^1G_4\ J'_z \mid C_3^{(5)} + C_{-3}^{(5)} \mid fd\ {}^1G_4\ J_z)$

J'_z \ J_z	0	∓ 1	∓ 2	± 3	± 4
0				$\frac{\mp 10}{33\sqrt{77}}$	
± 1			$\frac{\mp 10\sqrt{5}}{33\sqrt{22}}$		$\frac{\mp 20\sqrt{10}}{33\sqrt{77}}$
± 2		$\frac{\mp 10\sqrt{5}}{33\sqrt{22}}$			
± 3	$\frac{\pm 10}{33\sqrt{77}}$				
∓ 4		$\frac{\mp 20\sqrt{10}}{33\sqrt{77}}$			

Table IIIE. $(f^2\ {}^1G_4\ J_z' | C_3^{(5)} + C_{-3}^{(5)} | fd\ {}^1D_2\ J_z)$

J_z' \ J_z	0	∓ 1	∓ 2
± 1			$\dfrac{\pm 15}{11\sqrt{15\cdot 11}}$
± 2		0	
± 3	$\dfrac{\mp 15\sqrt{2}}{11\sqrt{5\cdot 77}}$		
∓ 4		$\dfrac{\mp 15\sqrt{2}}{11\sqrt{15\cdot 77}}$	

Table IIIF. $(f^2\ {}^1G_4\ J_z' | C_3^{(5)} + C_{-3}^{(5)} | fd\ {}^1P_1\ J_z)$

J_z' \ J_z	0	∓ 1
± 2		$\dfrac{\pm 4}{33\sqrt{11}}$
± 3	$\dfrac{\mp 8}{33\sqrt{77}}$	
∓ 4		$\dfrac{\mp 2}{33\sqrt{77}}$

Table IIIG. $(f^2\ {}^1G_4\ J_z' \,|C_3^{(5)} + C_{-3}^{(5)}|\ fd\ {}^1H_5\ J_z)$

J_z' \ J_z	0	∓ 1	∓ 2	± 3	± 4	± 5
0				$\frac{\pm 15\sqrt{2}}{11\sqrt{21\cdot 11}}$		
± 1			$\frac{\mp 5\sqrt{5}}{7\sqrt{77}}$		0	
± 2		0				$\frac{\mp 30}{11\sqrt{21\cdot 11}}$
± 3	$\frac{\pm 15\sqrt{2}}{11\sqrt{21\cdot 11}}$					
∓ 4		$\frac{\mp 5\sqrt{10}}{7\sqrt{77}}$				

Table IIIH. $(f^2\ {}^1G_4\ J_z' \,|\, C_3^{(5)} + C_{-3}^{(5)} \,|\, fd\ {}^1F_3\ J_z)$

J_z' \ J_z	0	∓ 1	∓ 2	± 3
0				$\dfrac{\mp 30}{7\sqrt{21\cdot 11}}$
± 1			$\dfrac{2\sqrt{5}}{7\sqrt{14\cdot 11}}$	
± 2		$\dfrac{\mp 18}{11\sqrt{14\cdot 11}}$		
± 3	$\dfrac{\mp 6}{11\sqrt{33}}$			
∓ 4		$\dfrac{\mp 4\sqrt{2}}{11\sqrt{11}}$		

Table IV. Shifts in $^1D_2$ and $^1G_4$ levels of f^2 arising from interaction with various levels of fd.

f^2 \ fd	^1P	^1D	^1F	^1G	^1H	Total
$^1D_2$ $J_z=\pm2$	-	-	-.1	-1.0	-1.8	-2.9
±1	-	-	-.1	- .3	-3.1	-3.5
0	-	-	-.0	-1.8	- .0	-1.8
$^1G_4$ $J_z=\pm4$	.0	-.1	-.8	-1.8	- .8	-3.5
±3	.0	-.4	-.3	- .0	- .5	-1.2
±2	.0	-	-.6	- .8	-1.0	-2.4
±1	-	-.4	-.0	-2.6	- .4	-3.4
0	-	-	-2.1	- .1	-1.0	-3.2

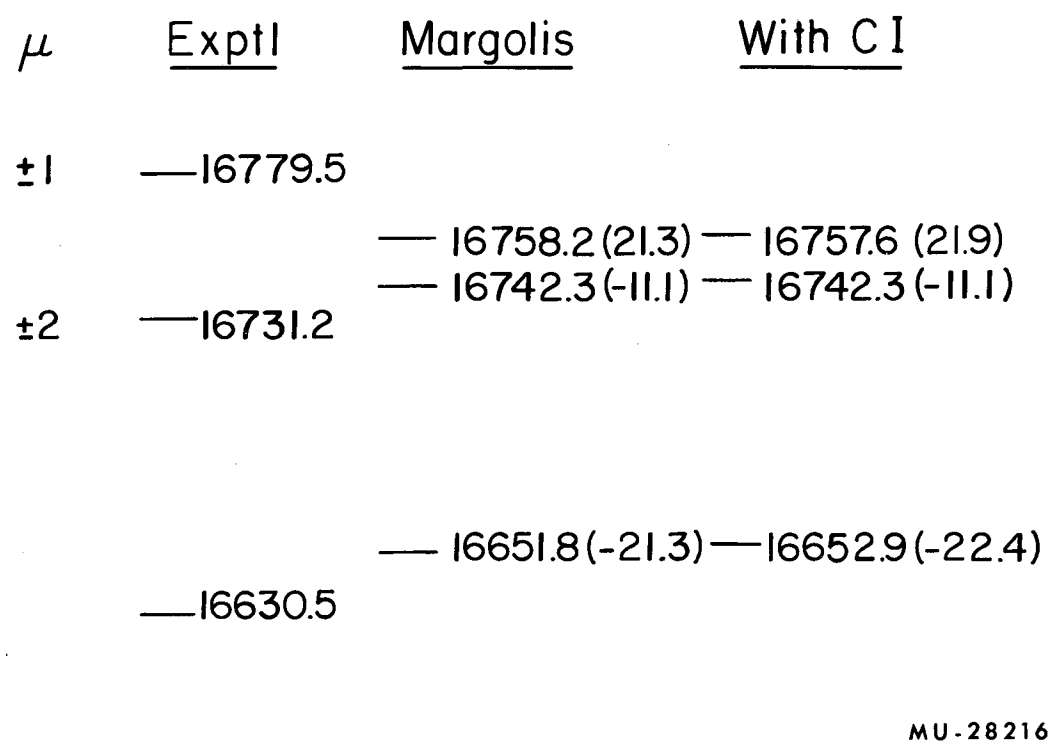

Fig. 2A. Levels of $^1D_2$ as a result of crystal field interaction with 4f5d.

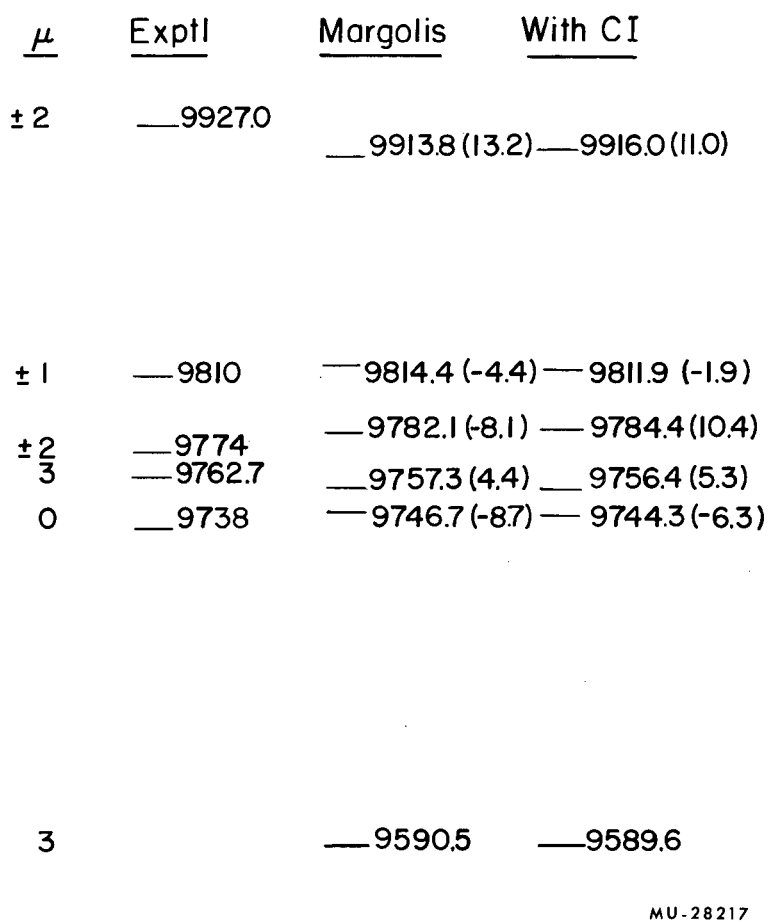

Fig. 2B. Levels of $^1G_4$ as a result of crystal field interaction with 4f5d.

interaction is in the opposite direction. The interaction of $|f^2\ {}^1D_2>$ with $|fd\ {}^1G_4>$ alone, however, comes closer to producing the correct ratios. (See Table IV). But the only way to reduce the contribution from interaction with ${}^1H_5$ is to assume that the ΔE used in that calculation was too small, i.e., that $|fd\ {}^1H_5>$ lies considerably higher in the fd configuration of Pr^{+3} than in LaII or CeIII. The effect of increasing this ΔE slightly, keeping the positions of the other levels fixed, is to make the shifts of all three components of ${}^1D_2$ more nearly equal and thereby reduce the measurable effect of this interaction. The fit of the ${}^1G_4$ levels is slightly improved by this mechanism.

The value of $A_5^3 < r_{fd}^5 >$ used in this calculation is also approximate. The $A_6^0 < r^6 >$ and $A_6^6 < r^6 >$ calculated by Wong [32] differ from those observed by Margolis[2] by nearly a factor of 4, but the calculated and observed ratios $A_6^0 < r^6 > / A_6^6 < r^6 >$ are nearly the same. This can be interpreted as an indication that the value of $< r^6 >$ computed from Ridley's free-ion 4f function[41] is too small by a factor of nearly 4. If such an effect arises from a simple outward scaling of the 4f function, as it seems to for the 3d function of Marshall and Stuart,[42] and if the 5d function is assumed to be affected in the same way in going from the free ion to the crystal, this would imply that the $< f_{fd}^5 >$ used in computing $A_5^3 < r_{fd}^5 >$ was too small by about a factor of 3. All of the computed shifts would then be increased by a factor of 9. If only the interaction with $|fd\ {}^1G_4 >$ is considered, a somewhat improved fit may be made to the ${}^1D_2$ levels, but it would also give absolutely unreasonable values for some of the shifts in ${}^1G_4$. Thus, one must conclude that while such a scaling may be applicable to the 4f function, the 5d function

must be changed in some more complex way and there is really no way to estimate the accuracy of the $A_5^3 < r_{fd}^5 >$ parameter used in this calculation. It is obvious, though, that any interaction of this type large enough to give appreciable improvement to the fit of the $^1D_2$ will also cause shifts of the same order of magnitude in the $^1G_4$ where the fit is already quite good. Thus a second-order crystal field interaction between configurations may contribute to crystal field splitting of $^1D_2$ but this mechanism alone cannot explain the observed discrepancy without greatly altering the already fairly good fit of the $^1G_4$ levels.

IV. APPROXIMATE EXCITED EIGENFUNCTIONS FOR Pr^{+3} AND Tm^{+3}

In this section, the greater part of which is taken from reference 43, the 5d, 6s, 6p and 5f radial wave functions that are necessary for any calculation of configuration interaction are obtained for Pr^{+3} and Tm^{+3}, these two ions being chosen because of the availability of ground state eigenfunctions from Ridley's SCF calculations.[41]

Since it was necessary to compute the effect of promoting one of the 4f electrons of Pr^{+3} to an excited orbital, the contribution of one of the 4f electrons was removed from the effective potential tabulated by Ridley. The resulting potential was treated as that of a core in whose field the excited electron moves, i.e., the 4f and excited electron were assumed to move in the same central field. The inner 4f and outer 5d, 6s, etc. electrons actually do see different fields, but the present functions are a good first approximation. They are certainly better than the presently available hydrogenic functions.

A. Calculations

In addition to the wave functions, Ridley's results include a tabulation of a total effective charge $Z_p(r)$ for the ion, and a contribution to Z from each shell of electrons. $Z_p(r)/r$ is the total potential at any point due to the nucleus and the average charge distribution of the electrons. For a single electron in a state of radial and angular momentum quantum numbers n and ℓ, the radial wave function is denoted by $P(n\ell;r)$, where $\int_0^\infty P^2(n\ell;r)\,dr = 1$. The effective charge due to one electron and one nuclear charge, $Z_p(n'\ell';r)$, i.e., the contribution to the total Z_p from a single electron, can be obtained from a differential

equation given by Ridley.[44]

$$Z_p(n'\ell';r) = 1 - \int_0^r P^2(n'\ell';r_1)dr_1 - r\int_r^\infty \frac{1}{r_1} P^2(n'\ell';r_1)\, dr_1$$

$$= Z(n\ell;r) - r\int_r^\infty \frac{1}{r_1} P^2(n'\ell';r_1)\, dr_1,$$

where $Z(n\ell;r)$ is defined[45] as $1 - \int_0^r P^2(n\ell;r)dr$. The total Z_p becomes[45]

$$Z_p(r) = \sum_{n'\ell'} q(n'\ell')Z_p(n'\ell';\, r) + i,$$

and the total effective potential is $- Z_p(r)/r$. The quantity $q(n'\ell')$ is the number of electrons in state $n'\ell'$, and i is the degree of ionization.

In terms of these quantities, the radial Schrödinger equation for an electron in a state $n\ell$ becomes[44]

$$\left\{ \frac{d^2}{dr^2} + \frac{2}{r}\left[1 + i + \sum_{n'\ell'} q(n'\ell')Z_p(n'\ell';r) - Z_p(n\ell;r)\right] + 2E - \frac{\ell(\ell+1)}{r^2} \right\}$$

$$\times\, P(n\ell;r) = 0, \qquad (40)$$

where the distances and energies are in atomic units. The potential is the total potential of the ion minus the contribution to the potential of the electron whose wave function is being calculated; in the present case a 4f electron,

$$V = Z_p(\text{total}) - (Z_p(n\ell;r) - 1).$$

$Z_p(n\ell;r)$ may be obtained from Ridley's tabulation as follows:

$$Z_p(n\ell;r) = Z(n\ell;r) - r\int_r^\infty \frac{1}{r_1} P^2(n\ell;r_1)\, dr_1$$

Making a change of variables in the integral to $\rho = \ln 1000r_1$ we get

$$Z_p(n\ell;r) = Z(n\ell;r) - r\int_r^\infty P^2(n\ell;\rho)d\rho.$$

$Z(n\ell;r)$ is tabulated by Ridley and the integral is easily evaluated numerically from her tabulated $P(n\ell;r)$.

For the present calculation the potential was assumed to be the same for all the states of interest, i.e., Eq. (40) becomes

$$\left\{\frac{d^2}{dr^2} + \frac{2}{r}\left[1 + i + \sum_{n'\ell'} q(n'\ell')\, Z_p(n'\ell';r) - Z_p\,(4f;r)\right] + 2E - \frac{\ell(\ell+1)}{r^2}\right\}$$

$$\times\, P(n\ell;r) = 0, \qquad (41)$$

where $n\ell$ = 4f, 5d, 6s, 6p, 5f. Equation (41) was solved on the IBM 7090 for both Pr^{+3} and Tm^{+3}. The resulting wave functions are shown in Figs. 3 and 4 and tabulated in Appendix C. Since $\langle r^2\rangle$, $\langle r^4\rangle$ and the R^k integral defined by Condon and Shortley[16]

$$R^k(n\ell,\ n\ell,\ n\ell\ n'\ell')$$

$$= \int_0^\infty\int_0^\infty \frac{r_<^k}{r_>^{k+1}}\, P^2(n\ell;r_1)\, P(n\ell;r_2)\, P(n'\ell';r_2)\, dr_1\, dr_2$$

are of interest in crystal field and configuration interaction calculations, these integrals are tabulated in Table V alone with the one-electron energies.

B. Discussion

Dieke *et al* have determined experimentally the centers of various excited configurations of doubly and triply ionized rare earths.[38] They found that for the doubly ionized atoms a plot of the center of the configuration, relative to the $4f^{n-1}6s$ taken as zero, vs atomic number, yields a straight line. Although experimental points are available only for Ce^{+3} and Yb^{+3}, they also draw straight lines on a

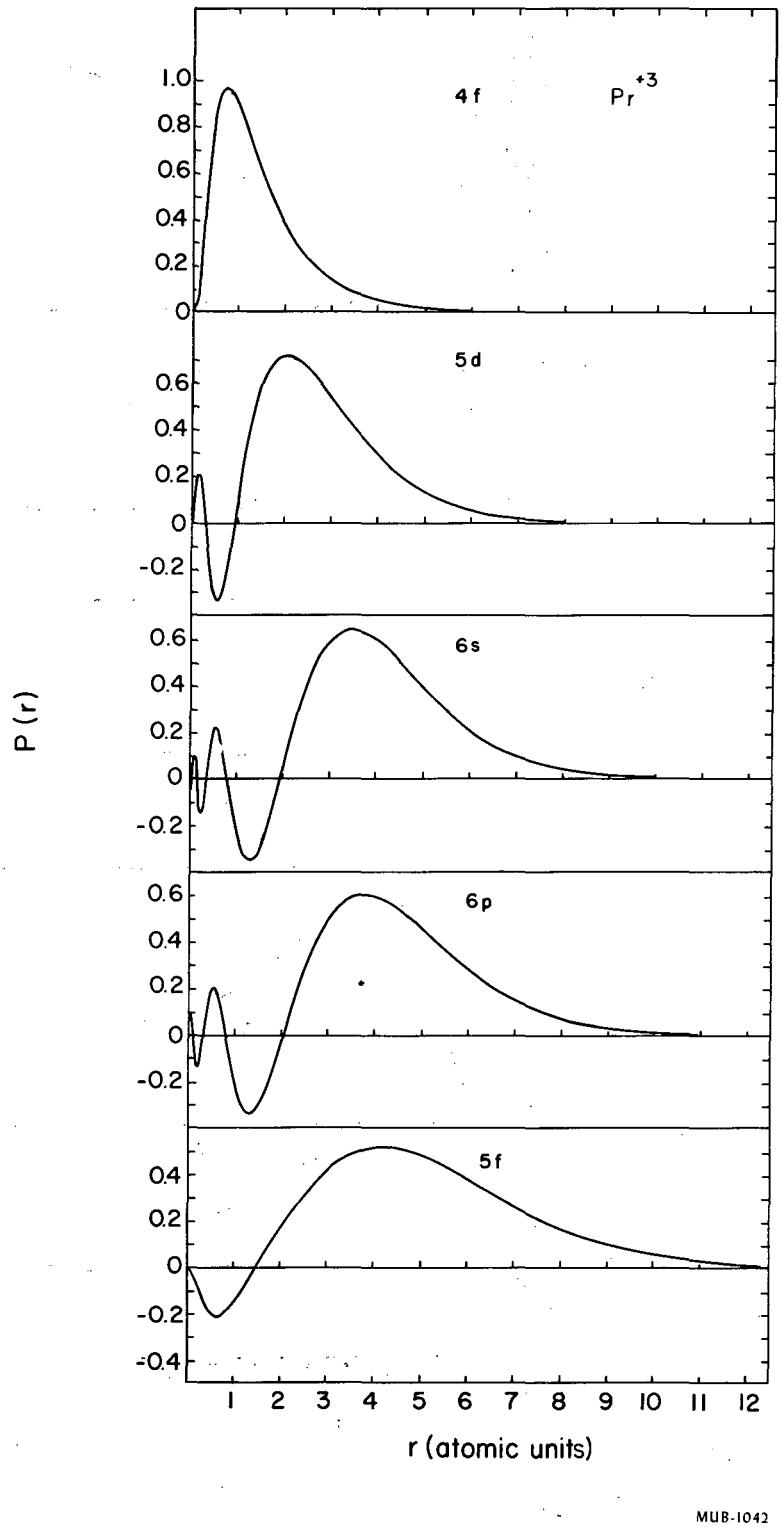

Fig. 3. Normalized radial eigenfunctions, P(r), for Pr^{+3}.

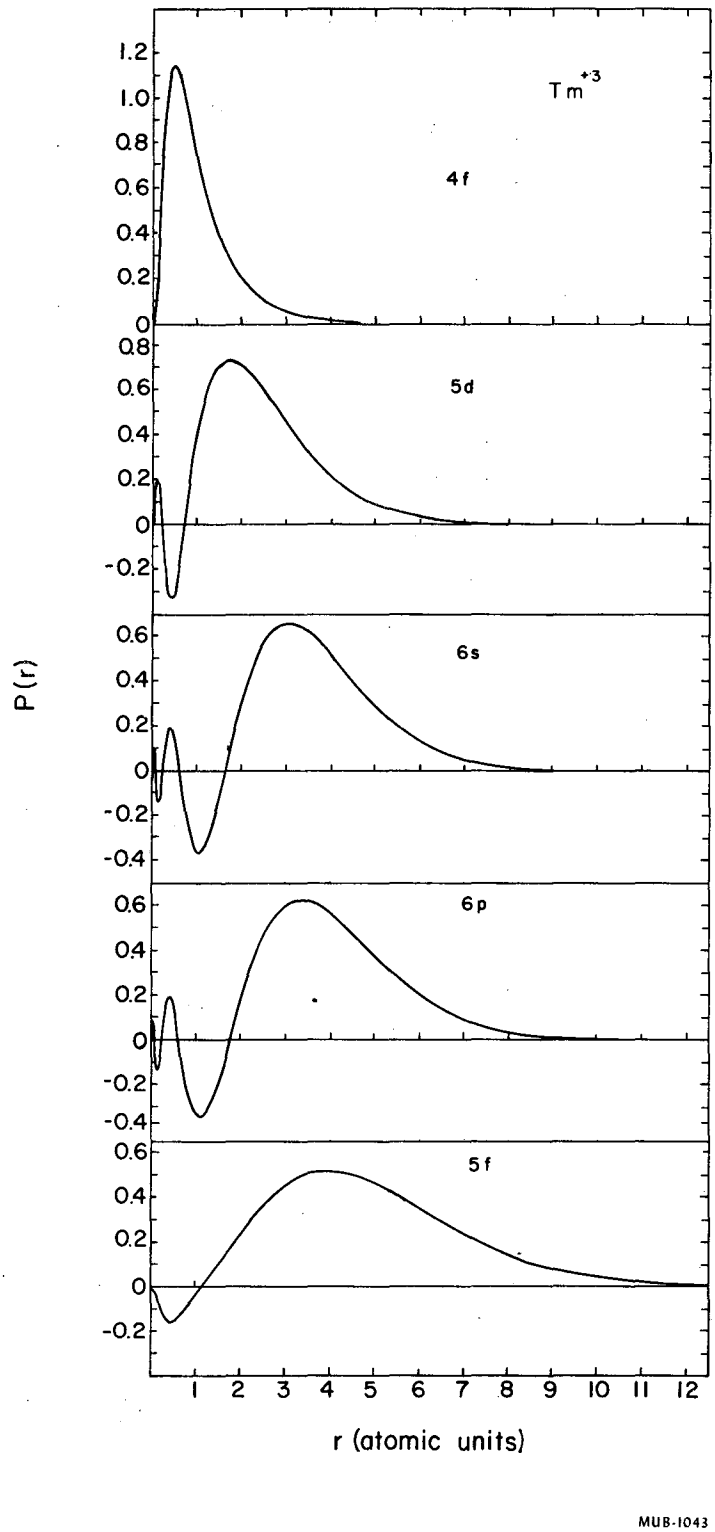

Fig. 4. Normalized radial eigenfunctions, P(r), for Tm^{+3}.

Table V. One-electron energies and radial integrals for excited orbitals of Pr^{+3} and Tm^{+3} (energies and integrals in atomic units).

	Pr^{+3}				Tm^{+3}			
		$R^k(4f4f,4fn\ell)$				$R^k(4f4f,4fn\ell)$		
	Energy	k=2	k=4	k=6	Energy	k=2	k=4	k=6
4f [a]	-1.159	.406	.253	.181	-1.452	.573	.358	.257
4f	-1.174	.408	.255	.186	-1.483	.576	.360	.259
5d	- .9822	—	—	—	-1.060	—	—	—
6s	- .8637	—	—	—	- .9631	—	—	—
6p	- .7352	-.0258	-.0172	—	- .8104	-.0140	-.0067	—
5f	- .4898	-.0592	-.0392	-.0224	- .5007	-.0547	-.0362	-.0263

[a] Entries in this row are those of Ridley (see reference 41).

similar plot for the triply ionized atoms. In Fig. 5 the calculated one-electron energies (relative to 6s) are plotted along with the experimental centers of configurations from Fig. 5 of Dieke et al. The results are remarkably good when one considers the approximations made. Since only the first ionization energy is available for Pr, it is impossible to compare absolute energies, but it is probable that in taking energy differences many of the errors have cancelled, yielding a reasonably good fit to the experimental spectrum.

The 4f energies differ slightly from those of Ridley. This is probably due to a slight difference in the potentials used, or the method of machine solution of the Schrödinger equation. However, the 4f functions differ only slightly from those of Ridley and the $F^k(4f,4f)$ integrals agree very well (see Table V).

Table VIA-B contains the $< r^k_{n\ell n'\ell'} >$ integrals necessary for the configuration interaction calculations. These integrals are not very sensitive to the grid size used in the numerical integration, but this is not true for the R^k integrals. A grid size ≈ 0.005 is necessary to obtain integrals that do not change appreciably with a change in grid size. It is felt that a further reduction of grid size would change the values given by less than $\pm 2 \times 10^{-4}$ a.u.

Wong[7] has used functions obtained in this manner to calculate Slater integrals connecting $4f^2$ and $5d^2$ configurations of Pr^{+3}. These have led to an appreciable improvement in the agreement between the calculated and observed spectra.

Without further experimental data it is difficult to establish any further criteria for the accuracy of these functions. An attempt

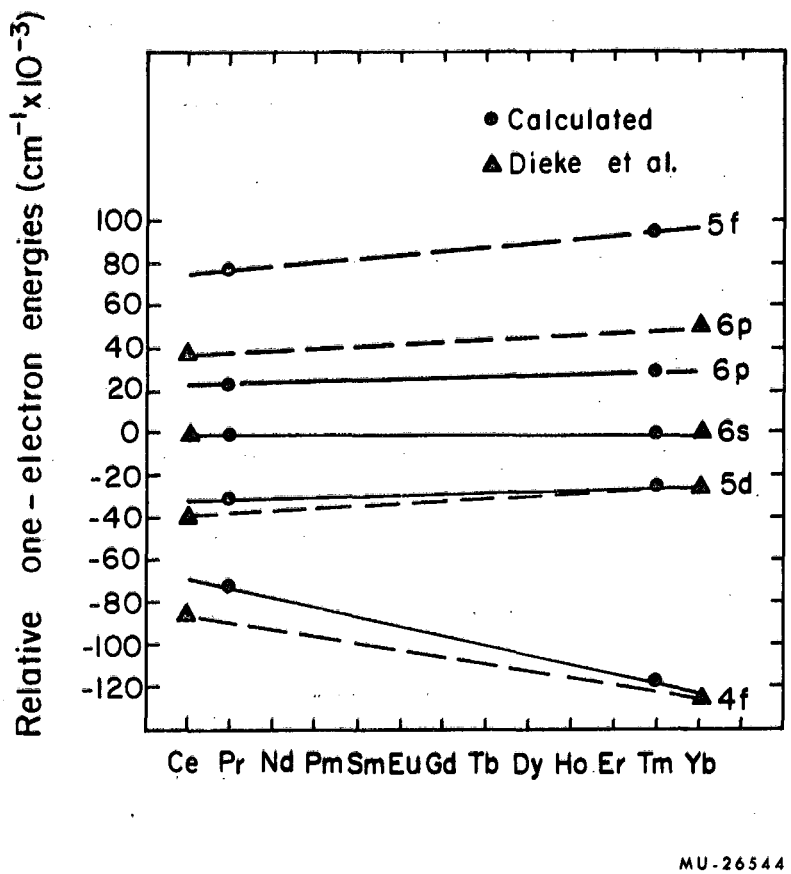

Fig. 5. Experimental centers of configurations of triply ionized rare-earth ions from Dieke et al. (see reference 38), and calculated one-electron energies.

Table VIA: Values of $< r^k_{n\ell n\ell'} >$ for Pr^{+3}

$< r^2 >$

	4f	5d	6s	6p	5f
4f	1.44			1.04	1.33
5d		6.65	7.61		
6s			14.2		
6p				17.6	
5f					23.8

$< r^4 >$

	4f	5d	6s	6p	5f
4f	5.17			19.2	20.4
5d		70.2	122.		
6s			279.		
6p				429.	
5f					831.

$< r^6 >$

	4f	5f
4f	37.4	430.
5f		39300

Table VIB. Values of $< r^k_{n\ell n\ell'} >$ for Tm^{+3}

$< r^2 >$

	4f	5d	6s	6p	5f
4f	0.747			0.439	0.589
5d		5.27	6.25		
6s			11.5		
6p				14.4	
5f					22.2

$< r^4 >$

	4f	5d	6s	6p	5f
4f	1.50			6.50	6.67
5d		46.3	82.5		
6s			184.		
6p				289.	
5f					731.

$< r^6 >$

	4f	5f
4f	6.72	109.
5f		33000

was made, however, to determine the sensitivity of the $R^k(4f4f,4f6p)$ and $R^k(4f4f,4f5f)$ integrals to slight changes in the wave functions. Since these integrals depend on the overlap of the 4f function with either the 6p or 5f, any change involving only the tail of the outer function will have little or no effect. The easiest way to change the whole function is simply to apply a scaling factor that moves the function in and out. If the 4f function is kept constant while the 5f and 6p are contracted or expanded by 10%, the integral $|R^2(4f4f,4f6p)|$ increases when the 6p function is contracted and decreases when it is expanded. $|R^2(4f4f,4f5f)|$, however, decreases with a 10% contraction of the 5f function and increases on expansion. The effect is about 20% for the 5f-interaction and 40% for the 6p. Therefore, unless the eigenfunctions are radically changed in going from the free ion to the crystal, a factor of 2 is probably a liberal estimate of the possible deviation from the integrals obtained here.

V. NUMERICAL RESULTS FOR Pr^{+3}

With the energies and integrals of the previous section, the shifts in the individual crystal field levels brought about by the various mechanisms considered may now be calculated. The corrections to the operator-equivalent factors due to interactions with the 4f6p and 4f5f configurations have been given in Eq. (28):

$$\alpha/\alpha_{ff} = 1 - \frac{2(f^2SL|Q|f\ell'SL)}{\Delta E} \quad \frac{\alpha_{f\ell'}}{\alpha_{ff}} \frac{\langle r^2_{f\ell'}\rangle}{\langle r^2_{ff}\rangle} \quad .$$

Using the Coulomb matrix elements from Table I, operator equivalent factors from Table II, and energy differences and radial integrals from Tables V and VI, these correction factors were computed. They are given in Table VIIA for the interaction with 4f6p, and in Table VIIB for 4f5f. For the interaction with 4f5f,

$$\frac{\alpha_{ff'}}{\alpha_{ff}} = \frac{\beta_{ff'}}{\beta_{ff}} = \frac{\gamma_{ff'}}{\gamma_{ff}} = \frac{1}{\sqrt{2}} ,$$

for all levels. Thus the correction factor is the same for each level within a given term.

Using the crystal field parameters of Margolis,[2] the following shifts were obtained for level of $^1D_2$:

	Interaction with		
μ	6p	5f	Total
±2	-0.9	-0.2	-1.1
±1	1.1	1.5	2.6
0	-0.4	-2.6	-3.0

Table VIIA. Corrections to α and β due to interaction with 4f6p

Level	α/α_{ff}	β/β_{ff}
$^1D_2$	0.963	1.019
$^3F_2$	0.969	1.173
$^3F_3$	0.969	1.173
$^3F_4$	0.969	1.173
$^1G_4$	1.088	0.856

Table VIIB. Corrections to α, β, and γ due to interaction with 4f5f

Term	α/α_{ff}	β/β_{ff}	γ/γ_{ff}
^3P	1.025	-	-
^1D	1.010	1.039	-
^3F	0.987	0.949	0.842
^1G	0.989	0.955	0.860
^3H	0.977	0.908	0.715
^1I	1.019	1.075	1.232

Table VIIC. Corrections to α, β and γ due to interaction with 4f6p and 4f5f

Term	α/α_{ff}	β/β_{ff}	γ/γ_{ff}
^1D	0.973	1.058	-
^3F	0.946	1.121	0.842
^1G	1.077	0.811	0.860
^3H	0.977	0.908	0.715
Cross term $\langle^3H\|V\|^3F\rangle$	0.991	0.886	0.779

Figure 6 shows these results, along with the results of Margolis,[2] without configuration interaction. The center of gravity has been adjusted to agree with the experimental spectrum. The sum of the two interactions has nearly the desired relative values, and the fit is somewhat improved by the inclusion of these terms. However, the average deviation is still much larger than the experimental error. If a screening factor of 10 or 15 is applied to A_2^0 (See Sec. IIIA) the fit of the upper two levels, particularly $J_z = \pm 2$, is appreciably improved, but the zero level is raised rather than depressed.

For the other levels the situation is not so simple. Whereas the $^1D_2$ is only weakly coupled to the other $J = 2$ states, the breakdown of LS coupling is quite large for the other states, particularly those with $J = 4$. The eigenvectors obtained by Margolis were provided by Dr. Wong and have been used to compute the shifts of the $^3H_4$, $^3F_4$ and $^1G_4$ levels due to the sum of the interactions with 4f5f and 4f6p:

$$^3H_4 = 0.98828 \mid {}^3H_4 > - 0.02779 \mid {}^3F_4 > + 0.15013 \mid {}^1G_4 > ,$$

$$^3F_4 = - 0.09772 \mid {}^3H_4 > - 0.87086 \mid {}^3F_4 > + 0.48213 \mid {}^1G_4 > ,$$

$$^1G_4 = - 0.11731 \mid {}^3H_4 > + 0.49115 \mid {}^3F_4 > + 0.86314 \mid {}^1G_4 > .$$

The phases have been adjusted to agree with the convention of this work.

The results are shown in Fig. 7. Some of these shifts are quite large and two of the $^1G_4$ levels are actually interchanged. The overall fit is worse than that of Margolis. Applying a shielding factor to A_2^0 has little effect on these levels because the dominant terms are, in nearly all cases, those involving A_6^0 and A_6^6. Thus the large

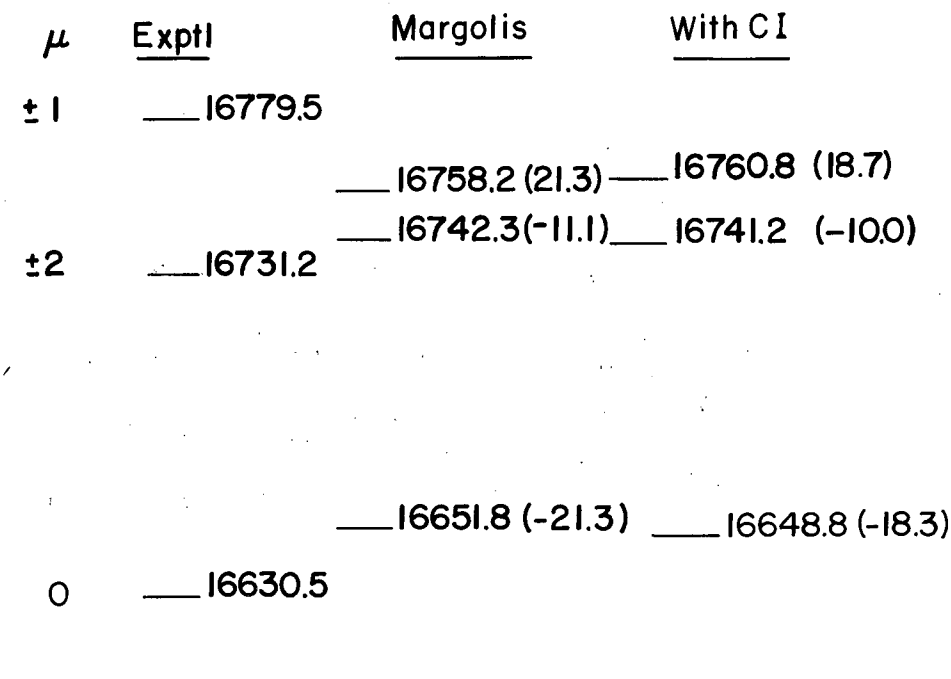

Fig. 6. The $^1D_2$ levels of Pr^{+3}.

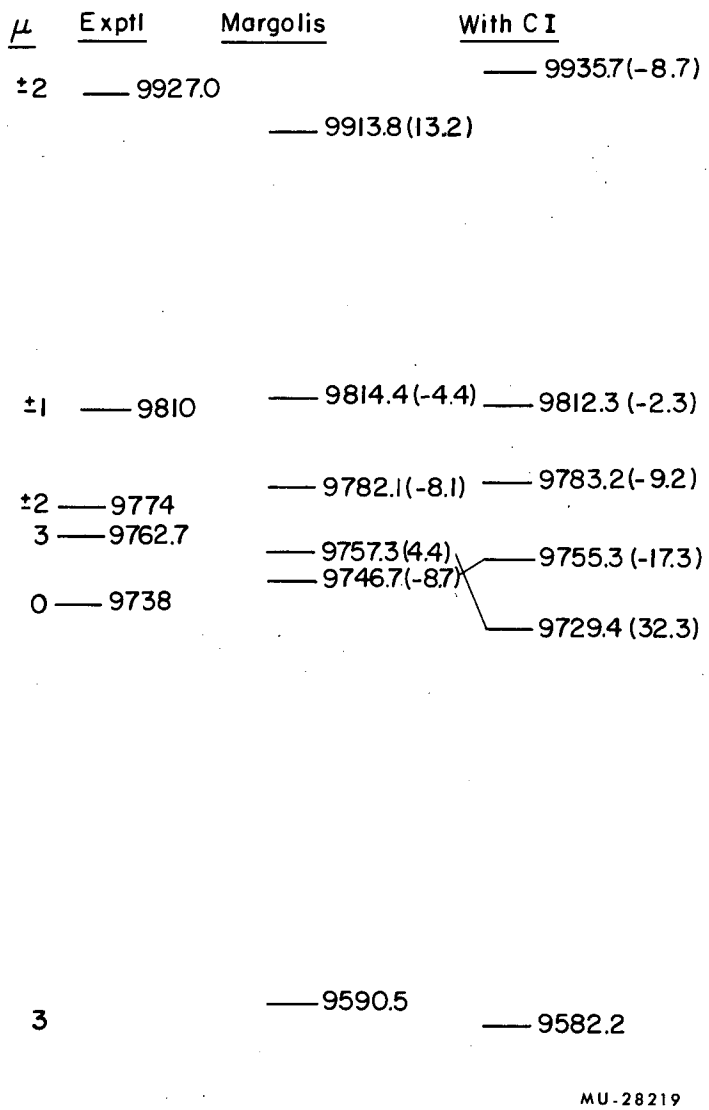

Fig. 7A. The $^1G_4$ levels of Pr^{+3}.

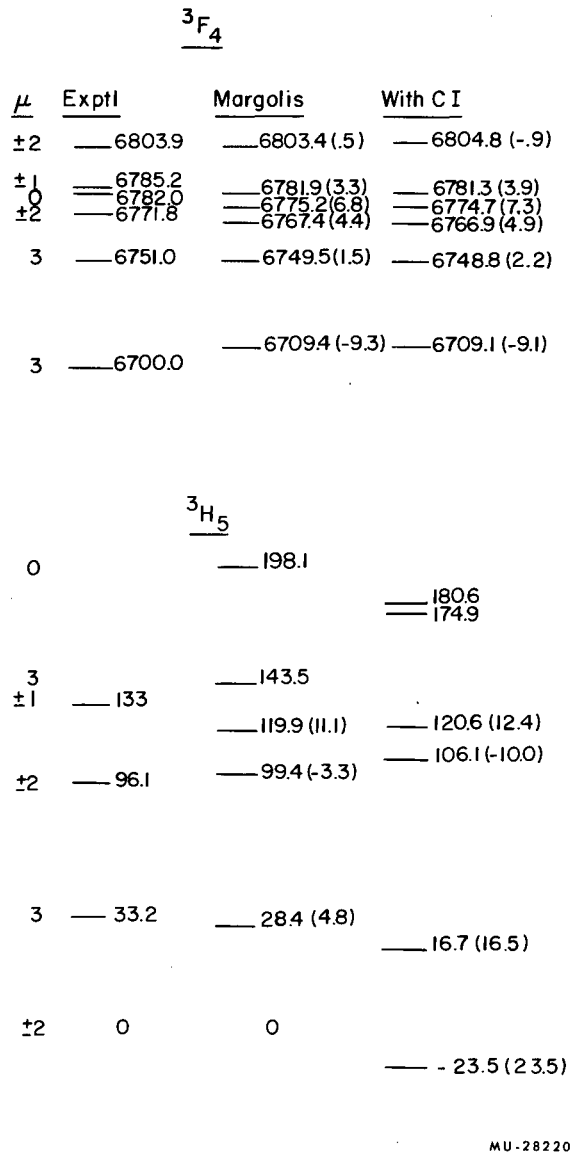

Fig. 7B. The $^3F_4$ and $^3H_5$ levels of Pr^{+3}.

shifts in the $\mu = 3, \pm 2$ components arise mainly from the corrections to γ in the 4f5f interaction. Since most of the matrix elements of V_6^0 and V_6^6 are quite large, a small correction to γ can lead to rather large shifts. This correction could be cut down without affecting the α and β terms by including second-order terms (see Appendix B), or by assuming that the calculated $< r_{ff'}^6 > / < r_{ff}^6 >$ is too large. If, as discussed in the previous section, it is assumed that $< r_{ff}^6 >$ is too small by a factor ≈ 4, the calculated shifts become reasonable. But there is really little justification for applying such a correction without some knowledge of the effect of the crystal on the free-ion 5f function. If it is scaled by the same amount as the 4f function, the present ratio is correct. If it remains unchanged while the 4f function is scaled outward, the present ratio is multiplied by about 0.85. This change is not sufficient to cause any appreciable difference in the results. There is also the possibility that the integrals $R^k(4f4f,4f5f)$ are too large but, in view of the results of Sec. IV, it is unlikely that this is more than a factor of 2. Such a correction is applicable to all terms in V, not just the sixth-order terms, however. Since many of the components are missing in the experimental spectrum and it was not expected to add anything to the general conclusions, the intermediate coupling calculations have not been carried out for the other levels.

Unfortunately, the discrepancy in the $^1D_2$ levels does not seem to arise from any single mechanism but must be the result of many small effects. None of the mechanisms considered are specific to the $^1D_2$, and produce shifts of at least the same order of magnitude in

other levels. If the present integrals are correct, the interaction of $4f^2$ with 4f5f and 4f6p is not negligible and the $R^k(4f4f,4f5f)$ and $R^k(4f4f,4f6p)$ integrals should really be treated as parameters in the intermediate coupling calculation. If this were done, the crystal field might then be fitted with a different set of crystal field parameters and many of the present difficulties might automatically be removed. Until good wave functions are available for Pr^{+3} in a chloride crystal, however, further attempts at calculation from first principles cannot be expected to give more than qualitative results.

VI. THE CONFIGURATION f^7 (Gd^{+3})

Whereas the Pr^{+3} spectrum is extremely well known, that of Gd^{+3} has received relatively little attention. The most recent work is that of Dieke and Leopold on $GdCl_3 \cdot 6H_2O$,[14] and Cook and Dieke on $GdAc_3 \cdot 4H_2O$ and $Gd_2(SO_4)_3 \cdot 8H_2O$,[46] in which they were able to assign the $^6P_{7/2}$, $^6P_{5/2}$, and $^6I_{7/2}$ levels in the chloride, and the $^6P_{3/2}$, $^6P_{5/2}$, and $^6P_{7/2}$ levels in the acetate and sulfate. From the Zeeman splitting factors in the chloride they determined that the lines A_3 and A_4 (Table VIII) are principally $J_z = 5/2$ and $7/2$, respectively. They were unwilling to assign J_z values to the other lines, however. But Judd has shown that only a small mixing of levels arising from deviations from perfect pseudo-hexagonal symmetry is necessary to explain the observed splitting factors.[15] He has made the assignment shown in Table VIII.

The $^6P_{7/2}$ and $^6P_{5/2}$ levels both exhibit total Stark splittings of approximately 80 cm^{-1}. There is no first-order crystal field splitting of the sextet states of f^7, however. This may be easily seen as follows. The crystal field matrix elements for the ^6P term are proportional to the operator equivalent factor α which is in turn proportional to a reduced matrix element of the operator $C^{(2)}$ (see Sec. III-A). In Appendix C it is shown that for the sextet states of f^7 the matrix elements $(f^7WU^6L \| C^{(2)} \| f^7WU^6L)$ are zero. Thus there should be no first-order Stark splitting of the sextet levels. Second-order effects can arise by three mechanisms: (1) a term that is first-order in both the spin orbit and crystal field interactions; (2) a second-order crystal field effect; (3) a term that is first order in both the Coulomb and crystal

Table VIII. Wave numbers of the lines in A and B groups of $GdCl_3 \cdot 6H_2O$ at 1.7^oK. [a]

		J_z
A_1	32065.60	1/2
A_2	090.95	3/2
A_3	121.49	5/2
A_4	144.86	7/2
B_1	658.67	1/2
B_2	698.57	3/2
B_3	739.19	5/2

[a] From reference 14.

field interactions between levels of the same L in different configurations. Judd has shown that the spin orbit interaction alone will not reproduce the observed splittings.[15] Thus there must also be some contribution from second-order crystal field effects or configuration interaction.

In this section, calculations are carried out for the interaction of $f^7(110)(11)^6P$ with the ^6P states of $f^6 6p$ in an attempt to account for this splitting. In view of the results obtained above for Pr^{+3}, the configuration of $4f^6 5f$ might have been a more judicious choice. However, $4f^6 6p$ is the lowest excited configuration of odd parity. Because of the greater number of allowed states, the calculation for $4f^6 5f$ would involve extremely long summations and calculation for $k = 6$ as well as the $k = 2$ and 4 which are necessary for the interaction with $4f^6 6p$.

Even though the Coulomb interaction Q has nonzero matrix elements only between states of the same S and L in different configurations, it can link $|4f^7(110)(11)^6P>$ to 5 different ^6P states of $4f^6 6p$. This may be readily seen by looking at the quintet and septet states of f^6 in Table IX. Any of these may couple with another electron to form a sextet, and all the S, P, and D states may couple with a p electron to form a ^6P state of $4f^6 6p$. Thus the interaction of $4f^7(110)(11)^6P$ with $4f^6 6p$ ^6P includes contributions from five separate matrix elements.

Table IX Classification of certain states of f^n [a]

		f^6					f^7		
n	ν	W	U	SL	n	ν	W	U	SL
6	6	(100)	(10)	^7F	7	7	(000)	(00)	^8S
	6	(210)	(11)	^5PH		7	(200)	(20)	^6DGI
			(20)	^5DGI		5	(110)	(10)	^6F
			(21)	^5DFGHKL				(11)	^6PH
	4	(111)	(00)	^5S					
			(10)	^5F					
			(20)	^5DGI					

[a] Taken from reference 47.

$$
\begin{aligned}
&(f^7{}_5(110)(11)^6P\ |Q|\ f^6{}_6(210)(11)^5P\ p\ ^6P)\\
&(f^7{}_5(110)(11)^6P\ |Q|\ f^6{}_6(210)(20)^5D\ p\ ^6P)\\
&(f^7{}_5(110)(11)^6P\ |Q|\ f^6{}_6(210)(21)^5D\ p\ ^6P)\\
&(f^7{}_5(110)(11)^6P\ |Q|\ f^6{}_4(111)(00)^5S\ p\ ^6P)\\
&(f^7{}_5(110)(11)^6P\ |Q|\ f^6{}_4(111)(20)^5D\ p\ ^6P)\ .
\end{aligned}
\tag{42}
$$

Each of these may be evaluated using Eq. (13). The sums over all intermediate states, of which there are many, make the calculation extremely long and tedious. Fortunately, however, some simplification can be made in Eq. (13) for the sextet states of f^7.

A. Calculations

For the $(110)(11)^6P$ state of Gd^{+3}, Eq. (13) becomes

$$
\begin{aligned}
&\left(f^7{}_5(110)(11)^6P\left|\sum_{i<j} 1/r_{ij}\right| f^6(\psi')\ p^6P\right)\\
&= 1/6 \sum_k \Bigg[\sum_{\psi''}(-1)^{1-L''}(f^7{}_5(110)(11)^6P\ ||\ C^{(k)}\ ||\ f^7\ W''U''S''L'')\\
&\qquad \times (f^7W''U''S''L''||C^{(k)}||f^6(\psi')p^6P)\\
&+ \sum_{\psi'',\,L'''}(-1)^{1-L'''}(f^7{}_5(110)(11)^6P||C^{(k)}||f^6(\psi'')pSL''')\\
&\quad \times (f^6(\psi'')pSL'''||C^{(k)}||f^6(\psi')\ p^6P)\Bigg]\ R^k(4f4f,4f6p)\\
&= 1/6 \sum_k \left[\sum_{\psi''}(-1)^{1-L''}A\cdot B + \sum_{\psi'',L'''}(-1)^{1-L'''}C\cdot D\right],
\end{aligned}
\tag{43}
$$

where k = 2 and 4.

Before embarking on such a series of summations let us consider briefly the effect of the crystal field. As was the case for Pr^{+3}, any Stark splitting which is first-order in configuration interaction arises from a product of crystal field and Coulomb matrix elements between the two configurations. Thus it will also be necessary to calculate matrix elements of the form $(f^7(110)(11)^6P|V|f^6(\psi')p\ ^6P)$ where

$$\begin{aligned}\psi' = {} & {}_6(210)(11)^5P \\ & {}_6(210)(20)^5D \\ & {}_6(210)(21)^5D \\ & {}_4(111)(00)^5S \\ & {}_4(111)(20)^5D\ .\end{aligned}$$

$GdCl_3 \cdot 6H_2O$ has only a C_2 symmetry axis.[48] If this is taken as the z axis the only terms in the crystal field potential which give nonzero matrix elements between ^6P states are

$$V = A_2^0\ (3z^2 - r^2) + A_2^2\ (x^2 - y^2).$$

However, the work of Dieke and Leopold[14] on $GdCl_3 \cdot 6H_2O$ and that of Eisenstein[49] on the isomophic $YbCl_3 \cdot 6H_2O$, show that these crystals also exhibit pseudo-hexagonal axes perpendicular to the C_2 axis. This implies a relationship between A_2^0 and A_2^2. If $A_2^2 = -3\ A_2^0$, the potential becomes

$$V = -2A_2^0(3x^2 - r^2).$$

This is simply a V_2^0 term with a new A_2^0 and referred to the pseudo-hexagonal axis perpendicular to the C_2 axis:

$$V = A_2^0\ (3z^2 - r^2). \tag{44}$$

The work of Judd[15] on $GdCl_3 \cdot 6H_2O$, as well as that of Eisenstein[49] on the Yb compound, has shown that even if $A_2^2 = -3\,A_2^0 + \delta$, the splittings caused by deviations from Eq. (44) will be small. Thus the matrix elements to be computed are

$$(f^7(110)(11)^6PJJ_z|V_2^0|f^6(\psi')p^6PJJ_z) = \alpha_{fp}\,A_2^0 < r^2_{fp} > \left[3J_z^{\,2} - J(J+1)\right].$$

An expression for α_{fp} may be obtained in exactly the same way as in Sec. III-B. This gives, for the ^6P term,

$$\alpha_{fp} = 36\sqrt{\frac{7}{5}}\,(2S+1)(-1)^{3J+\frac{5}{2}+L'+1}\left[\frac{(2J-2)!}{(2J+3)!}\right]^{1/2}\begin{Bmatrix} 1 & J & \frac{5}{2} \\ J & 1 & 2 \end{Bmatrix}\begin{Bmatrix} 3 & 1 & L' \\ 1 & 1 & 2 \end{Bmatrix}$$

$$\times\,(f^7(110)(11)^6P\left\{|f^6(\psi') + f\right)$$

The triangular conditions of the second 6-j symbol allow only $L \geqslant 2$. Thus the ^5P and ^5S states can immediately be eliminated from the possible ψ' given above. As will be seen below, the Coulomb interaction is zero for the $_4(111)(20)^5D$ state so we need calculate α_{fp} only for

$$\psi' = {}_6(210)(20)^5D$$
$$\phantom{\psi' = {}}{}_6(210)(21)^5D.$$

The coefficients of fractional parentage $(f^7\ WUSL\left\{|\ f^6\ W'U'S'L'\right) + f)$ which will be necessary for this and later calculations may be evaluated from Eq. (10) and the tables of Racah (IV). They are given in Table X. Table XI gives the operator equivalent factors α_{fp} for the $^6P_{3/2}$, $^6P_{5/2}$ and $^6P_{7/2}$ levels of Gd^{+3}.

Having eliminated two values of ψ', further simplification can be effected in Eq. (43). First consider the matrix elements

Table X. Fractional parentage coefficients $\left(f^7WUSL \left\{ \middle| f^6W'U'S'L' + f\right)\right.$.

ψ \ ψ'	(111)			(100)	(210)					
	$(10)^5F$	$(20)^5D$	$(20)^5G$	$(10)^7F$	$(11)^5P$	$(20)^5D$	$(20)^5G$	$(21)^5D$	$(21)^5F$	$(21)^5G$
${}_5(110)(11)^6P$	$\frac{-1}{\sqrt{21}}$	$\frac{-\sqrt{10}}{7}$	$\frac{\sqrt{11}}{7}$	$\frac{-1}{\sqrt{6}}$		$\frac{\sqrt{5}}{7\sqrt{7}}$	$\frac{-\sqrt{11}}{7\sqrt{14}}$	$\frac{\sqrt{55}}{7\sqrt{21}}$	$\frac{-\sqrt{11}}{2\sqrt{21}}$	$\frac{-3\sqrt{5\cdot 13}}{14\sqrt{21}}$
${}_7(200)(20)^6D$		0		$\frac{-1}{\sqrt{6}}$	$\frac{-\sqrt{3}}{7}$	$\frac{-4\sqrt{3}}{7\sqrt{14}}$		$\frac{3\sqrt{11}}{7\sqrt{14}}$		
${}_7(200)(20)^6G$			0	$\frac{-1}{\sqrt{6}}$	$\frac{\sqrt{11}}{7\sqrt{6}}$	$\frac{\sqrt{55}}{7\sqrt{14}}$		$\frac{4\sqrt{5}}{7\sqrt{42}}$		

Table XI. Operator-equivalent factors α_{fp} for $(f^7(110)(11)^6P|V|f^6(\psi')p\ ^6P)$.

Level	ψ'	α_{fp}
$^6P_{3/2}$	$(210)(20)^5D$	$\frac{-6}{7 \cdot 25\sqrt{30}}$
	$(210)(21)^5D$	$\frac{-2\sqrt{11}}{7 \cdot 25\sqrt{10}}$
$^6P_{5/2}$	$(210)(20)^5D$	$\frac{72}{25 \cdot 49\sqrt{30}}$
	$(210)(21)^5D$	$\frac{24\sqrt{11}}{25 \cdot 49\sqrt{10}}$
$^6P_{7/2}$	$(210)(20)^5D$	$\frac{-6}{5 \cdot 49\sqrt{30}}$
	$(210)(21)^5D$	$\frac{-2\sqrt{11}}{5 \cdot 49\sqrt{10}}$

$$A = (f^7\ WUSL||C^{(k)}||f^7\ W''U''S''L'')$$
$$= (f^7\,{}_5(110)(11)^6P||C^{(k)}||f^7\ W''U''S''L''),$$

where the ψ'' includes all the sextet states of f^7, i.e.,

$$\psi'' = {}_7(200)(20)^6DGI$$
$${}_5(110)(10)^6F$$
$$(11)^6PH.$$

Judd has shown that the summation involved in Eq. (14) for the matrix elements A can be carried out explicitly,[15] leaving a very simple expression;

$$A = (f^7WUSL||C^{(k)}||f^7W''U''S''L'')$$
$$= 14(-1)^{L+1}\left[(2L+1)(2L''+1)\right]^{1/2}\begin{Bmatrix} L & L'' & k \\ 3 & 3 & 3 \end{Bmatrix}\begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}\delta(S,S'), \quad (45)$$

for $L + L''$ odd. For $L + L''$ even, $A = 0$. The proof is given in Appendix D.

Thus the matrix elements A are zero unless $L + L''$ is odd. With $L = 1$ this means L'' must be even and we have

$$(f^7\,{}_5(110)(11)^6P||C^{(k)}||f^7W''U''^6L'')$$
$$= 14\left[3(2L''+1)\right]^{1/2}\begin{Bmatrix} 1 & L'' & k \\ 3 & 3 & 3 \end{Bmatrix}\begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}, \quad (46)$$

where L'' is even. But the triangular conditions on $(1, L'', k)$ in the 6-j symbol require $L'' \leqslant 1 + k$. This gives $L'' = 2$ for $k = 2$, and $L'' = 4$ for $k = 4$. Thus it is only necessary to compute two matrix elements, using Eq. (46),

$$(f^7{}_5(110)(11)^6P||C^{(2)}||f^7{}_7(200)(20)^6D) = -2/\sqrt{10},$$

and

$$(f^7{}_5(110)(11)^6P||C^{(4)}||f^7{}_7(200)(20)^6G) = \sqrt{\frac{10}{11}} \quad . \tag{47}$$

Since Eq. (43) involves the sum $\sum_{\psi''} A \cdot B$, it only remains to calculate the B terms which will be multiplied by nonzero A terms, i.e.,

$$B = (f^7W''U''S''L''||C^{(k)}||f^6(\psi')p^6P)$$

where

$$\psi'' = (200)(20)^6D \qquad \text{when } k = 2,$$

and

$$\psi'' = (200)(20)^6G \qquad \text{when } k = 4.$$

Whereas A was independent of ψ', B is not, and for each ψ'', B must be computed for the three values of ψ',

$$\psi' = {}_6(210)(20)^5D$$
$$\quad\;\; {}_6(210)(21)^5D$$
$$\quad\;\; {}_4(111)(20)^5D.$$

From Eq. (18) we obtain

$$B = \sqrt{7}\,(f^7W''U''S''L''\Big\{|\, f^6(\psi')fS''L'')(-1)^{L'+L''}$$
$$\times\, 3\Big[7(2L''+1)\Big]^{1/2}\begin{Bmatrix} 3 & L'' & L' \\ 1 & 1 & k \end{Bmatrix}\begin{pmatrix} 3 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}. \tag{48}$$

The c.f.p. have already been given in Table IX. The matrix elements B are given in Table XII.

Using the results in Eq. (47) and Table XI, the first term in Eq. (43) now becomes

$$X = 1/6 \sum_k \sum_{\psi''} (-1)^{1-L''} A \cdot B = \frac{-12}{35\sqrt{30}} R^2(4f4f,4f6p) + \frac{5}{14\sqrt{30}} R^4(4f4f,4f6p)$$

Table XII. $B = (f^7W''U''S''L''||C^{(k)}||f^6(\psi')p^6P)$.

ψ'' \ ψ'	$(210)(20)^5D$		$(210)(21)^5D$		$(110)(20)^5D$	
	k=2	k=4	k=2	k=4	k=2	k=4
$(200)(20)^5D$	$\frac{-36}{35\sqrt{3}}$	0	$\frac{9\sqrt{11}}{35}$	0	0	0
$(200)(20)^5G$	0	$\frac{-3\sqrt{11}}{14\sqrt{3}}$	0	$\frac{-2}{7}$	0	0

for $\psi' = (210)(20)^5D$,

and
$$X = \frac{3\sqrt{11}}{35\sqrt{10}} R^2(4f4f,4f6p) + \frac{10\sqrt{11}}{21\cdot 11\sqrt{10}} R^4(4f4f,4f6p)$$

for $\psi' = (111)(21)^5D$.

For $\psi' = (111)(20)^5D$, $X = 0$.

Unfortunately, the calculation of the terms C and D is not nearly as easy. From Eq. (19) we have

$$C = (f^7{}_5(110)(11)^6P||C^{(k)}||f^6(W''U''S''L'')p\ {}^6L''')$$
$$= 7\left[9(2L'''+1)\right]^{1/2}(f^7{}_5(110)(11)^6P\left\{|f^6(W''U''S''L'') + f)(-1)^{1+L''}\right.$$
$$\times \begin{Bmatrix} 3 & 1 & L'' \\ L''' & 1 & k \end{Bmatrix} \begin{pmatrix} 3 & k & 1 \\ 0 & 0 & 0 \end{pmatrix}, \qquad (49)$$

where L''' includes all sextets of f^6p, and ψ'' includes the septets and quintets of f^6. The triangular conditions of the 6-j symbol immediately eliminate a few terms but there are still many to be computed. The results are given in Table XIII.

If Eq. (20) instead of Eq. (21) is used for the matrix elements

$$D = (f^6(\psi'')p^6L'''||C^{(k)}||f^6(\psi')p\ {}^6P),$$

they may be written in terms of reduced matrix elements of the unit tensor $U^{(k)}$ in the configuration f^6. $U^{(k)}$ is defined by

$$(\ell||U^{(k)}||\ell) = 1, \text{ or } (\ell||C^{(k)}||\ell) = (-1)^{\ell}\ (2\ell + 1)\begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}(\ell||U^{(k)}||\ell). \qquad (50)$$

When we change $C^{(k)}$ to $U^{(k)}$, Eq. (20) becomes, for L = 1 and k even,

Table XIII. $C = (f^7{}_5(110)(11)^6P||C^{(k)}||f^6(W''U''S''L'')p\ {}^6L''')$.

ψ'' \ L'''	1 k=2	2 k=2	3 k=2	3 k=4	5 k=4	6 k=4
$(210)(20)^5D$	$\frac{3^2}{35}$	$\frac{\sqrt{15}}{35}$	$\frac{\sqrt{3}}{35\sqrt{7}}$	$\frac{-2\sqrt{5}}{7\sqrt{7}}$	0	0
$(210)(21)^5D$	$\frac{3\sqrt{33}}{35}$	$\frac{\sqrt{55}}{35}$	$\frac{\sqrt{11}}{35\sqrt{7}}$	$\frac{-2\sqrt{55}}{7\sqrt{21}}$	0	0
$(111)(20)^5D$	$\frac{-9\sqrt{2}}{5\sqrt{7}}$	$\frac{-\sqrt{30}}{5\sqrt{7}}$	$\frac{-\sqrt{6}}{35}$	$\frac{2\sqrt{10}}{7}$	0	0
$(210)(21)^5F$	0	$\frac{-\sqrt{22}}{\sqrt{35}}$	$\frac{-\sqrt{11}}{2\sqrt{35}}$	$\frac{-\sqrt{11}}{4\sqrt{21}}$	$\frac{\sqrt{55}}{4\sqrt{7}}$	0
$(111)(10)^5F$	0	$\frac{-2\sqrt{2}}{\sqrt{35}}$	$\frac{-1}{\sqrt{35}}$	$\frac{-1}{2\sqrt{21}}$	$\frac{\sqrt{5}}{2\sqrt{7}}$	0
$(210)(20)^5D$	0	0	$\frac{-3\sqrt{33}}{7\sqrt{70}}$	$\frac{\sqrt{11}}{18\cdot 7\sqrt{14}}$	$\frac{-\sqrt{11}}{42\sqrt{2}}$	$\frac{22}{63\sqrt{2}}$
$(210)(21)^5G$	0	0	$\frac{-9\sqrt{13}}{14\sqrt{7}}$	$\frac{\sqrt{65}}{84\sqrt{21}}$	$\frac{-\sqrt{65}}{28\sqrt{3}}$	$\frac{\sqrt{55\cdot 13}}{21\sqrt{3}}$
$(111)(21)^5G$	0	0	$\frac{3\sqrt{33}}{7\sqrt{5}}$	$\frac{-\sqrt{11}}{9\cdot 14}$	$\frac{\sqrt{11}}{6\sqrt{7}}$	$\frac{-22}{9\sqrt{7}}$

$$D = (-1)^{L''+1}\, 7 \left[3(2L''' + 1)\right]^{1/2} \begin{Bmatrix} L'' & L''' & 1 \\ 1 & L' & k \end{Bmatrix} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times\, (f^6 W'' U'' S'' L'' \| U^{(k)} \| f^6 W' U' S' L') + \delta(\psi', \psi'')(-1)^{L'+L'''}$$

$$\times\, 3 \left[3(2L''' + 1)\right]^{1/2} \begin{Bmatrix} 1 & L''' & L' \\ 1 & 1 & k \end{Bmatrix} \begin{pmatrix} 1 & k & 1 \\ 0 & 0 & 0 \end{pmatrix} . \qquad (51)$$

All of the necessary matrix elements of $U^{(2)}$, and those of $U^{(4)}$ except for $L' = L'' = 2$, were kindly provided by Dr. Judd. The latter were computed from

$$(f^6 W'' U''^5 D \| U^{(4)} \| f^6 W' U'^5 D) = 6 \sum_{\psi_1} (f^6 W'' U''^5 D \{\!| f^5 W_1 U_1 S_1 L_1 + f)$$

$$\times\, (f^6 W' U'^5 D \{\!| f^5 W_1 U_1{}^5 D + f)(-1)^{L_1+5}\, 5 \begin{Bmatrix} 3 & 2 & L_1 \\ 2 & 3 & 4 \end{Bmatrix} . \qquad (52)$$

Equation (52) was derived in exactly the same way that Eq. (21) was obtained from Eq. (20). The c.f.p. for $(f^6 \psi'' \{\!| f^5(\psi') + f)$ are given in Table XIV and the matrix elements of $U^{(2)}$ and $U^{(4)}$ in f^6 in Table XVA and Table XVB, respectively.

These matrix elements may now be substituted in Eq. (51) to obtain the matrix elements D which are given in Tables XVIA, XVIB, and XVIC, for $\psi' = (210)(20)^5D$, $(210)(21)^5D$, and $(111)(20)^5D$, respectively. Now the results of Table XIII and Tables XVIA, XVIB, and XVIC may be combined to give the second term in Eq. (43):

$$Y = 1/6 \sum_{\psi'', L'''} (-1)^{1-L'''}\, C \cdot D.$$

These values are shown in Table XVII, along with the values of X obtained earlier and the total Coulomb matrix elements for various ψ'.

Here again it may be noted that X = Y (see Appendix A). Some attempt was made to show under what conditions this equality should hold, but the summations always involve products of 6-j symbols and

TABLE XIV. $(f^6 WUSL \{ f^5(W'U'S'L') + f)$.

$f^5(\gamma')$	$_5(110)$			$_5(211)$													$_3(111)$		
$f^6(\gamma)$	$(10)^6P$	$(11)^6P$	$(11)^6H$	$(10)^4P$	$(11)^4P$	$(11)^4H$	$(20)^4D$	$(20)^4G$	$(21)^4D$	$(21)^4P$	$(21)^4G$	$(21)^4H$	$(30)^4P$	$(30)^4F$	$(30)^4G$	$(30)^4H$	$(10)^4P$	$(20)^4D$	$(20)^4G$
$_6(210)(11)^5P$	$\frac{1}{\sqrt{5}}$	0		$\frac{2}{\sqrt{30}}$	0		$\frac{-2\sqrt{5}}{7\sqrt{3}}$	$\frac{2\sqrt{11}}{7\sqrt{6}}$	$\frac{-\sqrt{110}}{42}$	$\frac{\sqrt{11}}{6\sqrt{2}}$	$\frac{\sqrt{65}}{14\sqrt{2}}$								
$_6(210)(20)^5D$	$\frac{\sqrt{7}}{3\sqrt{5}}$	$\frac{-\sqrt{6}}{7\sqrt{5}}$	$\frac{-2\sqrt{11}}{21\sqrt{5}}$	$\frac{-2\sqrt{14}}{9\sqrt{15}}$	$\frac{16}{21\sqrt{5}}$	$\frac{16\sqrt{22}}{63\sqrt{15}}$	$\frac{8\sqrt{2}}{21\sqrt{7}}$	$\frac{-2\sqrt{22}}{7\sqrt{21}}$	$\frac{5\sqrt{11}}{14\sqrt{21}}$	$\frac{5\sqrt{11}}{18\sqrt{14}}$	$\frac{\sqrt{65}}{42\sqrt{14}}$	$\frac{-\sqrt{55\cdot 13}}{18\sqrt{21}}$	$\frac{2\sqrt{11}}{21\sqrt{5}}$	$\frac{2\sqrt{55\cdot 13}}{45\sqrt{42}}$	$\frac{-2\sqrt{55}}{15\sqrt{14}}$	$\frac{4\sqrt{55\cdot 13}}{35\cdot 9\sqrt{2}}$	0	0	0
$_6(210)(21)^5D$	0	$\frac{-\sqrt{22}}{7\sqrt{5}}$	$\frac{3\sqrt{3}}{7\sqrt{5}}$	0	$\frac{-\sqrt{11}}{14\sqrt{15}}$	$\frac{3}{14\sqrt{10}}$	$\frac{\sqrt{33}}{7\sqrt{14}}$	$\frac{4}{7\sqrt{14}}$	$\frac{-5}{14\sqrt{7}}$	$\frac{-\sqrt{2}}{\sqrt{21}}$	$\frac{\sqrt{22\cdot 13}}{7\sqrt{105}}$	$\frac{-\sqrt{13}}{2\sqrt{35}}$	$\frac{17}{14\sqrt{15}}$	$\frac{-\sqrt{13}}{\sqrt{70}}$	$\frac{-\sqrt{5}}{\sqrt{42}}$	$\frac{-\sqrt{65}}{14\sqrt{6}}$	0	0	0
$_4(111)(20)^5D$	$\frac{-\sqrt{2}}{3\sqrt{5}}$	$\frac{-\sqrt{3}}{\sqrt{35}}$	$\frac{-\sqrt{22}}{3\sqrt{35}}$	$\frac{1}{36\sqrt{15}}$	$\frac{1}{3\sqrt{70}}$	$\frac{\sqrt{11}}{9\sqrt{105}}$	$\frac{-1}{21}$	$\frac{\sqrt{11}}{28\sqrt{3}}$	$\frac{\sqrt{11}}{7\sqrt{6}}$	$\frac{\sqrt{11}}{18}$	$\frac{\sqrt{13}}{42\sqrt{5}}$	$\frac{-\sqrt{143}}{9\sqrt{30}}$	$\frac{-\sqrt{11}}{3\sqrt{70}}$	$\frac{-\sqrt{143}}{18\sqrt{15}}$	$\frac{\sqrt{11}}{6\sqrt{5}}$	$\frac{-\sqrt{143}}{9\sqrt{35}}$	$\frac{-1}{4}$	$\frac{-1}{\sqrt{7}}$	$\frac{\sqrt{33}}{4\sqrt{7}}$
$_6(210)(21)^5F$	0			0			$\frac{-\sqrt{55}}{42}$	$\frac{-2}{7\sqrt{11}}$	$\frac{\sqrt{10}}{7\sqrt{3}}$	$\frac{-1}{2\sqrt{3}}$	$\frac{\sqrt{65}}{14\sqrt{3}}$								
$_4(111)(10)^5F$	$-\frac{\sqrt{2}}{15}$			$\frac{-1}{4\sqrt{5}}$			$\frac{-\sqrt{5}}{12}$	$\frac{-1}{4}$	0	0	0								
$_6(210)(20)^5G$	$\frac{\sqrt{7}}{3\sqrt{5}}$			$\frac{-2\sqrt{14}}{9\sqrt{15}}$			$\frac{-2\sqrt{110}}{21\sqrt{21}}$	$\frac{10\sqrt{10}}{21\sqrt{77}}$	$\frac{10\sqrt{5}}{63\sqrt{7}}$	$\frac{5\sqrt{2}}{9\sqrt{77}}$	$\frac{10\sqrt{13}}{21\sqrt{42}}$								
$_6(210)(21)^5G$	0			0			$\frac{\sqrt{13}}{42\sqrt{7}}$	$\frac{2\sqrt{13}}{7\sqrt{21}}$	$\frac{\sqrt{22\cdot 13}}{21\sqrt{21}}$	$\frac{-5\sqrt{13}}{6\sqrt{105}}$	$\frac{-23\sqrt{11}}{42\sqrt{35}}$								
$_4(111)(20)^5G$	$\frac{-\sqrt{2}}{3\sqrt{5}}$			$\frac{1}{36\sqrt{15}}$			$\frac{\sqrt{55}}{84\sqrt{3}}$	$\frac{-5\sqrt{5}}{84\sqrt{11}}$	$\frac{2\sqrt{10}}{63}$	$\frac{2}{9\sqrt{11}}$	$\frac{2\sqrt{13}}{21\sqrt{3}}$								

Table XVA. $(f^6\ WU\ {}^5L\ \|U^{(2)}\|\ f^6\ W'U'\ {}^5L')$.[a]

WUSL \ W'U'S'L'	$(210)(20)^5D$	$(210)(21)^5D$	$(111)(20)^5D$	$(210)(21)^5F$	$(111)(10)^5F$	$(210)(20)^5G$	$(210)(21)^5G$	$(111)(20)^5G$
$(210)(20)^5D$	$\frac{52\sqrt{6}}{441}$	$\frac{5\sqrt{22}}{49}$	$\frac{67\sqrt{21}}{441}$	$\frac{-\sqrt{22}}{21}$	$\frac{-8\sqrt{2}}{21}$	$\frac{32\sqrt{11}}{147}$	$\frac{-5\sqrt{390}}{147}$	$\frac{-2\sqrt{154}}{147}$
$(210)(21)^5D$	$\frac{5\sqrt{22}}{49}$	$\frac{11\sqrt{6}}{98}$	$\frac{2\sqrt{77}}{49}$	$\frac{3\sqrt{6}}{14}$	$\frac{-\sqrt{66}}{14}$	$\frac{-4\sqrt{3}}{147}$	$\frac{-\sqrt{1430}}{98}$	$\frac{-31\sqrt{42}}{294}$
$(111)(20)^5D$	$\frac{67\sqrt{21}}{441}$	$\frac{2\sqrt{77}}{49}$	$\frac{-17\sqrt{6}}{126}$	$\frac{2\sqrt{77}}{21}$	$\frac{-2\sqrt{7}}{21}$	$\frac{-2\sqrt{154}}{147}$	$\frac{-2\sqrt{1365}}{147}$	$\frac{-2\sqrt{11}}{21}$
$(210)(21)^5F$	$\frac{\sqrt{22}}{21}$	$\frac{-3\sqrt{6}}{14}$	$\frac{-2\sqrt{77}}{21}$	$\frac{-1}{6}$	$\frac{-\sqrt{11}}{6}$	$\frac{2\sqrt{6}}{7}$	$\frac{\sqrt{715}}{70}$	$\frac{-\sqrt{21}}{14}$
$(111)(10)^5F$	$\frac{8\sqrt{2}}{21}$	$\frac{\sqrt{66}}{14}$	$\frac{2\sqrt{7}}{21}$	$\frac{-\sqrt{11}}{6}$	$\frac{1}{6}$	$\frac{-2\sqrt{66}}{21}$	$\frac{\sqrt{65}}{70}$	$\frac{-\sqrt{231}}{42}$
$(210)(20)^5G$	$\frac{32\sqrt{11}}{147}$	$\frac{-4\sqrt{3}}{147}$	$\frac{-2\sqrt{154}}{147}$	$\frac{-2\sqrt{6}}{7}$	$\frac{2\sqrt{66}}{21}$	$\frac{13}{49\sqrt{33}}$	$\frac{4\sqrt{130}}{490}$	$\frac{-20}{7\sqrt{462}}$
$(210)(21)^5G$	$\frac{-5\sqrt{390}}{147}$	$\frac{-\sqrt{1430}}{98}$	$\frac{-2\sqrt{1365}}{147}$	$\frac{-\sqrt{715}}{70}$	$\frac{-\sqrt{65}}{70}$	$\frac{4\sqrt{130}}{490}$	$\frac{429}{98\sqrt{33}}$	$\frac{31\sqrt{455}}{490}$
$(111)(20)^5G$	$\frac{-2\sqrt{154}}{147}$	$\frac{-31\sqrt{42}}{294}$	$\frac{-2\sqrt{11}}{21}$	$\frac{\sqrt{21}}{14}$	$\frac{\sqrt{231}}{42}$	$\frac{-20}{7\sqrt{462}}$	$\frac{31\sqrt{455}}{490}$	$\frac{1}{14\sqrt{33}}$

[a] These matrix elements have also been calculated on a computer by C. W. Nielson of M.I.T. (unpublished). These results agree with his tables.

Table XVB. $(f^6\ WU\ {}^5L\ \|U^{(4)}\|f^6\ W'U'\ {}^5L')$.[a]

WUSL \ W′U′S′L′	$(210)(20)^5D$	$(210)(21)^5D$	$(111)(20)^5D$	$(210)(21)^5F$	$(111)(10)^5F$	$(210)(20)^5G$	$(210)(21)^5G$	$(111)(20)^5G$
$(210)(20)^5D$	$\frac{32\sqrt{55}}{9\cdot 49}$	$\frac{-19\sqrt{15}}{6\cdot 49}$	$\frac{-4\sqrt{55}}{63\sqrt{14}}$	$\frac{11\sqrt{30}}{252}$	$\frac{2\sqrt{330}}{63}$	$\frac{13\sqrt{165}}{4851}$	$\frac{19\sqrt{26}}{196}$	$\frac{-10\sqrt{2310}}{4851}$
$(210)(21)^5D$	$\frac{-19\sqrt{15}}{6\cdot 49}$	$\frac{5\cdot 59\sqrt{5}}{6\cdot 49\sqrt{11}}$	$\frac{\sqrt{30}}{7\sqrt{7}}$	$\frac{2\sqrt{110}}{77}$	$\frac{-2\sqrt{10}}{21}$	$\frac{-170\sqrt{5}}{539}$	$\frac{4\sqrt{858}}{539}$	$\frac{-34\sqrt{70}}{539}$
$(111)(20)^5D$	$\frac{-4\sqrt{55}}{63\sqrt{14}}$	$\frac{\sqrt{30}}{7\sqrt{7}}$	$\frac{-2\sqrt{55}}{63}$	$\frac{5\sqrt{105}}{63}$	$\frac{\sqrt{33\cdot 35}}{126}$	$\frac{10\sqrt{2310}}{4851}$	$\frac{-3\sqrt{91}}{49}$	$\frac{\sqrt{165}}{1386}$
$(210)(21)^5F$	$\frac{-11\sqrt{30}}{252}$	$\frac{-2\sqrt{110}}{77}$	$\frac{-5\sqrt{105}}{63}$	$\frac{17}{66}$	$\frac{-2\sqrt{11}}{33}$	$\frac{19\sqrt{10}}{231}$	$\frac{-5\sqrt{429}}{462}$	$\frac{-38\sqrt{35}}{231}$
$(111)(10)^5F$	$\frac{-2\sqrt{330}}{63}$	$\frac{2\sqrt{10}}{21}$	$\frac{-\sqrt{33\cdot 35}}{126}$	$\frac{-2\sqrt{11}}{33}$	$\frac{1}{6}$	$\frac{10\sqrt{110}}{231}$	$\frac{2\sqrt{39}}{21}$	$\frac{5\sqrt{385}}{462}$
$(210)(20)^5G$	$\frac{13\sqrt{165}}{4851}$	$\frac{-170\sqrt{5}}{539}$	$\frac{-10\sqrt{2310}}{4851}$	$\frac{-19\sqrt{10}}{231}$	$\frac{-10\sqrt{110}}{231}$	$\frac{29\sqrt{13}}{539}$	$\frac{25\sqrt{330}}{1617}$	$\frac{38\sqrt{182}}{539}$
$(210)(21)^5G$	$\frac{19\sqrt{26}}{196}$	$\frac{4\sqrt{858}}{539}$	$\frac{-3\sqrt{91}}{49}$	$\frac{5\sqrt{429}}{462}$	$\frac{-2\sqrt{39}}{21}$	$\frac{25\sqrt{330}}{1617}$	$\frac{151\sqrt{13}}{1274}$	$\frac{10\sqrt{77\cdot 15}}{1617}$
$(111)(20)^5G$	$\frac{-10\sqrt{2310}}{4851}$	$\frac{-34\sqrt{70}}{539}$	$\frac{\sqrt{165}}{1386}$	$\frac{38\sqrt{35}}{231}$	$\frac{-5\sqrt{385}}{462}$	$\frac{38\sqrt{182}}{539}$	$\frac{10\sqrt{77\cdot 15}}{1617}$	$\frac{-15\sqrt{13}}{154}$

[a] See the footnote to Table XVA.

Table XVIA. $(f^6(\psi')\ p\,^6L'''\|C^{(k)}\|f^6(210)(20)\,^5Dp\ ^6P)$.

ψ'' \ L'''	1	2	3		4	5
	k=2	k=2	k=2	k=4	k=4	k=4
$(210)(20)^5D$	$\frac{-16\sqrt{2}}{210\sqrt{15}}$	$\frac{-29\sqrt{2}}{18\cdot 35}$	$\frac{-142\sqrt{2}}{9\cdot 35\sqrt{35}}$	$\frac{32\sqrt{6}}{63\sqrt{7}}$	0	0
$(210)(21)^5D$	$\frac{-\sqrt{22}}{7\sqrt{5}}$	$\frac{-\sqrt{22}}{7\sqrt{3}}$	$\frac{-2\sqrt{22}}{7\sqrt{105}}$	$\frac{-19\sqrt{2}}{14\sqrt{77}}$	0	0
$(111)(20)^5D$	$\frac{-67\sqrt{21}}{9\cdot 35\sqrt{5}}$	$\frac{-67\sqrt{7}}{9\cdot 35}$	$\frac{-134}{9\cdot 35\sqrt{5}}$	$\frac{-4\sqrt{3}}{63}$	0	0
$(210)(21)^5F$	0	$\frac{-4\sqrt{11}}{5\sqrt{21}}$	$\frac{-2\sqrt{22}}{15\sqrt{21}}$	$\frac{-11\sqrt{10}}{24\sqrt{77}}$	$\frac{-11\sqrt{6}}{24\sqrt{77}}$	0
$(111)(10)^5D$	0	$\frac{-32}{15\sqrt{21}}$	$\frac{-16\sqrt{2}}{15\sqrt{21}}$	$\frac{-\sqrt{10}}{3\sqrt{7}}$	$\frac{-\sqrt{6}}{3\sqrt{7}}$	0
$(210)(20)^5G$	0	0	$\frac{-64\sqrt{11}}{105\sqrt{7}}$	$\frac{13\sqrt{55}}{18\cdot 7\sqrt{21}}$	$\frac{13\sqrt{15}}{18\cdot 35\sqrt{11}}$	$\frac{26\sqrt{15}}{105\cdot 99}$
$(210)(21)^5G$	0	0	$\frac{2\sqrt{30\cdot 13}}{21\sqrt{7}}$	$\frac{19\sqrt{26}}{24\cdot 7\sqrt{7}}$	$\frac{19\sqrt{26}}{8\cdot 35}$	$\frac{19\sqrt{26}}{210\sqrt{11}}$
$(111)(20)^5G$	0	0	$\frac{4\sqrt{22}}{105}$	$\frac{-5\sqrt{30\cdot 11}}{63\cdot 33}$	$\frac{-\sqrt{30\cdot 77}}{63\cdot 11}$	$\frac{-4\sqrt{210}}{27\cdot 77}$

Table XVIB. $(f^6(\psi'')p\,^6L''''\|C^{(k)}\|f^6(210)(21)^5Dp\ ^6P)$

ψ'' \ L''''	1 k=2	2 k=2	3 k=2	3 k=4	4 k=4	5 k=4
$(210)(20)^5D$	$\frac{-\sqrt{22}}{7\sqrt{5}}$	$\frac{-\sqrt{22}}{7\sqrt{3}}$	$\frac{-2\sqrt{22}}{7\sqrt{105}}$	$\frac{-19\sqrt{2}}{14\sqrt{77}}$	0	0
$(210)(21)^5D$	$\frac{-27\sqrt{2}}{35\sqrt{15}}$	$\frac{16\sqrt{2}}{35}$	$\frac{-2\cdot 79\sqrt{2}}{35\sqrt{35}}$	$\frac{5\cdot 59\sqrt{6}}{42\cdot 11\sqrt{7}}$	0	0
$(111)(20)^5D$	$\frac{-2\sqrt{11}}{5\sqrt{35}}$	$\frac{-2\sqrt{77}}{35\sqrt{3}}$	$\frac{-4\sqrt{11}}{35\sqrt{15}}$	$\frac{6}{7\sqrt{11}}$	0	0
$(210)(21)^5F$	0	$\frac{6}{5\sqrt{7}}$	$\frac{3\sqrt{2}}{5\sqrt{7}}$	$\frac{-\sqrt{30}}{11\sqrt{7}}$	$\frac{-6}{11\sqrt{14}}$	0
$(111)(10)^5F$	0	$\frac{-2\sqrt{11}}{5\sqrt{7}}$	$\frac{-\sqrt{22}}{5\sqrt{7}}$	$\frac{\sqrt{30}}{3\sqrt{77}}$	$\frac{\sqrt{2}}{\sqrt{77}}$	0
$(210)(20)^5G$	0	0	$\frac{8\sqrt{3}}{105\sqrt{7}}$	$\frac{-85\sqrt{5}}{21\cdot 11\sqrt{7}}$	$\frac{-17\sqrt{5}}{77}$	$\frac{-4\cdot 17\sqrt{5}}{21\cdot 11\sqrt{11}}$
$(210)(21)^5G$	0	0	$\frac{\sqrt{22\cdot 13}}{7\sqrt{35}}$	$\frac{2\sqrt{66\cdot 13}}{21\cdot 11\sqrt{7}}$	$\frac{2\sqrt{66\cdot 13}}{35\cdot 11}$	$\frac{8\sqrt{6\cdot 13}}{15\cdot 77}$
$(111)(20)^5G$	0	0	$\frac{31\sqrt{6}}{105}$	$\frac{-17\sqrt{10}}{21\cdot 11}$	$\frac{-17\sqrt{70}}{35\cdot 11}$	$\frac{-4\cdot 17\sqrt{70}}{15\cdot 77\sqrt{11}}$

Table XVIC. $(f^6(\psi'')\ p^6L'''\|C^{(k)}\|f^6(111)(20)^5D_p\ {}^6P)$

ψ'' \ L'''	1	2	3		4	5
	k=2	k=2	k=2	k=4	k=4	k=4
$(210)(20)^5D$	$\frac{-67\sqrt{7}}{105\sqrt{15}}$	$\frac{-67\sqrt{7}}{9\cdot 35}$	$\frac{-134}{9\cdot 35\sqrt{5}}$	$\frac{-4\sqrt{3}}{63}$	0	0
$(210)(21)^5D$	$\frac{-2\sqrt{77}}{35\sqrt{5}}$	$\frac{-2\sqrt{77}}{35\sqrt{3}}$	$\frac{-4\sqrt{11}}{35\sqrt{15}}$	$\frac{6}{7\sqrt{11}}$	0	0
$(111)(20)^5D$	$\frac{4\sqrt{2}}{15\sqrt{15}}$	$\frac{-\sqrt{2}}{9}$	$\frac{-4\cdot 43\sqrt{2}}{45\sqrt{35}}$	$\frac{-2\sqrt{6}}{9\sqrt{7}}$	0	0
$(210)(21)^5F$	0	$\frac{4\sqrt{22}}{15\sqrt{3}}$	$\frac{4\sqrt{11}}{15\sqrt{3}}$	$\frac{-5\sqrt{5}}{6\sqrt{11}}$	$\frac{-5}{2\sqrt{33}}$	0
$(111)(10)^5F$	0	$\frac{-4\sqrt{2}}{15\sqrt{3}}$	$\frac{-4}{15\sqrt{3}}$	$\frac{-\sqrt{5}}{12}$	$\frac{-\sqrt{3}}{12}$	0
$(210)(20)^5G$	0	0	$\frac{4\sqrt{22}}{105}$	$\frac{-5\sqrt{30}}{189\sqrt{11}}$	$\frac{-2\sqrt{35}}{21\sqrt{66}}$	$\frac{-4\sqrt{30}}{9\cdot 33}$
$(210)(21)^5G$	0	0	$\frac{4\sqrt{39}}{21\sqrt{5}}$	$\frac{-\sqrt{13}}{14}$	$\frac{-3\sqrt{13}}{10\sqrt{7}}$	$\frac{-2\sqrt{13}}{5\sqrt{77}}$
$(111)(20)^5G$	0	0	$\frac{4\sqrt{11}}{15\sqrt{7}}$	$\frac{\sqrt{15}}{108\sqrt{77}}$	$\frac{\sqrt{15}}{36\cdot 5\sqrt{11}}$	$\frac{\sqrt{15}}{27\cdot 55}$

Table XVII. $(f^7(110)(10)\,{}^6P|\sum_{i<j} 1/r_{ij}|f^6(W'U'S'L')p\;{}^6P)$

ψ'	X = first term in Eq. (2)	Y = second term in Eq. (2)	Total Matrix Element
$(210)(20)\,{}^5D$	$\frac{-12}{35\sqrt{30}}R^2(4f4f,4f6p)$ $+\frac{5}{14\sqrt{30}}R^4(4f4f,4f6p)$	$\frac{-12}{35\sqrt{30}}R^2(4f4f,4f6p)$ $+\frac{5}{14\sqrt{30}}R^4(4f4f,4f6p)$	$\frac{-24}{35\sqrt{30}}R^2(4f4f,4f6p)$ $+\frac{5}{7\sqrt{30}}R^4(4f4f,4f6p)$
$(210)(21)\,{}^5D$	$\frac{3\sqrt{11}}{35\sqrt{10}}R^2(4f4f,4f6p)$ $\frac{10\sqrt{11}}{21\cdot 11\sqrt{10}}R^4(4f4f,4f6p)$	$\frac{3\sqrt{11}}{35\sqrt{10}}R^2(4f4f,4f6p)$ $\frac{10\sqrt{11}}{21\cdot 11\sqrt{10}}R^4(4f4f,4f6p)$	$\frac{6\sqrt{11}}{35\sqrt{10}}R^2(4f4f,4f6p)$ $+\frac{20\sqrt{11}}{21\cdot 11\sqrt{10}}R^4(4f4f,4f6p)$
$(111)(20)\,{}^5D$	0	0	0

c.f.p. for which there are no sum rules known. There is also the problem that the c.f.p. have no analytic form which nearly always forces one to reduce the problem to specific cases. A formula which is just twice the second term obtained above has recently been derived by Wybourne for the matrix elements of $C_i^{(k)} \cdot C_j^{(k)}$ between the configurations ℓ^n and $\ell^{n-1}\ell'$.[51] This proves that the equality always holds when $\ell \neq \ell'$. For $\ell = \ell'$ matrix elements of $C_i^{(k)} \cdot C_i^{(k)}$ must be subtracted out but the equality still holds (see Sec. II-B). Judd has been able to give an explicit proof of this relationship.[15] It is surprising that a division of a summation over all intermediate states into sums over two different kinds of intermediates should divide the sum into two equal parts. If there is some group theoretical reason for this it is not obvious at this time.

B. Results and Discussion

Since the operator equivalent factor α in f^7 is zero the crystal field matrix elements for the ^6P states of Gd^{+3} become, to first order in the configuration interaction

$$(f^7(110)(11)^6P|V_2^0|f^7(110)(11)^6P) = -2 \sum_{\psi'} \frac{(f^7(110)(11)^6P|Q|f^6(\psi')p\ ^6P)}{\Delta E}$$

$$\times\ (f^6(\psi')^6P\ JJ_z|V_2^0|f^7(110)(11)^6P\ JJ_z)$$

$$= -2 \sum_{\psi'} \frac{(f^7(110)(11)^6P|Q|f^6(\psi')p^6P)}{\Delta E}\ \alpha_{fp}(\psi')\ A_2^0 < r^2_{fp} > [3J_z^2 - J(J+1)],$$

where the Coulomb matrix elements are given in Table XVII and the operator equivalent factors in Table XI. No radial wave functions for Gd^{+3} are available for evaluating the radial integrals involved in the Coulomb matrix elements, but a reasonable estimate may be made by

interpolating between the Pr^{+3} and Tm^{+3} integrals given in Table V. This gives

$$\Delta E = 0.540 \text{ a.u.}$$
$$R^2(4f4f, 4f6p) = -0.0199 \text{ a.u.}$$
$$R^4(4f4f, 4f6p) = -0.0120 \text{ a.u.}$$
$$\langle r^2_{fp} \rangle = .74 \text{ (a.u.)}^2$$
$$\langle r^2_{ff} \rangle = 1.10 \text{ (a.u.)}^2.$$

Substituting these numbers in the matrix elements in Table XVII, and using the operator equivalent factors in Table XI, we obtain

J	$\sum_{\psi'} \frac{(f^7(110)(10)^6P\|Q\|f^6(\psi')p\ ^6P)}{\Delta E} \alpha_{fp}(\psi')$
7/2	0.0663×10^{-3}
5/2	-0.159×10^{-3}
1/2	0.0928×10^{-3}

Figure 8 shows the observed spectrum along with that calculated by Judd for mechanisms 1 and 2 and that obtained above for mechanism 3. The relative spacings within a level are the same for all three mechanisms, except that for $J = 5/2$ the crystal field levels are inverted by mechanisms 2 and 3 relative to mechanism 1. Since the parameters necessary to calculate absolute splittings are not available, it is perhaps more meaningful to consider the total splitting of the 7/2 level relative to that of the 5/2 level. If the overall splitting of the $J = 7/2$ level is denoted by $s_{7/2}$ and that of the 5/2 level by $s_{5/2}$ the observed ratio $\frac{s_{7/2}}{s_{5/2}} \approx 1$, whereas the ratio calculated from spin orbit interaction is 2.08, and that from second-order crystal field effects or configuration interaction is -0.83. Since mechanisms 2 and 3 also have the same J dependence, it

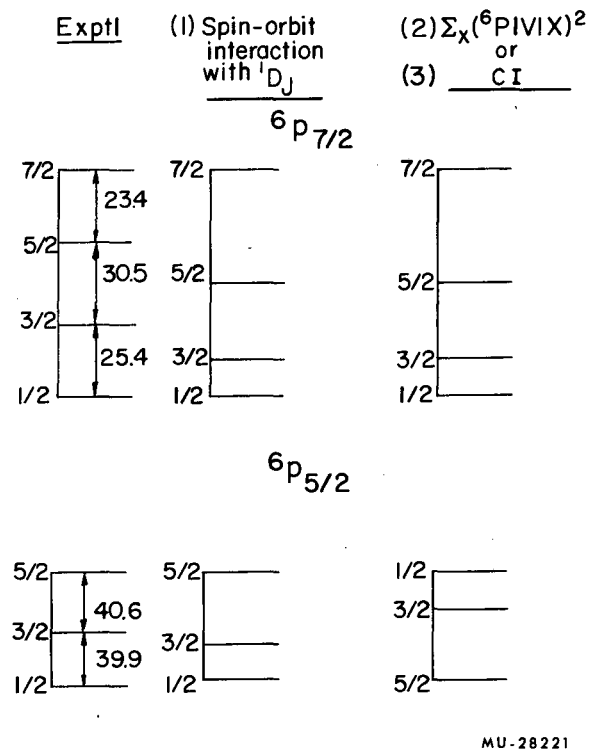

Fig. 8. Experimental splitting of the $^6P_{7/2}$ and $^6P_{5/2}$ levels of $GdCl_3 \cdot 6H_2O$ and relative spacing due to spin-orbit interaction with ^1D_J, second-order crystal field effects, and configuration interaction.

is impossible to distinguish between them on the basis of relative splittings alone. However, it is possible to calculate that part of the overall splittings $s_{7/2}$ and $s_{5/2}$ which would have to come from mechanisms 2 and 3 in order for the two to be nearly equal. The result is that about 30% of the energy difference between $|^6P_{7/2}\ 7/2>$ and $|^6P_{7/2}\ 1/2>$ must come from mechanisms 2 and 3. If all of this were to come from configuration interaction, it would require $A_2^0 < r^2_{fp}> =$ 10400 cm^{-1}. The only crystal field parameters that have been determined for hydrated rare-earth chlorides are those of Eisenstein for $YbCl_3 \cdot 6H_2O$.[49] He obtained $A_2^0 < r^2_{ff}> = 48.2\ cm^{-1}$. If one assumes that the value of $A_2^0 < r^2_{ff}>$ is not greatly different in the Yb and Gd compounds this would imply that an $A_2^0 < r^2_{fp}>$ of about 39 cm^{-1} could be expected for $GdCl_3 \cdot 6H_2O$. Even if a screening factor of 10 to 15 were allowed (see Sec. III-A), this would give $A_2^0 < r^2_{fp}>$ of only 400 to 600 cm^{-1}, still a factor of $\sim$ 20 too small. This means that either the radial integrals are wrong by a factor of $\approx$ 20, which in view of the results in Sec. IV seems unlikely, or configuration interaction with $4f^6 6p$ can account for perhaps 1 cm^{-1} of the observed 80 cm^{-1} splitting of the $^6P_{7/2}$ state. Thus the greater part of the splitting must arise from spin orbit interaction and second-order crystal field effects, interaction with some configuration other than $4f^6 6p$, or some higher-order mechanism that has not yet been considered.

VII. CONCLUSIONS

In the case of $PrCl_3$, configuration interaction is certainly not negligible. Because the corrections to the Stark levels involve sums of many terms, often with opposite signs, it is possible that more accurate knowledge of the parameters involved would decrease the unreasonably large shifts in some of the $^1G_4$ and $^3H_5$ levels, and also improve the fit of the $^1D_2$ levels. However, this will require more extensive experimental data on the higher configurations, as well as wave functions for Pr^{+3} in the chloride crystal. Until these are available, further calculations can be expected to give only qualitative results.

The only other approach is to put the necessary $R^k(4f4f,4fn'\ell')$ integrals into the intermediate coupling calculations and determine them to give the best fit to the experimental spectrum. However, such a calculation should also include interaction with $5d^2$ and other 2 electron excitations and there are soon more parameters than terms. Even if this could be done there still remains the problems of shielding and the different values of A_2^0 in $A_2^0 < r^2 >$ and $A_2^0 < r^2_{f\ell'} >$. Thus at the present time, there does not seem to be much hope for appreciable improvement of these calculations. It does not seem, however, that the discrepancies in the $^1D_2$ levels can be explained by any one mechanism and they must arise from the sum of many small terms.

For $GdCl_3 \cdot 6H_2O$ slightly more definite conclusions may be drawn. Without assuming unreasonably large values of $A_2^0 < r^2 >$, the interaction of $4f^7$ with $4f^6 6p$ cannot explain more than about 1 cm^{-1} of the 80 cm^{-1} splitting of the $^6P_{7/2}$ level. However, judging from the results for the $PrCl_3$, interaction with $4f^6 5f$ may be quite important. But until more

experimental data are available so that exact contributions from the spin-orbit and ctystal field acting linearly and second-order crystal field effects within the configuration f^7 can be determined it does not seem worthwhile to undertake such a tedious calculation.

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APPENDICES

A. Matrix Elements $(\ell^2||C_i^{(k)}\cdot C_j^{(k)}||\ell\ell')$

For the case of 2 electrons it may be shown that the 2 summations in Eq. (13) are equal and that the expression for the matrix elements of Q between the configurations ℓ^2 and $\ell\ell'$ as obtained from Eq. (13) reduces to that which could be obtained more easily from Eq. (6).

First let

$$X = \Sigma_{\psi''}(-1)^{L-L''}(\ell^n\alpha SL||\Sigma_i C_i^{(k)}||\ell^n\alpha''S''L'')$$

$$\times\ (\ell^n\alpha''S''L''||\Sigma_i C_i^{(k)}||\ell^{n-1}(\alpha'S'L')\ell'SL) = \Sigma_{\psi''}(-1)^{L-L''}A\cdot B,$$

and

$$Y = \Sigma_{\psi''}\Sigma_{\psi'''}(-1)^{L-L''}(\ell^n\alpha SL||\Sigma_i C_i^{(k)}||\ell^{n-1}(\alpha'''S'''L''')\ell'SL'')$$

$$\times\ (\ell^{n-1}(\alpha'''S'''L''')\ell'SL''||\Sigma_i C_i^{(k)}||f^{n-1}(\alpha'S'L')\ell'S\ L)$$

$$= \Sigma_{\psi''}\Sigma_{\psi'''}(-1)^{L-L''}C\cdot D.$$

The problem is then to show under what conditions X = Y. Using (27)III and Eq. (8) to partially evaluate B, one obtains

$$X = \Sigma_{\psi''}(-1)^{L+L'+\ell'+k}\sqrt{n}\ (\ell||C^{(k)}||\ell')(\ell^n\alpha SL||\Sigma_i C_i^{(k)}||\ell^n\alpha''SL'')$$

$$\times\ \left(\ell^n\alpha''SL''\left\{|\ \ell^{n-1}(\alpha'S'L')SL''\right)\left[(2L+1)(2L''+1)\right]^{1/2}\begin{Bmatrix}\ell & L'' & L\\ L & \ell' & k\end{Bmatrix}\right.\ .$$

If we let n = 2, then $L' = \ell$, and all the c.f.p. = 1. This gives

$$X = \Sigma_{\psi''}(-1)^{L+\ell+\ell'+k}\left[2(2L+1)(2L''+1)\right]^{1/2}(\ell||C^{(k)}||\ell')$$

$$\times\ (\ell^2\alpha SL||\Sigma_i C_i^{(k)}||\ell^2\alpha''S\ L'')\begin{Bmatrix}\ell & L'' & \ell\\ L & \ell' & k\end{Bmatrix}\ .$$

If $\Sigma_i C_i^{(k)}$ is now broken into its two separate parts, and formulae (7) and (8) are applied to the matrix elements of $C_1^{(k)}$ and $C_2^{(k)}$ respectively, one obtains

$$X = \Sigma_{L''} (2L+1)(2L''+1)\sqrt{2}\,(\ell||C^{(k)}||\ell')(\ell||C^{(k)}||\ell)(-1)^{L+\ell+\ell'+L''}$$

$$\times \begin{Bmatrix} \ell & L'' & \ell \\ L & \ell' & k \end{Bmatrix} \begin{Bmatrix} \ell & L & \ell \\ L'' & \ell & k \end{Bmatrix}$$

$$+ \Sigma_{L''}(2L+1)(2L''+1)\sqrt{2}\,(\ell||C^{(k)}||\ell')(\ell||C^{(k)}||\ell)(-1)^{L+\ell+\ell'+L}$$

$$\times \begin{Bmatrix} \ell & L'' & \ell \\ L & \ell' & k \end{Bmatrix} \begin{Bmatrix} \ell & L & \ell \\ L'' & \ell & k \end{Bmatrix}$$

There are two sum rules involving products of 6-j symbols which may be applied to simplify these expressions:[51]

$$\Sigma_{j_{23}} (-1)^{j_{23}+j_{31}+j_{12}}(2j_{23}+1) \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix} \begin{Bmatrix} j_2 & j_3 & j_{23} \\ j_1 & j & j_{31} \end{Bmatrix} = \begin{Bmatrix} j_3 & j_1 & j_{31} \\ j_2 & j & j_{12} \end{Bmatrix} .$$

By rearranging the rows of the 6-j symbols and applying this formula one obtains

$$\Sigma_{L''}(-1)^{L+\ell'+\ell\ L''}(2L''+1) \begin{Bmatrix} \ell & L'' & \ell \\ L & \ell' & k \end{Bmatrix} \begin{Bmatrix} \ell & L & \ell \\ L'' & \ell & k \end{Bmatrix} = (-1)^L \begin{Bmatrix} \ell & L & \ell \\ \ell & k & \ell' \end{Bmatrix} .$$

Similarly, using the relationship

$$\Sigma_j (2j+1)(2j''+1) \begin{Bmatrix} j_1 & j_2 & j' \\ j_3 & j_4 & j \end{Bmatrix} \begin{Bmatrix} j_3 & j_2 & j \\ j_1 & j_4 & j'' \end{Bmatrix} = \delta\,(j',j'')$$

on the second term, one obtains

$$\Sigma_{L''}(2L''+1) \begin{Bmatrix} L & \ell & \ell' \\ \ell & k & L'' \end{Bmatrix} \begin{Bmatrix} \ell & \ell & L'' \\ L & k & \ell \end{Bmatrix} = \frac{\delta(\ell',\ell)}{(2\ell+1)} .$$

This gives, for n = 2

$$X = (2L+1)\sqrt{2}\,(\ell||C^{(k)}||\ell')(\ell||C^{(k)}||\ell) \left[(-1)^L \begin{Bmatrix} \ell & L & \ell \\ \ell & k & \ell' \end{Bmatrix} + \frac{\delta(\ell,\ell')}{(2\ell+1)} \right] .$$

In an exactly analogous manner, by first evaluating D, putting n = 2, using Eqs. (7) and (8) on the two parts of C, and using the sum rules an expression for Y is obtained.

$$Y = (2L+1)\sqrt{2}\,(\ell||C^{(k)}||\ell')(\ell||C^{(k)}||\ell)\left[(-1)^L \begin{Bmatrix} \ell' & L & \ell \\ \ell & k & \ell \end{Bmatrix} + \frac{\delta(\ell,\ell')}{(2\ell'+1)}\right].$$

Owing to the symmetry relations for the 6-j symbol, the two 6-j symbols are equal. Thus for any $\ell \neq \ell'$,

$$X = Y = (2L+1)\sqrt{2}\,(\ell||C^{(k)}||\ell')(\ell||C^{(k)}||\ell)(-1)^L \begin{Bmatrix} \ell' & L & \ell \\ \ell & k & \ell \end{Bmatrix}. \qquad \text{(A-1)}$$

The correction for $\ell = \ell'$ (see Sec. II-B) is merely to subtract the delta function term so that Eq. (A-1) is applicable for any ℓ'.

From Eqs. (12) and (13), we obtain

$$(\ell^2 SL||\sum_{i<j} C_i^{(k)} \cdot C_j^{(k)}||\ell\ell' SL) = \frac{1}{2}(\ell^2 SL||\left[\Sigma_i C_i^{(k)}\right]^2||\ell\ell' SL) = \frac{2X}{2(2L+1)},$$

or

$$(\ell^2 SL||\sum_{i<j} C_i^{(k)} \cdot C_j^{(k)}||\ell\ell' SL) = (-1)^L\sqrt{2}\,(\ell||C^{(k)}||\ell')(\ell||C^{(k)}||\ell) \begin{Bmatrix} \ell' & L & \ell \\ \ell & k & \ell \end{Bmatrix}. \qquad \text{(A-2)}$$

Except for a factor of $(-1)^{\ell+\ell'}\sqrt{2}$ this is the same result that would have been obtained by using Eq. (6) instead of Eqs. (12) and (13). Since Q acts only between configurations of the same parity, $\ell+\ell'$ is always even. The $\sqrt{2}$ arises from the fact that $|\ell\ell'>$ is really $(1/\sqrt{2})$ $(|\ell\ell'> \pm |\ell\ell'>)$, which gives two identical matrix elements, or a factor of $(2/\sqrt{2}) = \sqrt{2}$ times the result computed by Eq. (6). In using (27)III of Racah, this is automatically taken into account.

B. Corrections to α, β, and γ from $\frac{(f^2SL|Q|f\ell'SL)^2}{(\Delta E)^2}(f\ell'SLJJ_z|V|f\ell'SLJJ_z')$

To compute the effect of terms quadratic in

$$a=\frac{(f^2SL|Q|f\ell'SL)}{\Delta E}$$

in Eq. (26), matrix elements of the form

$$(f\ell'SLJJ_z|V_2^0|f\ell'SLJJ_z) = 2A_2^0\,(-1)^{J-J_z}\begin{pmatrix} J & 2 & J \\ -J_z & 0 & J_z \end{pmatrix}$$

$$\times\left[(f\ell'SLJ\|C_f^{(2)}\|f\ell'SLJ) < r_{ff}^2 > + (f\ell'SLJ\|C_{\ell'}^{(2)}\|f\ell'SLJ) < r_{\ell'\ell'}^2 >\right]$$

$$=\left[\alpha_{ff}^{\ell'} A_2^0 < r_{ff}^2 > + \alpha_{\ell'\ell'}^{f} A_2^0 < r_{\ell'\ell'}^2 > f_1(J,J_z)\right] \qquad \text{(B-1)}$$

are necessary. The operator equivalent factors are given by

$$\alpha_{ff}^{p} = \frac{56}{\sqrt{105}}(-1)^{3J+S+3}(2J+1)(2L+1)\left[\frac{(2J-2)!}{(2J+3)!}\right]^{\frac{1}{2}}\begin{Bmatrix} L & J & S \\ J & L & 2 \end{Bmatrix}\begin{Bmatrix} 3 & L & 1 \\ L & 3 & 2 \end{Bmatrix},$$

$$\alpha_{pp}^{f} = \frac{12\sqrt{2}}{\sqrt{15}}(-1)^{S+3J+1}(2J+1)(2L+1)\left[\frac{(2J-2)!}{(2J+3)!}\right]^{\frac{1}{2}}\begin{Bmatrix} L & J & S \\ J & L & 2 \end{Bmatrix}\begin{Bmatrix} 1 & L & 3 \\ L & 1 & 2 \end{Bmatrix}, \qquad \text{(B-2)}$$

$$\alpha_{ff}^{f'} = \alpha_{f'f'}^{f} = \frac{1}{2}\alpha_{ff},$$

$$\beta_{ff}^{p} = \frac{28\sqrt{2}}{\sqrt{77}}(-1)^{3J+S}(2L+1)(2J+1)\left[\frac{(2J-4)!}{(2J+5)!}\right]^{\frac{1}{2}}\begin{Bmatrix} L & J & S \\ J & L & 4 \end{Bmatrix}\begin{Bmatrix} 3 & L & 1 \\ L & 3 & 4 \end{Bmatrix},$$

$$\beta_{pp}^{f} = 0,$$

$$\beta_{ff}^{f'} = \beta_{f'f'}^{f} = \frac{1}{2}\beta_{ff},$$

$$\gamma_{ff}^{f'} = \beta_{f'f'}^{f} = \frac{1}{2}\gamma_{ff}.$$

The correction to α is then

$$\frac{\alpha^{\ell'}_{ff}}{\alpha_{ff}} + \frac{\alpha^{f}_{\ell'\ell'}}{\alpha_{ff}} \frac{< r^2_{\ell'\ell'} >}{< r^2_{ff} >} ,$$

with similar expressions for the corrections to β and γ. Using the expressions in Eq. (B-2) and the results in Tables I, II, V, and VI, these corrections can be calculated for the various terms of f^2. In all cases the largest contribution is from the second term in Eq. (B-1) because of the relatively large values of $< r^k_{\ell'\ell'} >$.

Table B-I shows the resulting correction along with those from the terms linear in a. The quadratic terms are in most cases less than 10% of the linear terms. The exception is in the corrections to γ. These corrections can only be regarded as approximate, however, since they depend on $< r^6_{f'f'} >$, which is highly dependent on the exact form of the 5f wave function. Therefore they were neglected in the calculation. The a and a^2 corrections to γ are all of opposite sign, however, and if the second-order terms really are as large as shown in Table B-I, they will decrease the computed shifts given in Sec. V.

Table B-I. Corrections to α, β, and γ.

	$\frac{\alpha}{\alpha_{ff}}-1$			
	6p		5f	
	from a	from a^2	from a	from a^2
^3P	—	—	.025	—
^1D	-.037	-.001	.010	.000
^3F	-.031	.002	-.013	.000
^1G	.088	.015	-.011	.000
^3H	—	—	-.023	.001

	$\frac{\beta}{\beta_{ff}}-1$				$\frac{\gamma}{\gamma_{ff}}-1$	
	6p		5f		5f	
	from a	from a^2	from a	from a^2	from a	from a^2
^1D	.019	.000	.039	.002	—	—
^3F	.173	.000	-.051	.004	-.158	.029
^1G	-.144	.000	-.045	.003	-.140	.019
^3H	—	—	-.092	.012	-.285	.079

C. Radial Wave Functions For Pr^{+3} and Tm^{+3}

Table C-I. Radial Wave Functions, P(r), for Pr^{+3}

r (atomic units)	4f	5d	6s	6p	5f
.01	.0000	.0008	-.0611	.0141	.0000
.02	.0002	.0055	-.0554	.0412	.0000
.03	.0008	.0155	-.0190	.0677	-.0002
.04	.0022	.0305	.0247	.0867	-.0005
.05	.0047	.0496	.0630	.0960	-.0011
.06	.0086	.0715	.0900	.0953	-.0021
.07	.0141	.0948	.1040	.0860	-.0034
.08	.0214	.1183	.1055	.0698	-.0051
.09	.0304	.1408	.0964	.0487	-.0073
.10	.0414	.1616	.0788	.0245	-.0100
.11	.0541	.1798	.0553	-.0010	-.0130
.12	.0687	.1950	.0281	-.0266	-.0165
.13	.0849	.2070	-.0008	-.0509	-.0204
.14	.1027	.2154	-.0297	-.0733	-.0247
.15	.1220	.2202	-.0572	-.0929	-.0293
.16	.1426	.2216	-.0823	-.1094	-.0343
.17	.1643	.2196	-.1042	-.1225	-.0395
.18	.1871	.2144	-.1224	-.1322	-.0449
.19	.2108	.2062	-.1368	-.1384	-.0506
.20	.2352	.1954	-.1470	-.1412	-.0564
.21	.2602	.1821	-.1532	-.1409	-.0624
.22	.2857	.1666	-.1556	-.1376	-.0685
.23	.3116	.1493	-.1542	-.1317	-.0746
.24	.3376	.1304	-.1495	-.1233	-.0808
.25	.3639	.1102	-.1417	-.1129	-.0871
.26	.3901	.0890	-.1312	-.1006	-.0933
.27	.4163	.0669	-.1184	-.0868	-.0995
.28	.4423	.0442	-.1035	-.0718	-.1056
.29	.4680	.0212	-.0870	-.0558	-.1116

r (atomic units)	4f	5d	6s	6p	5f
.30	.4934	-.0020	-.0691	-.0391	-.1176
.31	.5184	-.0252	-.0503	-.0220	-.1235
.32	.5430	-.0482	-.0308	-.0046	-.1292
.33	.5670	-.0709	-.0109	.0129	-.1347
.34	.5903	-.0931	.0091	.0302	-.1402
.35	.6131	-.1147	.0290	.0473	-.1454
.36	.6352	-.1356	.0487	.0639	-.1504
.37	.6565	-.1558	.0677	.0799	-.1553
.38	.6772	-.1750	.0862	.0953	-.1600
.39	.6970	-.1934	.1038	.1098	-.1645
.40	.7161	-.2107	.1205	.1236	-.1687
.41	.7343	-.2271	.1361	.1364	-.1728
.42	.7518	-.2423	.1506	.1482	-.1766
.43	.7684	-.2565	.1639	.1590	-.1802
.44	.7842	-.2695	.1760	.1688	-.1836
.45	.7993	-.2815	.1867	.1775	-.1868
.46	.8135	-.2923	.1962	.1851	-.1898
.47	.8269	-.3019	.2044	.1917	-.1926
.48	.8395	-.3105	.2112	.1972	-.1951
.49	.8514	-.3180	.2167	.2017	-.1975
.50	.8625	-.3233	.2210	.2051	-.1996
.52	.8826	-.3339	.2257	.2089	-.2033
.54	.8998	-.3394	.2257	.2089	-.2063
.56	.9145	-.3410	.2212	.2054	-.2086
.58	.9268	-.3392	.2128	.1986	-.2101
.60	.9368	-.3340	.2007	.1890	-.2111
.62	.9448	-.3258	.1855	.1767	-.2115
.64	.9509	-.3148	.1675	.1622	-.2113
.66	.9552	-.3014	.1472	.1457	-.2107
.68	.9580	-.2858	.1250	.1277	-.2096
.70	.9593	-.2683	.1013	.1082	-.2080

r (atomic units)	4f	5d	6s	6p	5f
.72	.9593	-.2490	.0764	.0877	-.2061
.74	.9580	-.2282	.0507	.0664	-.2037
.76	.9557	-.2061	.0245	.0445	-.2011
.78	.9523	-.1828	-.0019	.0222	-.1981
.80	.9481	-.1587	-.0284	-.0002	-.1948
.82	.9430	-.1338	-.0546	-.0227	-.1912
.84	.9371	-.1083	-.0803	-.0450	-.1874
.86	.9306	-.0824	-.1054	-.0670	-.1833
.88	.9234	-.0560	-.1298	-.0885	-.1790
.90	.9157	-.0295	-.1532	-.1096	-.1745
.92	.9074	-.0029	-.1756	-.1299	-.1698
.94	.8987	.0237	-.1969	-.1496	-.1649
.96	.8896	.0503	-.2170	-.1684	-.1599
.98	.8801	.0767	-.2358	-.1864	-.1547
1.00	.8703	.1029	-.2532	-.2035	-.1494
1.10	.8174	.2282	-.3197	-.2741	-.1209
1.20	.7608	.3406	-.3514	-.3187	-.0902
1.30	.7030	.4371	-.3514	-.3380	-.0581
1.40	.6461	.5171	-.3247	-.3349	-.0253
1.50	.5913	.5811	-.2771	-.3128	-.0078
1.60	.5395	.6304	-.2145	-.2758	.0408
1.70	.4911	.6665	-.1418	-.2272	.0736
1.80	.4464	.6912	-.0632	-.1705	.1058
1.90	.4053	.7060	-.0175	-.1083	.1375
2.00	.3676	.7125	.0978	-.0431	.1685
2.10	.3333	.7119	.1755	.0232	.1987
2.20	.3020	.7054	.2490	.0890	.2280
2.30	.2736	.6940	.3171	.1531	.2563
2.40	.2477	.6786	.3791	.2144	.2835
2.50	.2242	.6600	.4344	.2721	.3096
2.60	.2028	.6389	.4830	.3258	.3334
2.70	.1835	.6159	.5246	.3749	.3579

r (atomic units)	4f	5d	6s	6p	5f
2.80	.1659	.5914	.5595	.4192	.3799
2.90	.1499	.5659	.5878	.4587	.4005
3.00	.1354	.5397	.6098	.4931	.4195
3.10	.1223	.5132	.6260	.5226	.4369
3.20	.1103	.4866	.6367	.5474	.4527
3.30	.0995	.4603	.6424	.5675	.4669
3.40	.0897	.4343	.6436	.5832	.4794
3.50	.0808	.4088	.6407	.5946	.4903
3.60	.0728	.3840	.6342	.6022	.4996
3.70	.0655	.3599	.6245	.6062	.5072
3.80	.0589	.3367	.6121	.6068	.5133
3.90	.0529	.3145	.5974	.6044	.5178
4.00	.0476	.2932	.5807	.5992	.5209
4.25	.0363	.2442	.5328	.5764	.5226
4.50	.0276	.2016	.4796	.5427	.5166
4.75	.0209	.1651	.4249	.5018	.5038
5.00	.0158	.1341	.3712	.4570	.4857
5.25	.0119	.1083	.3204	.4107	.4632
5.50	.0089	.0868	.2737	.3648	.4376
5.75	.0066	.0693	.2316	.3207	.4099
6.00	.0050	.0550	.1943	.2794	.3809
6.25	.0037	.0434	.1618	.2415	.3514
6.50	.0027	.0341	.1338	.2071	.3220
6.75	.0020	.0267	.1100	.1765	.2933
7.00	.0015	.0209	.0900	.1494	.2656
7.25	.0011	.0162	.0732	.1259	.2392
7.50	.0008	.0126	.0592	.1054	.2145
7.75	.0006	.0097	.0477	.0879	.1914
8.00	.0004	.0075	.0383	.0730	.1700
8.25	.0003	.0057	.0306	.0604	.1505
8.50	.0002	.0044	.0244	.0497	.1326
8.75	.0002	.0034	.0194	.0408	.1165
9.00	.0001	.0026	.0153	.0334	.1020
9.25	.0001	.0020	.0121	.0272	.0890

r (atomic units)	4f	5d	6s	6p	5f
9.50	.0001	.0015	.0095	.0221	.0774
9.75	.0000	.0011	.0075	.0179	.0671
10.00	-	.0008	.0058	.0145	.0581
10.25	-	.0006	.0046	.0117	.0501
10.50	-	.0005	.0036	.0094	.0431
10.75	-	.0004	.0028	.0076	.0369
11.00	-	.0003	.0022	.0060	.0316
11.25	-	.0002	.0017	.0048	.0270
11.50	-	.0002	.0013	.0038	.0229
11.75	-	.0001	.0010	.0031	.0194
12.00	-	.0001	.0008	.0024	.0164
12.25	-	.0001	.0006	.0019	.0138
12.50	-	.0000	.0004	.0015	.0115
12.75	-	-	.0003	.0012	.0095
13.00	-	-	.0002	.0009	.0078
13.25	-	-	.0002	.0007	.0063
13.50	-	-	.0001	.0005	.0050

Table C-II. Radial Wave Functions, P(r), for Tm^{+3}

r (atomic units)	4f	5d	6s	6p	5f
.01	.0000	.0014	-.0639	.0183	.0000
.02	.0005	.0087	-.0459	.0505	-.0001
.03	.0024	.0235	.0024	.0780	-.0003
.04	.0064	.0448	.0510	.0929	-.0009
.05	.0135	.0705	.0863	.0938	-.0019
.06	.0242	.0981	.1036	.0824	-.0033
.07	.0388	.1254	.1036	.0617	-.0054
.08	.0575	.1508	.0893	.0349	-.0079
.09	.0803	.1727	.0645	.0051	-.0111
.10	.1069	.1902	.0332	-.0252	-.0148
.11	.1372	.2027	-.0009	-.0538	-.0189
.12	.1707	.2099	-.0351	-.0793	-.0236
.13	.2070	.2119	-.0669	-.1006	-.0286
.14	.2456	.2087	-.0949	-.1171	-.0339
.15	.2863	.2008	-.1178	-.1286	-.0394
.16	.3284	.1886	-.1350	-.1351	-.0452
.17	.3716	.1726	-.1464	-.1367	-.0512
.18	.4155	.1533	-.1519	-.1338	-.0572
.19	.4597	.1313	-.1520	-.1269	-.0632
.20	.5039	.1070	-.1470	-.1164	-.0692
.21	.5478	.0811	-.1375	-.1030	-.0752
.22	.5910	.0540	-.1240	-.0870	-.0810
.23	.6334	.0261	-.1073	-.0692	-.0868
.24	.6748	-.0021	-.0880	-.0499	-.0924
.25	.7148	-.0303	-.0666	-.0296	-.0977
.26	.7533	-.0582	-.0439	-.0088	-.1029
.27	.7903	-.0854	-.0202	.0122	-.1078
.28	.8256	-.1117	-.0038	.0330	-.1125
.29	.8590	-.1369	.0278	.0532	-.1168

r (atomic units)	4f	5d	6s	6p	5f
.30	.8906	-.1609	.0513	.0728	-.1210
.31	.9203	-.1834	.0740	.0913	-.1248
.32	.9480	-.2043	.0957	.1087	-.1284
.33	.9738	-.2236	.1160	.1248	-.1316
.34	.9977	-.2413	.1348	.1395	-.1346
.35	1.020	-.2572	.1519	.1527	-.1372
.36	1.040	-.2713	.1672	.1644	-.1396
.37	1.058	-.2837	.1807	.1745	-.1418
.38	1.074	-.2943	.1923	.1830	-.1436
.39	1.089	-.3032	.2020	.1898	-.1452
.40	1.102	-.3104	.2097	.1952	-.1466
.41	1.113	-.3160	.2155	.1990	-.1477
.42	1.123	-.3200	.2195	.2013	-.1486
.43	1.132	-.3225	.2217	.2022	-.1492
.44	1.138	-.3234	.2221	.2017	-.1496
.45	1.144	-.3231	.2209	.2000	-.1499
.46	1.149	-.3213	.2181	.1970	-.1499
.47	1.152	-.3183	.2139	.1928	-.1498
.48	1.154	-.3141	.2082	.1876	-.1495
.49	1.156	-.3088	.2013	.1813	-.1490
.50	1.156	-.3025	.1932	.1742	-.1484
.52	1.154	-.2868	.1737	.1573	-.1468
.54	1.149	-.2678	.1507	.1377	-.1446
.56	1.141	-.2459	.1247	.1157	-.1420
.58	1.131	-.2215	.0965	.0920	-.1390
.60	1.119	-.1951	.0668	.0670	-.1356
.62	1.105	-.1670	.0360	.0411	-.1320
.64	1.090	-.1376	.0047	.0147	-.1281
.66	1.074	-.1072	-.0266	-.0119	-.1239
.68	1.057	-.0761	-.0577	-.0384	-.1196
.70	1.039	-.0445	-.0880	-.0644	-.1150

r (atomic units)	4f	5d	6s	6p	5f
.72	1.021	-.0127	-.1175	-.0899	-.1103
.74	1.002	.0192	-.1457	-.1146	-.1055
.76	.9829	.0511	-.1726	-.1384	-.1005
.78	.9634	.0826	-.1979	-.1611	-.0955
.80	.9437	.1139	-.2215	-.1826	-.0903
.82	.9238	.1446	-.2433	-.2028	-.0851
.84	.9010	.1748	-.2633	-.2218	-.0798
.86	.8841	.2043	-.2814	-.2394	-.0744
.88	.8644	.2331	-.2976	-.2555	-.0690
.90	.8447	.2611	-.3119	-.2703	-.0635
.92	.8252	.2884	-.3242	-.2836	-.0580
.94	.8059	.3147	-.3347	-.2954	-.0525
.96	.7868	.3402	-.3432	-.3059	-.0469
.98	.7679	.3648	-.3500	-.3150	-.0413
1.00	.7493	.3885	-.3549	-.3227	-.0357
1.10	.6607	.4932	-.3553	-.3417	-.0075
1.20	.5804	.5756	-.3213	-.3324	.0208
1.30	.5089	.6380	-.2620	-.3004	.0490
1.40	.4457	.6828	-.1855	-.2516	.0770
1.50	.3903	.7128	-.0989	-.1908	.1048
1.60	.3419	.7305	-.0076	-.1224	.1325
1.70	.2996	.7381	.0840	-.0497	.1600
1.80	.2628	.7373	.1729	.0246	.1872
1.90	.2306	.7298	.2567	.0983	.2140
2.00	.2025	.7168	.3339	.1696	.2404
2.10	.1779	.6994	.4034	.2375	.2663
2.20	.1564	.6787	.4648	.3008	.2915
2.30	.1375	.6552	.5176	.3590	.3159
2.40	.1210	.6298	.5620	.4117	.3394
2.50	.1064	.6029	.5982	.4584	.3619
2.60	.0936	.5750	.6266	.4993	.3832
2.70	.0824	.5466	.6476	.5342	.4032

r (atomic units)	4f	5d	6s	6p	5f
2.80	.0725	.5179	.6617	.5632	.4219
2.90	.0637	.4894	.6695	.5867	.4392
3.00	.0560	.4611	.6717	.6048	.4549
3.10	.0493	.4333	.6689	.6180	.4691
3.20	.0433	.4063	.6616	.6264	.4818
3.30	.0380	.3800	.6506	.6305	.4928
3.40	.0334	.3547	.6363	.6307	.5023
3.50	.0293	.3304	.6192	.6274	.5102
3.60	.0257	.3072	.6000	.6209	.5165
3.70	.0226	.2851	.5789	.6117	.5213
3.80	.0198	.2641	.5565	.6000	.5246
3.90	.0173	.2443	.5331	.5863	.5266
4.00	.0152	.2256	.5090	.5708	.5271
4.25	.0109	.1836	.4477	.5263	.5228
4.50	.0078	.1482	.3875	.4767	.5115
4.75	.0055	.1187	.3308	.4254	.4942
5.00	.0039	.0944	.2790	.3746	.4724
5.25	.0028	.0747	.2329	.3262	.4470
5.50	.0020	.0587	.1926	.2812	.4191
5.75	.0014	.0459	.1580	.2402	.3897
6.00	.0010	.0357	.1286	.2035	.3597
6.25	.0007	.0277	.1040	.1712	.3297
6.50	.0005	.0213	.0836	.1431	.3003
6.75	.0003	.0164	.0668	.1189	.2719
7.00	.0002	.0126	.0531	.0982	.2448
7.25	.0002	.0096	.0420	.0807	.2193
7.50	.0001	.0073	.0331	.0660	.1955
7.75	.0001	.0055	.0260	.0538	.1736
8.00	.0000	.0042	.0203	.0437	.1534
8.25	--	.0032	.0158	.0353	.1351
8.50	--	.0024	.0123	.0284	.1185
8.75	--	.0018	.0095	.0228	.1036

r (atomic units)	4f	5d	6s	6p	5f
9.00	--	.0013	.0074	.0183	.0903
9.25	--	.0010	.0057	.0146	.0784
9.50	--	.0007	.0044	.0116	.0679
9.75	--	.0006	.0033	.0092	.0586
10.00	--	.0004	.0026	.0073	.0505
10.25	--	.0003	.0019	.0058	.0434
10.50	--	.0002	.0015	.0046	.0371
10.75	--	.0002	.0011	.0036	.0317
11.00	--	.0001	.0008	.0028	.0270
11.25	--	.0001	.0006	.0022	.0230
11.50	--	.0001	.0005	.0017	.0194
11.75	--	.0000	.0004	.0013	.0164
12.00	--	--	.0003	.0010	.0138
12.25	--	--	.0002	.0008	.0116
12.50	--	--	.0002	.0006	.0096
12.75	--	--	.0001	.0005	.0079
13.00	--	--	.0001	.0004	.0065
13.25	--	--	.0001	.0003	.0052
13.50	--	--	.0000	.0002	.0041

D. Matrix Elements $(f^7WUSL\|C^{(k)}\|f^7W'U'S'L')$

A double tensor U^{hk} may be defined as a tensor operator, such as $S \cdot L$, which operates on two parts of the system, and is of rank h with respect to the first part and rank k with respect to the second.[17] If the terms of $\ell^{2\ell+1}$ are divided into two classes:

(1) those with seniority numbers $\nu = 1,5,9, \ldots,$

(2) those with seniority numbers $\nu = 3,7,11, \ldots,$

there are no matrix elements of U^{hk} between terms of different classes if h + k is odd, and none between terms of the same class if h + k is even.[27]

The sextet terms of f^7 (see Table IX) may be divided into

(1) $\nu = 5$ $\quad {}^6DGI,$

(2) $\nu = 7$ $\quad {}^6PFH.$

It is easily seen that two terms characterized by L and L′ are in the same class if L + L′ is even, and in different classes if L + L′ is odd. Thus we have

$$(f^7WUSL\|U^{0k}\|f^7W'U'S'L') = 0, \quad \text{if } L + L' \text{ is even,}$$

and

$$(f^7WUSL\|U^{1k}\|f^7W'U'S'L') = 0, \quad \text{if } L + L' \text{ is odd.}$$

Using the equations of Judd,[27] we may write, for L + L′ even,

$$\begin{aligned}(f^7WUSL\|U^{0k}\|f^7W'U'S'L') &= 0 \\ &= 7 \sum_{\bar{\Psi}} (f^7WUSL\{|f^6(\bar{\Psi})fSL)(f^7W'U'S'L'\{|f^6(\bar{\Psi})fS'L')(2S+1) \\ &\quad \times [(2L+1)(2L'+1)]^{\frac{1}{2}} (-1)^{\bar{L}+\bar{S}+3+\frac{1}{2}+S+L} \begin{Bmatrix} \frac{1}{2} & S & \bar{S} \\ S' & \frac{1}{2} & 0 \end{Bmatrix} \begin{Bmatrix} 3 & L & \bar{L} \\ L' & 3 & k \end{Bmatrix}. \qquad \text{(D-1)}\end{aligned}$$

For the sextet states (S = 5/2), $\bar{S}$ has only two values, $\bar{S} = 2,3$. But, according to Table IX, there is only one state of f^6 with $\bar{S} = 3$, the

$(100)(10)^7F$ term. The sum (D-1) may then be broken into two parts, one over quintets and one over septets. The latter may be explicitly evaluated. This gives

$$(f^7WUSL\{|\, f^6\ (100)(10)^7F)(f^6W'U'S'L'\{|\, f^6(100)(10)^7F)\begin{Bmatrix}3 & L & 3\\ L' & 3 & k\end{Bmatrix}$$

$$= \sum_{\substack{\Psi\\ \text{(quintets)}}} (f^7WUSL\{|\, f^6(\overline{\Psi})fSL)(f^7W'U'S'L'\{|\, f^6(\overline{\Psi})fS'L')(-1)^L \begin{Bmatrix}3 & L & \overline{L}\\ L' & 3 & k\end{Bmatrix} \quad \text{(D-2)}$$

This is only for $S = 5/2$ and $L + L'$ and k even. Using Eqs. (14) and (15), where $U^{(k)}$ is the tensor operator defined in Eq. (50),

$$(f^7WUSL\|U^{(k)}\|f^7W'U'S'L')$$

$$= 7 \sum_{\Psi} (f^7WUSL\{|\, f^6(\overline{\Psi})fSL)(f^7W'U'S'L'\{|\, f^6(\overline{\Psi})fS'L')$$

$$\times\ (-1)^{\overline{L}+3+L+k}\ [(2L'+1)(2L+1)]^{\frac{1}{2}} \begin{Bmatrix}3 & L & \overline{L}\\ L' & 3 & k\end{Bmatrix}$$

$$= 7\ [(2L+1)(2L'+1)]^{\frac{1}{2}}\ (-1)^{L+3}\Bigg[(f^7WUSL\{|\, f^6(100)(10)^7F\ fSL)$$

$$\times\ (f^7W'U'S'L'\{|\, f^6(100)(10)^7F\ fS'L')(-1)^3\begin{Bmatrix}3 & L & 3\\ L' & 3 & k\end{Bmatrix}$$

$$+ \sum_{\substack{\Psi\\ \text{(quintets)}}} (f^7WUSL\{|\, f^6(\overline{\Psi})fSL)(f^7W'U'S'L'\{|f^6(\overline{\Psi})fS'L')(-1)^{\overline{L}} \begin{Bmatrix}3 & L & \overline{L}\\ L' & 3 & k\end{Bmatrix}\Bigg]$$

But the summation may be evaluated from Eq. (D-2) for $L + L'$ and k even and $S = 5/2$.

$$(f^7WUSL\|U^{(k)}\|f^7W'U'S'L') = 7[(2L+1)(2L'+1)]^{\frac{1}{2}}(-1)^{L+3}$$

$$\times\Bigg[(f^7WUSL\{|f^6(100)(10)^7FfSL)\ (f^7W'U'S'L'\{|f^6(100)(10)^7F\ fS'L')(-1)^3\begin{Bmatrix}3 & L & 3\\ L' & 3 & k\end{Bmatrix}$$

$$+ (f^7WUSL\{|f^6(100)(10)^7F\ fSL)\ \ (f^7W'U'S'L'\{|f^6(100)(10)^7F\ fS'L')\begin{Bmatrix}3 & L & 3\\ L' & 3 & k\end{Bmatrix}\Bigg] = 0.$$

Thus
$$(f^7WUSL\|U^{(k)}\|f^7W'U'S'L') = 0, \qquad \text{(D-4)}$$
for sextet states with k and $L + L'$ even.

Now consider the matrix elements of the double tensor U^{1k}. For $L + L'$ odd, the matrix elements of U^{1k} are zero, i.e.,

$$(f^7WUSL\|U^{1k}\|f^7W'U'S'L')$$
$$= 7 \sum_{\bar\psi} (f^7WUSL\{|f^6(\bar\psi)fSL)(f^7W'U'S'L'\{|f^6(\bar\psi)f\ S'L')(2S+1)$$
$$\times\ [(2L+1)(2L'+1)]^{\frac{1}{2}}(-1)^{\bar L+\bar S+\frac{1}{2}+S+L} \begin{Bmatrix} \frac{1}{2} & S & \bar S \\ S & \frac{1}{2} & 1 \end{Bmatrix} \begin{Bmatrix} 3 & L & \bar L \\ L' & 3 & k \end{Bmatrix} = 0.$$

For $S = 5/2$, $\bar S = 3,2$ only, and for $\bar S = 3$ the sum over $\bar\psi$ includes only $(100)(10)^7F$. Thus

$$(f^7WUSL\{|f^6(100)(10)^7FfSL)(f^7W'U'S'L'\{|f^6(100)(10)^7FfS'L')\begin{Bmatrix} \frac{1}{2} & 5/2 & 3 \\ 5/2 & \frac{1}{2} & 1 \end{Bmatrix}\begin{Bmatrix} 3 & L & 3 \\ L' & 3 & k \end{Bmatrix}$$

$$= \sum_{\bar\psi} (f^7WUSL\{|f^6(\bar\psi)fSL)(f^7W'U'S'L'\{|f^6(\bar\psi)f\ S'L')(-1)^{\bar L}\begin{Bmatrix} \frac{1}{2} & 5/2 & 2 \\ 5/2 & \frac{1}{2} & 1 \end{Bmatrix}\begin{Bmatrix} 3 & L & \bar L \\ L' & 3 & k \end{Bmatrix}$$
(quintets)

Evaluating the 6-j symbols involving spin, one obtains

$$-5/7\ (f^7WUSL\{|f^6(100)(10)^7FfSL)(f^7W'U'S'L'\{|f^6(100)(10)^7F\ f\ S'L')\begin{Bmatrix} 3 & L & 3 \\ L' & 3 & k \end{Bmatrix}$$

$$= \sum_{\bar\psi} (f^7WUSL\{|f^6(\bar\psi)\ fSL)(f^7W'U'S'L'\{|f^6(\bar\psi)f\ S'L')(-1)^{\bar L}\begin{Bmatrix} 3 & L & \bar L \\ L' & 3 & k \end{Bmatrix}. \qquad \text{(D-5)}$$

If the summation in (D-3) is now evaluated from (D-5) one finds that

$$(f^7WUSL\|U^{(k)}\|f^7W'U'S'L') = 12(-1)^L[(2L+1)(2L'+1)]^{\frac{1}{2}}$$
$$\times\ (f^7WUSL\{|f^6(100)(10)^7FfSL)$$
$$(f^7W'U'S'L'\{|f^6(100)(10)^7FfS'L')\begin{Bmatrix} L & L' & k \\ 3 & 3 & 3 \end{Bmatrix}. \qquad \text{(D-6)}$$

If the c.f.p. for all values of ψ' are evaluated from Racah's tables, one finds that for any ψ

$$(f^7\ (\psi)\{|\ f^6(100)(10)^7F\ fSL) = -\frac{1}{\sqrt{6}}$$

Putting this result into (D-6), we obtain for S = 5/2 and even values of k,

$$(f^7WUSL\|U^{(k)}\|f^7W'U'S'L') = 2(-1)^L\ [(2L+1)(2L'+1)]^{\frac{1}{2}} \begin{Bmatrix} L & L' & k \\ 3 & 3 & 3 \end{Bmatrix} \quad \text{(D-7)}$$

for L + L′ odd, and

$$(f^7WUSL\|U^{(k)}\|f^7W'U'S'L') = 0$$

for L + L′ even.

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