(Note that $f^\alpha\theta^\alpha=N!$.) Thus

$$G_1{}^\alpha\Phi\chi=(f/2^m\theta)\mathcal{A}[(P_1N_1P_1\Phi)\chi].$$

But

$$\chi=\alpha(1)\beta(2)\alpha(3)\beta(4)\cdots\alpha(2m-1)\beta(2m)\times\alpha(2m+1)\cdots\alpha(N), \quad \text{(D3)}$$

and thus $\nu\chi=\chi$ for any $\nu\in\mathfrak{N}$.

Hence

$$\mathcal{A}\Psi\chi=\zeta_\nu\mathcal{A}[(\nu\Psi)(\nu\chi)]=\zeta_\nu\mathcal{A}[(\nu\Psi)\chi]$$

for any spatial function Ψ, and thus

$$\mathcal{A}(N_1\Psi)\chi=n!m!\mathcal{A}(\Psi\chi). \quad \text{(D4)}$$

Hence $\mathcal{A}[(N_1P_1N_1P_1\Phi)\chi]=n!m!\mathcal{A}[(P_1N_1P_1\Phi)\chi]$. But from p. 19 of Ref. 9 $N_1P_1N_1P_1=\theta N_1P_1$; thus

$$n!m!\mathcal{A}[(P_1N_1P_1\Phi)\chi]=\theta\mathcal{A}[(N_1P_1\Phi)\chi].$$

Similarly, using (D4), we have

$$\mathcal{A}[(N_1P_1\Phi)\chi]=n!m!\mathcal{A}[(P_1\Phi)\chi];$$

thus

$$G_1{}^\alpha\Phi\chi=(f/n!m!2^m)\mathcal{A}[(N_1P_1\Phi)\chi]=(f/2^m)\mathcal{A}[(P_1\Phi)\chi]. \quad \text{(D5)}$$

This expression is used in the discussion of paired-type wave functions.

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Intra-Atomic Magnetic Interactions for *f* Electrons*

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An examination is made of the effects of spin-spin and spin-other-orbit interactions on the energy levels of f-electron configurations. The theory is applied to several rare-earth atoms and ions under a number of simplifying assumptions. Considerable improvements in the fits between experiment and theory are obtained, particularly for the sextets of Gd IV. Electrostatically correlated spin-orbit interaction is studied and found not to be susceptible to parametric absorption into the ordinary spin-orbit and spin-other-orbit interactions. The various contributions to the effective Hamiltonian for two electrons are decomposed into parts having well-defined group-theoretical properties, in preparation for their calculation for any configuration f^N.

I. INTRODUCTION

TERM analyses of complex atomic configurations are usually performed with a Hamiltonian comprising two parts: the Coulomb interaction between the electrons and the spin-orbit coupling. The procedure introduces as parameters certain Slater integrals (such as the F^k, or, equivalently, the linear combinations E^k of Racah[1]), and a few spin-orbit coupling constants ζ_l.[2] In recent years, most efforts at improvement have been centered on the study of configuration interaction. This has as its origin the large off-diagonal matrix elements of the Coulomb interaction. Its effect can be accommodated by introducing effective operators that act only within the configuration under study. The additional parameters that enter in the lowest order of perturbation theory are associated with two-electron operators (the parameters α and β of Trees[3] fall in this class) or with three-electron operators.[4] Under these limitations, the total number of parameters necessary to describe a configuration f^N is 14 [corresponding to ζ_f, $F^k(k=0, 2, 4, 6)$, α, β, γ, and six parameters T^k for the three-electron operators].

A parametrization of such a kind neglects the contributions to the Hamiltonian coming from the Breit operator H_B, given by [5]

$$H_B=-\tfrac{1}{2}e^2\sum_{i>j}[(\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j)r_{ij}^{-1}+(\boldsymbol{\alpha}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\alpha}_j\cdot\mathbf{r}_{ij})r_{ij}^{-3}].$$

In the nonrelativistic limit, H_B separates out into parts that are easy to interpret.[6] Some of them produce effects that can be taken into account by changes in the electrostatic parameters (e.g., the parameters F^k, α, β, and γ for f^N). Into this category fall the retardation of the Coulomb interaction, the magnetic interactions between the electrons produced by their orbital motion, and the contact interaction between electron spins. Other parts produce effects that cannot be absorbed into the param-

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* Work partially supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Contract No. 49(638)-1497, and by the U. S. Atomic Energy Commission.

[1] G. Racah, Phys. Rev. **76**, 1352 (1949).

[2] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935).

[3] R. E. Trees, Phys. Rev. **83**, 756 (1951); **85**, 382 (1952); J. Opt. Soc. Am. **54**, 651 (1964).

[4] B. R. Judd, Phys. Rev. **141**, 4 (1966); S. Feneuille, Compt. Rend. Acad. Sci. Paris **262**, 23 (1966); J. Phys. (Paris) **28**, 61 (1967); **28**, 315 (1967); **28**, 497 (1967); **28**, 701 (1967).

[5] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Julius Springer-Verlag, Berlin, 1957).

[6] L. Armstrong, J. Math. Phys. **7**, 1891 (1966).

etrization procedure. They are the spin-spin interaction H_{ss} and the interaction between the spin of one electron and the orbit of another—the so-called spin-other-orbit interaction H_{soo}. For equivalent electrons, they can be conveniently described in tensorial form as follows[7]:

$$H_{\mathrm{ss}}=-2\sum_{i\neq j}\sum_{k}[(k+1)(k+2)(2k+3)]^{1/2}M^{k}(l\|C^{(k)}\|l)\times(l\|C^{(k+2)}\|l)\{\mathbf{w}_i^{(1k)}\mathbf{w}_j^{(1\,k+2)}\}^{(22)0}, \quad (1)$$

$$\begin{aligned}H_{\mathrm{soo}}=\sum_{i\neq j}\sum_{k}&[(k+1)(2l+k+2)(2l-k)]^{1/2}\\&\times[\{\mathbf{w}_i^{(0\,k+1)}\mathbf{w}_j^{(1k)}\}^{(11)0}\{M^{k-1}(l\|C^{(k+1)}\|l)^{2}\\&+2M^{k}(l\|C^{(k)}\|l)^{2}\}+\{\mathbf{w}_i^{(0k)}\mathbf{w}_j^{(1\,k+1)}\}^{(11)0}\\&\times\{M^{k}(l\|C^{(k)}\|l)^{2}+2M^{k-1}(l\|C^{(k+1)}\|l)^{2}\}]. \quad (2)\end{aligned}$$

In these expressions, $\mathbf{w}_i^{(\kappa k)}$ is a double tensor (for electron i) of rank κ in the spin space and rank k in the orbital space; its magnitude is defined by

$$(l\|w^{(\kappa k)}\|l)=(2\kappa+1)^{1/2}(2k+1)^{1/2}.$$

The quantities M^k are the radial integrals of Marvin,[8] i.e.,

$$M^{k}=(e^{2}\hbar^{2}/8m^{2}c^{2})\langle(nl)^{2}|(r_{<}^{k}/r_{>}^{k+3})|(nl)^{2}\rangle,$$

where $r_<$ and $r_>$ are the lesser and greater, respectively, of r_1 and r_2.

Although H_{ss} and H_{soo} produce overt effects that demand additional parameters, their use in atomic spectroscopy has been somewhat sporadic. They play an important role in accounting for the peculiar structures of the triplets ^3P in the configurations $1snp$ of He I.[5] However, their Z^3 dependence on an effective nuclear charge Z, when contrasted with the Z^4 dependence of the ordinary spin-orbit effects, means that they become relatively less important for heavy atoms. Interest in such cases dates from the work of Marvin.[8] Trees[9] included H_{ss} in his analysis of Fe III $3d^6$, and found the levels shifted by roughly 10 cm^{-1}. The role of H_{soo} in a number of configurations of p electrons was studied by Horie[10] and by Obi and Yanagawa.[11] Garstang[12] considered the combined effect of H_{ss} and H_{soo} for $(2p)^N$, and found that the values of M^0 required to fit the experimental data could be obtained quite accurately from eigenfunctions derived from a self-consistent field. Jucys and his collaborators have examined more complex configurations from a theoretical standpoint, thereby extending and correcting earlier tables of matrix elements.[13,14] The possibility of calculating ordinary spin-orbit parameters ζ_f from the sums of the magnetic two-electron interactions (instead of through the intermediary of a central field) led Blume and Watson to study H_{soo} in detail.[15] Hartree-Fock values for the integrals M^k were found for a number of atoms and ions, and these results were then applied to the calculation of H_{ss}.[16] More recently, Dunn and Li[17] have considered H_{soo} in an attempt to reduce the discrepancies in the theoretical fit with the levels of Mn III $3d^5$.

The purpose of the present paper is to introduce H_{ss} and H_{soo} into the analysis of f-electron systems. It has recently been shown[18] that the Hartree-Fock values for the parameters M^k lead to level shifts in Gd IV $4f^7$ that exceed 100 cm^{-1}. This figure is of the same order of magnitude as the discrepancies in a typical term analysis in which H_{soo} is ignored. The neglect of H_{soo} can obviously no longer be justified if improvements in the fit are sought. As for H_{ss}, it turns out that it is an order of magnitude less important than H_{soo}, displacements of 10 cm^{-1} in the level schemes of rare-earth ions being typical. By including H_{soo} and H_{ss} into term analyses, the number of magnetic parameters is increased from one (ζ_f) to four (ζ_f, M^0, M^2, M^4). This redresses somewhat the imbalance in the number of electrostatic parameters compared with the number of magnetic parameters in the 14-parameter analysis mentioned above.

II. MATRIX ELEMENTS

As can be seen from Eqs. (1) and (2), both H_{ss} and H_{soo} are the scalar parts of double tensors of equal rank in the orbital and spin spaces. We write

$$H_{\mathrm{ss}}=(5)^{1/2}\mathbf{T}^{(22)0},\quad H_{\mathrm{soo}}=-(3)^{1/2}\mathbf{T}^{(11)0}.$$

The matrix elements of H_{ss} and H_{soo} are then given by

$$\langle\gamma SLJ|H|\gamma' S'L'J'\rangle=\delta(J,J')(-1)^{S'+L+J}\times\begin{Bmatrix}S' & L' & J\\ L & S & t\end{Bmatrix}(\gamma SL\|T^{(tt)}\|\gamma' S'L'). \quad (3)$$

In this equation, we take $t=2$ for $H\equiv H_{\mathrm{ss}}$ and $t=1$ for $H\equiv H_{\mathrm{soo}}$. The J dependence is contained in the 6-j symbol.

A standard procedure for calculating matrix elements for a configuration l^N is to relate them to the matrix

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[7] B. R. Judd, Physica **33**, 174 (1967).

[8] H. H. Marvin, Phys. Rev. **71**, 102 (1947).

[9] R. E. Trees, Phys. Rev. **82**, 683 (1951).

[10] H. Horie, Progr. Theoret. Phys. (Kyoto) **10**, 296 (1953).

[11] S. Obi and S. Yanagawa, Publ. Astron. Soc. Japan **7**, 125 (1955).

[12] R. H. Garstang, Monthly Notices Roy. Astron. Soc. (London) **111**, 115 (1951).

[13] A. Jucys and R. Dagys, Trudy Akad. Nauk Litovsk S. S. R. **B1**, 41 (1960).

[14] A. Jucys and R. Dagys, Trudy Akad. Nauk Litovsk S. S. R. **B1**, 59 (1960); R. Dagys and J. Vizbaraite, *ibid.* **B1**, 71 (1960); A. Jucys, R. Dagys, J. Vizbaraite, and S. Zvironaite, *ibid.* **B3**, 53 (1961); Z. Rudzikas, J. Vizbaraite, and A. Jucys, Lietuvos Fizikos Rinkinys **V1**, 37 (1965); Z. Rudzikas, J. Vizbaraite, R. Karazija, and A. Jucys, *ibid.* **V1**, 49 (1965).

[15] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A270**, 127 (1962); **A271**, 565 (1963). See also M. Blume, A. J. Freeman, and R. E. Watson, Phys. Rev. **134**, A320 (1964).

[16] R. E. Watson and M. Blume, Phys. Rev. **139**, A1209 (1965).

[17] T. M. Dunn and Wai-Kee Li, J. Chem. Phys. **46**, 2907 (1967).

[18] B. R. Judd, Phys. Rev. **162**, 28 (1967).

TABLE I. Reduced matrix elements of $\mathbf{T}^{(22)}$ for the configuration f^2.

ψ	ψ'	$(\psi\|T^{(22)}\|\psi')$
${}^3P$	${}^3P$	$-12M^0-24M^2-(300/11)M^4$
${}^3P$	${}^3F$	$(8/3^{1/2})[3M^0+M^2-(100/11)M^4]$
${}^3F$	${}^3F$	$(4/3)(14)^{1/2}[-M^0+8M^2-(200/11)M^4]$
${}^3F$	${}^3H$	$(8/3)(11/2)^{1/2}[2M^0-(23/11)M^2-(325/121)M^4]$
${}^3H$	${}^3H$	$(4/3)(143)^{1/2}[M^0-(34/11)M^2-(1325/1573)M^4]$

elements of l^{N-1} through the equation

$$(l^N\psi\|T^{(tt)}\|l^N\psi')=[N/(N-2)]\sum(\psi\{|\bar{\psi})(\psi'\{|\bar{\psi}')(-1)^x$$
$$\times\{(2S+1)(2S'+1)(2L+1)(2L'+1)\}^{1/2}$$
$$\times\begin{Bmatrix}S & t & S'\\ \bar{S}' & s & \bar{S}\end{Bmatrix}\begin{Bmatrix}L & t & L'\\ \bar{L}' & l & \bar{L}\end{Bmatrix}(l^{N-1}\bar{\psi}\|T^{(tt)}\|l^{N-1}\bar{\psi}'),\quad (4)$$

where $x=\bar{S}+\bar{L}+s+l+S'+L'$, and the symbols ψ, ψ', $\bar{\psi}$, and $\bar{\psi}'$ are abbreviations for the sets of quantum numbers (γSL), $(\gamma' S'L')$, $(\bar{\gamma}\bar{S}\bar{L})$, and $(\bar{\gamma}'\bar{S}'\bar{L}')$, respectively.[9] The sum in Eq. (4) runs over the parent states $\bar{\psi}$ and $\bar{\psi}'$ of l^{N-1}. The coefficients of fractional parentage, $(\psi\{|\bar{\psi})$, are known for $l\leq 3$.[19] Thus, all the matrix elements for f electrons can be calculated by a chain procedure once those for the starting configuration f^2 are specified. To do this, the detailed forms of H_{ss} and H_{soo}, as given in Eqs. (1) and (2), are required; the results of the calculation for f^2 are set out in Tables I and II. These are consistent with the tables of Jucys and Dagys,[13] except for the entry of 146 in the column headed M_0 in the f^2 part of their Table 2; this number should be 143. It is worth noting that

$$(\psi\|T^{(tt)}\|\psi')=(-1)^{L-S-L'+S'}(\psi'\|T^{(tt)}\|\psi),$$

so that for f^2 (for which $L+S$ and $L'+S'$ are even), the states ψ and ψ' may be interchanged without introducing a phase factor. All matrix elements for f^2 not given in Tables I and II are zero.

It is often convenient to introduce effective operators for diagonal matrix elements. Operators having the correct tensorial characters can be constructed from the basic vectors $\mathbf{S}$ and $\mathbf{L}$, and we write

$$H_{ss}\equiv-\rho[(\mathbf{L}\cdot\mathbf{S})^2+\tfrac{1}{2}(\mathbf{L}\cdot\mathbf{S})-\tfrac{1}{3}L(L+1)S(S+1)],$$
$$H_{soo}\equiv\lambda'\mathbf{L}\cdot\mathbf{S}.$$

TABLE II. Reduced matrix elements of $\mathbf{T}^{(11)}$ for the configuration f^2.

ψ	ψ'	$(\psi\|T^{(11)}\|\psi')$
${}^1S$	${}^3P$	$6M^0+2M^2+(10/11)M^4$
${}^3P$	${}^3P$	$-36M^0-72M^2-(900/11)M^4$
${}^3P$	${}^1D$	$-(2/15)^{1/2}[27M^0+14M^2+(115/11)M^4]$
${}^1D$	${}^3F$	$(2/5)^{1/2}[23M^0+6M^2-(195/11)M^4]$
${}^3F$	${}^3F$	$2(14)^{1/2}[-15M^0-M^2+(10/11)M^4]$
${}^3F$	${}^1G$	$(11)^{1/2}[-6M^0+(64/33)M^2-(1240/363)M^4]$
${}^1G$	${}^3H$	$(2/5)^{1/2}[39M^0-(728/33)M^2-(3175/363)M^4]$
${}^3H$	${}^3H$	$8(55)^{-1/2}[-132M^0+23M^2+(130/11)M^4]$
${}^3H$	${}^1I$	$(26)^{1/2}[-5M^0-(30/11)M^2-(375/1573)M^4]$

Once the proportionality constants ρ and λ' have been specified, the contributions of H_{ss} and H_{soo} to any given multiplet can be rapidly determined. Values of ρ for all terms of maximum multiplicity in the f shell have already been given.[20] The corresponding values of λ' are set out in Table III; they were obtained by relating the eigenvalues of $\mathbf{L}\cdot\mathbf{S}$ to the 6-j symbol

$$\begin{Bmatrix}S & L & J\\ L & S & 1\end{Bmatrix},$$

and then using Eqs. (3) and (4). As a check, the L symmetry about the quarter-filled shell [as exemplified by Eq. (10) of Ref. 18] was used to derive the relation

$$N\lambda'(f^N,{}^{N+1}L)+(7-N)\lambda'(f^{7-N},{}^{8-N}L)$$
$$=-36M^0+2M^2+(10/11)M^4.$$

The generalization to arbitrary l runs

$$N\lambda'(l^N,{}^{N+1}L)+(2l+1-N)\lambda'(l^{2l+1-N},{}^{2l+2-N}L)$$
$$=-12lM^0+3\Xi,$$

where

$$\Xi=\sum_{k>0}M^k(l\|C^{(k)}\|l)^2(k+1)(2l+k+2)(2l-k)/$$
$$(k+2)l(2l+1)(l+1).$$

TABLE III. Spin-other-orbit splitting factors for terms of maximum multiplicity in f^N.

Configuration	Term	λ'
f	${}^2F$	0
f^2	${}^3P$	$-6M^0-12M^2-(150/11)M^4$
	${}^3F$	$-5M^0-(1/3)M^2+(10/33)M^4$
	${}^3H$	$-(16/5)M^0+(92/165)M^2+(104/363)M^4$
f^3	${}^4D$	$-(58/15)M^0+(62/15)M^2+(48/11)M^4$
	${}^4F$	$-(11/2)M^0\qquad\qquad+(5/22)M^4$
	${}^4G$	$-(151/30)M^0-(544/495)M^2-(3131/2178)M^4$
	${}^4I$	$-(14/3)M^0+(6/11)M^2+(140/363)M^4$
f^4	${}^5D$	$-(61/10)M^0-(26/10)M^2-(67/22)M^4$
	${}^5F$	$-(39/8)M^0+(1/2)M^2+(5/88)M^4$
	${}^5G$	$-(209/40)M^0+(437/330)M^2+(3791/2904)M^4$
	${}^5I$	$-(11/2)M^0+(1/11)M^2-(15/242)M^4$
f^5	${}^6P$	$-(24/5)M^0+(26/5)M^2+(62/11)M^4$
	${}^6F$	$-(26/5)M^0+(8/15)M^2+(2/33)M^4$
	${}^6H$	$-(148/25)M^0+(146/825)M^2+(122/1815)M^4$
f^6	${}^7F$	$-6M^0+(1/3)M^2+(5/33)M^4$
f^7	${}^8S$	0

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[19] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* (The MIT Press, Cambridge, Mass., 1963).

[20] B. R. Judd, Proc. Phys. Soc. (London) **A69**, 157 (1956).

Table IV. Effect of parameters M^k on mean error.

Configuration	Ion	Number of levels	Mean error (cm^{-1}) $M^k=0$	Mean error (cm^{-1}) $M^0=M^2=M^4$	M^0(cm^{-1}) expt.	M^0(cm^{-1}) H.F.[e]
$4f^2$	Ce III[a]	9	34	3.7	0.78	1.76
$4f^2$	Pr IV[b]	13	36	10.7	1.55	2.24
$4f^5$	Pm I[c]	12	24	6.0	2.64	2.53[f]
$4f^7$	Gd IV[d]	15	66	9.2	1.71	3.70

[a] J. Sugar, J. Opt. Soc. Am. **55**, 33 (1965).
[b] H. M. Crosswhite, G. H. Dieke, and W. J. Carter, J. Chem. Phys. **43**, 2047 (1965); see also J. Sugar, Phys. Rev. Letters **14**, 731 (1965).
[c] J. Reader and S. P. Davis (private communication).
[d] Reference 21.
[e] Reference 15, with interpolations where necessary.
[f] The M^0 value for the $4f^56s^2$ configuration of Pm I is taken to be the same as that for Pm III $4f^5$.

By setting $l=2$, we may verify Horie's results.[10] Only λ' values for the first half of the f shell are given in Table III; the others can be calculated from the general formula

$$\langle l^{4l+2-N}\psi | H_{\text{soo}} | l^{4l+2-N}\psi' \rangle = \langle l^N\psi | H_{\text{soo}} | l^N\psi' \rangle + \zeta' \langle l^N\psi | \sum_i (\mathbf{s}\cdot\mathbf{l})_i | l^N\psi' \rangle,$$

where

$$\zeta' = (8l-2)M^0 - \Xi.$$

If, however, the ordinary spin-orbit interaction is parametrized, the effect of ζ' will be absorbed into ζ_l. This means that we can take the matrix elements of H_{soo} in the second half of the shell to be equal to the corresponding ones in the first half.

III. COMPARISON WITH EXPERIMENT

As has already been mentioned, the inclusion of H_{ss} and H_{soo} in the term analysis for a configuration f^N introduces three new parameters, i.e., M^0, M^2, and M^4. The constraints which we impose on the M^k in a fitting procedure are a matter of choice. At one extreme, we may simply take the Hartree-Fock values[15] and see whether the agreement between experiment and theory is improved. However, it is well known that the Hartree-Fock method leads to appreciable discrepancies for the two-electron Coulomb integrals F^k, and there is no guarantee that the M^k might not be even more susceptible to error. If, on the other hand, the M^k are allowed to freely vary, the improvement in the fits that are obtained appear to be less striking because of the use of as many as three additional parameters. Since our primary aim in this paper is to demonstrate the importance of additional magnetic parameters in as direct a way as possible, it was decided early in the analysis to impose a limited number of constraints on the M^k. An obvious choice is to set M^2/M^0 and M^4/M^0 equal to their Hartree-Fock values (roughly 0.56 and 0.38, respectively, for all triply ionized rare-earth atoms). A few tests with $4f^2$ soon indicated, however, that the ratio M^2/M^0 appeared to be seriously underestimated—a value exceeding unity being more appropriate. This is, of course, inconsistent with the definition of M^k (which, like F^k, must decrease as k increases). As a compromise, it was decided to set the M^k at their theoretical limit by imposing the conditions

$$M^0 = M^2 = M^4. \tag{5}$$

This choice has the merit of simplicity and serves as a good starting point for more complete analyses. This assumption will be examined more critically in Sec. IV, where the role of configuration interaction in affecting multiplet splittings is studied.

The level schemes of several atoms and ions have been studied both with and without the additional magnetic parameter M^0. The details are given in Tables IV and V. Where data are meager, additional con-

Table V. Summary of experimental parameters (in cm^{-1}).

Parameter	Ce III	Ce III	Pr IV	Pr IV	Pr IV	Pm I	Pm I	Gd IV	Gd IV
E^1	3642.	3651.	4865.	4864.	4862.7	[5032.]	[5049.]	6047.	6044.
E^2	18.5	18.42	23.14	23.19	23.142	[26.34]	[26.43]	32.64	33.15
E^3	417.	416.2	488.1	487.4	487.63	508.8	510.5	628.4	630.9
ζ_f	554.	547.	758.4	769.3	773.27	919.	987.	1465.	1497.
α	28	28.18	23.70	23.76	24.01	[20]	[20]	[20]	[20]
β	[0]	[0]	−586.	−602.	−595.	[0]	[0]	[0]	[0]
γ	[0]	[0]	728.	742.	729.	[0]	[0]	[0]	[0]
M^0	[0]	0.78	[0]	1.55	1.560	[0]	2.64	[0]	1.71
M^2	[0]	[0.78]	[0]	[1.55]	0.537	[0]	[2.64]	[0]	[1.71]
M^4	[0]	[0.78]	[0]	[1.55]	0.249	[0]	[2.64]	[0]	[1.71]
P^6	[0]	[0]	[0]	[0]	−962.	[0]	[0]	[0]	[0]

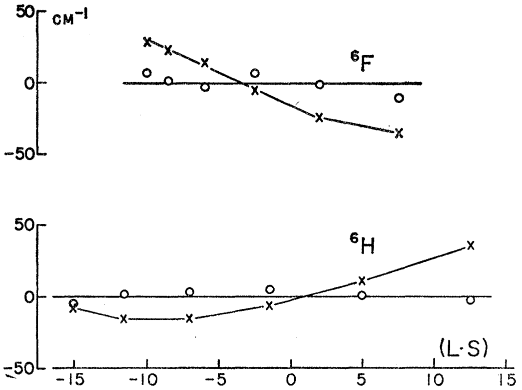

FIG. 1. Calculated energies minus observed energies for low $4f^5$ sextets of Pm I. Crosses: spin orbit (ζ) only. Circles: spin-orbit, spin–other-orbit, and spin-spin (two parameters, ζ, and $M^0=M^2=M^4$).

straints are imposed on the electrostatic parameters. The values of those so constrained are given in brackets in Table V. The row labeled P^6 refers to a parameter to be introduced in Sec. IV.

The f^2 configurations were diagonalized completely, using the matrix elements of Tables I and II for H_{ss} and H_{soo}. On the addition of a single parameter, substantial reductions in the mean errors are obtained; these are given in Table V. Even more striking, however, are the improvements brought about for the sextets of f^5 and f^7. At present, the matrix elements of H_{ss} and H_{soo} are known only for pure LS states; but, as Russell-Saunders coupling is quite well obeyed, this limitation is not serious. Given this approximation for calculating the matrix elements of H_{ss} and H_{soo} for the sextets (and ignoring their effects in other multiplets), complete diagonalizations were made using the parameters of Table V. The resulting deviations are plotted in Figs. 1 and 2.

Some comment on the fitting procedures should be made. The separation between the ^6F and ^6H multiplets of f^5 is determined in first order only by E^3, and this is therefore the most sensitive electrostatic parameter. Since no information is available for Pm I on the higher levels, we have constrained E^1 and E^2 to have their hydrogenic ratios relative to E^3. To make the results more physically meaningful, we have taken $\alpha = 20$ cm⁻¹. The parameter analysis of the two multiplet structures then gives the values for E^3, ζ_f, and M^0 entered in Table V. The effects of H_{ss} and H_{soo} are both represented through a single parameter, since we insist that Eqs. (5) be satisfied.

TABLE VI. Spin-spin factors ρ for the sextets of f^7.

Term	ρ
^6P	$(6/25)[-4M^0+6M^2+(75/11)M^4]$
^6D	$(2/525)[-44M^0+26M^2-(575/11)M^4]$
^6F	$(4/225)[-2M^0-2M^2+(125/11)M^4]$
^6G	$(4/1925)[6M^0-(130/11)M^2-(3425/121)M^4]$
^6H	$(2/9)[(4/25)M^0-(2/55)M^2-(233/1573)M^4]$
^6I	$(2/165)[4M^0-(50/11)M^2-(7225/1573)M^4]$

Complete Stark manifolds are known for Gd^{3+} in $LaCl_3$ for the ^8S, ^6P, ^6D, and ^6I multiplets.[21] From these four terms, the four electrostatic parameters E^k have been determined. We again assume $\alpha = 20$ cm⁻¹. The effects of J mixing turn out to be negligible. Values of ρ for the sextets of f^7 have been calculated by Morrison,[22] and are set out in Table VI; the corresponding factors λ' are given elsewhere.[18]

An obvious step to reduce still further the mean errors is to relax the condition that all the M^k be equal. However, we are at present reluctant to do this for several reasons. In the first place, the effect of configuration interaction—to be discussed in the next section—is as yet an unknown factor. Secondly, the spin–other-orbit splitting factors λ' for the sextets of f^5 and f^7 are dominated by M^0, so that any change in the assumed ratios M^2/M^0 and M^4/M^0 has a comparatively small effect.

In spite of these limitations, the analysis yields valuable information on M^0. For the four atoms considered in Table IV, it turns out to be positive, and of the same order of magnitude as the Hartree-Fock values. The fact that there is a tendency for the empirical values of M^0 to be smaller than these theoretical figures (at any rate, for the ions) suggests the existence of screening effects similar to those that lower the values of the F^k.

Studies have also been made of Nd IV $4f^3$, Sm IV $4f^5$. Dy IV $4f^9$, Ho IV $4f^{10}$, Er IV $4f^{11}$, and Tm IV $4f^{12}$. The results for the parameters M^k are consistent with those reported above. However, the experimental data all come from ions in crystals. In these cases, it is often difficult to deduce the centers of gravity of the levels, since many Stark manifolds are incomplete and J mixing is difficult to estimate. These factors give an imprecision to the analysis, and it was felt not to be worthwhile to include them in the present paper.

IV. CONFIGURATION INTERACTION

The noncentral part C of the Coulomb interaction is the largest of the terms in the perturbative Hamiltonian, and is mainly responsible for mixing configurations. All matrix elements $\langle\psi|H|\psi'\rangle$ of the ground configuration (where $H = H_{\text{ss}} + H_{\text{soo}}$) should thus be corrected by terms of the type

$$-\sum_{\chi}\langle\psi|H|\chi\rangle\langle\chi|C|\psi'\rangle/E-\sum_{\chi}\langle\psi|C|\chi\rangle\langle\chi|H|\psi'\rangle/E,$$

where χ runs over the states of the perturbing configurations, situated at energies E above the ground configuration. However, there exists a much more impor-

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[21] A. H. Piksis, G. H. Dieke, and H. M. Crosswhite, J. Chem. Phys. 47, 5083 (1967); R. L. Schwiesow (private communication).

[22] J. Morrison (private communication).

tant type of correction. It is given by

$$\langle\psi|H_{\mathrm{ci}}|\psi'\rangle,$$

where

$$H_{\mathrm{ci}}=-\sum_{\chi}\sum_{h}\xi(r_h)(\mathbf{s}_h\cdot\mathbf{l}_h)|\chi\rangle\langle\chi|C/E$$
$$-\sum_{\chi}\sum_{h}C|\chi\rangle\langle\chi|\xi(r_h)(\mathbf{s}_h\cdot\mathbf{l}_h)/E,$$

and represents what has been called electrostatically correlated spin-orbit interaction.[23] Its importance lies in the fact that the effective operator H_{ci} has very similar properties to H_{soo}; for example, it includes a scalar two-electron operator with ranks of unity in both the spin and orbital spaces. We denote this by H_{ci}'. Furthermore, the combined effects of the spin-orbit interaction and the Coulomb interaction may be large enough to offset the energy denominator E, and thus give contributions to the displacements of the energy levels that are of the same order of magnitude as H_{soo} itself.

It has been stated[23] that the effect of H_{ci} for a ground configuration l^N can be absorbed by the spin-orbit interaction and the spin–other-orbit interactions. In other words, by treating ζ_l and the M^k associated with H_{soo} (distinct now from the M^k associated with H_{ss}) as variable parameters, the effect of H_{ci} is automatically taken into account. This is not the case. The error appears to have been made by too superficial a comparison between H_{ci} and H_{soo}. The distinctive character of H_{ci} becomes apparent if we write $H_{\mathrm{ci}}'=-(3)^{1/2}\mathbf{t}^{(11)0}$, and tabulate the reduced matrix elements of $\mathbf{t}^{(11)}$ for f^2. This is done in Table VII. No single choice of the M^k of Table II can reproduce all the entries of this table. The parameters P_k that appear are related to certain quantities P^k by the equations

$$P_0=P^0,\quad P_2=P^2/225,\quad P_4=P^4/1089,\quad P_6=25P^6/184041$$

(which parallel the definition[2] of the F_k for f electrons). The P^k, in turn, are given by

$$P^k=6\sum_{f'}\zeta_{ff'}R^k(ff,ff')/E_{ff'}. \tag{6}$$

The symbol f' denotes a radial eigenfunction (with $l=3$) distinct from that of the configuration f^N under study. The quantity $E_{ff'}$ is the (positive) difference in the energy eigenvalues for the two radial eigenfunctions f and f'. As usual, $\zeta_{ff'}$ and $R^k(ff,ff')$ are the off-diagonal radial integrals of the spin-orbit and Coulomb interactions, respectively:

$$\zeta_{ff'}=\langle f|\xi(r)|f'\rangle,$$
$$R^k(ff,ff')=e^2\langle f_1f_2|(r_<^k/r_>^{k+1})|f_1f_2'\rangle.$$

As can readily be verified, the coefficients P^0 in Table VII are proportional to the reduced matrix elements of the double tensor $(\mathbf{s}_1\mathbf{l}_1+\mathbf{s}_2\mathbf{l}_2)$. It follows that the effect of P^0 is absorbed by ζ_f. The three remaining parameters P^k considerably widen the scope for fitting experimental levels. It would be out of place here to begin a detailed analysis, but we must not overlook the possibility that the P^k parameters might be as effective as the M^k in fitting the experimental data. (Since there are three triplets in f^2 and three additional

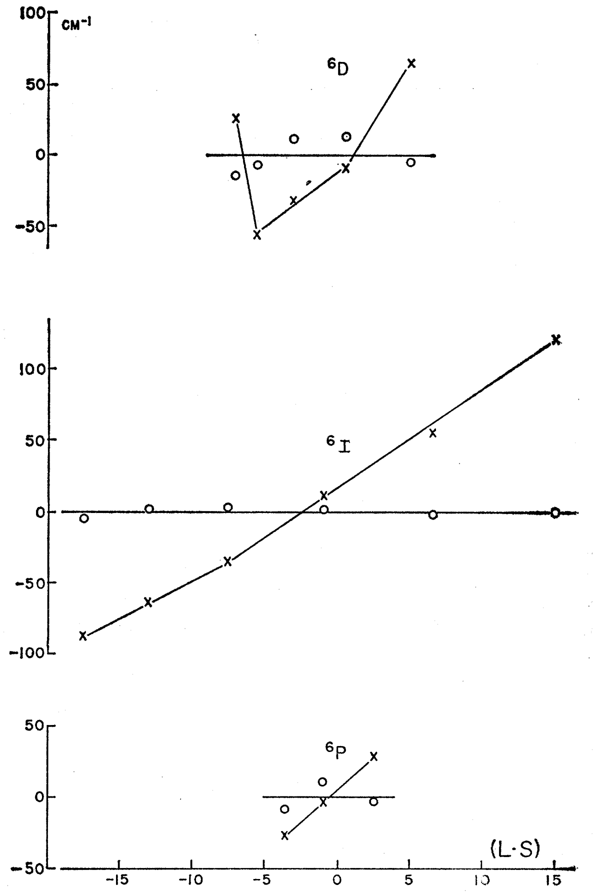

FIG. 2. Calculated energies minus observed energies for lowest $4f^7$ sextets of Gd IV. Crosses: spin-orbit (ζ) only. Circles: spin-orbit, spin–other-orbit, and spin-spin (two parameters, ζ, and $M^0=M^2=M^4$).

TABLE VII. Reduced matrix elements of $\mathbf{t}^{(11)}$ for the configuration f^2.

ψ	ψ'	$(\psi\|t^{(11)}\|\psi')$
^1S	^3P	$-2P_0-105P_2-231P_4-429P_6$
^3P	^3P	$-P_0-45P_2-33P_4+1287P_6$
^3P	^1D	$(15/2)^{1/2}[P_0+32P_2-33P_4-286P_6]$
^1D	^3F	$(10)^{1/2}[-P_0-(9/2)P_2+66P_4-(429/2)P_6]$
^3F	^3F	$(14)^{1/2}[-P_0+10P_2+33P_4+286P_6]$
^3F	^1G	$(11)^{1/2}[P_0-20P_2+32P_4-104P_6]$
^1G	^3H	$(10)^{1/2}[-P_0+(55/2)P_2-23P_4-(65/2)P_6]$
^3H	^3H	$(55)^{1/2}[-P_0+25P_2+51P_4+13P_6]$
^3H	^1I	$(13/2)^{1/2}[P_0-21P_4-6P_6]$

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[23] K. Rajnak and B. G. Wybourne, Phys. Rev. **134**, A596 (1964).

TABLE VIII. Operators and parameters for $H_{\text{soo}}+H_{\text{ci}}$.

z_i	${}^{2K+1}(\sigma)WU^{2\kappa+1}k$	a_i
z_5	${}^5(1111000)(211)(11)^3P$	$(7/15)[M^0+(8/21)M^2-(5/33)M^4]+(11/30)[5P_2+6P_4-91P_6]$
z_6	${}^5(1111000)(211)(30)^3P$	$-(1/9)[33M^0+148M^2+(1805/11)M^4]-(55/6)[5P_2+6P_4-91P_6]$
z_7	${}^1(2200000)(211)(11)^3P$	$(49/30)[M^0+(8/21)M^2-(5/33)M^4]+(11/60)[5P_2+6P_4-91P_6]$
z_8	${}^1(2200000)(211)(30)^3P$	$-(7/18)[33M^0+148M^2+(1805/11)M^4]-(55/12)[5P_2+6P_4-91P_6]$
z_9	${}^1(2200000)(110)(11)^3P$	$(1/40)[-627M^0+29M^2+(145/11)M^4]+(21/80)[35P_2+77P_4+143P_6]$
z_{10}	${}^1(2200000)(310)(30)^3P$	$(1/24)[33M^0-296M^2+(1805/11)M^4]+(55/16)[19P_2-50P_4+91P_6]$
z_{11}	${}^1(2200000)(310)(31)^3P$	$(1/16)[429M^0-(1455/11)M^4]+(2145/32)[3P_2-2P_4-21P_6]$
z_{12}	${}^1(1100000)(110)(11)^3P$	$(1/24)[27M^0-5M^2-(25/11)M^4]+(1/3)P_0+(1/16)[35P_2+77P_4+143P_6]$
z_{13}	${}^3(1100000)(110)(11)^3P$	$-33M^0+3M^2+(15/11)M^4-6P_0+(3/2)[35P_2+77P_4+143P_6]$
z_{14}	${}^5(1100000)(110)(11)^3P$	$(1/5)[12M^0-(2/3)M^2-(10/33)M^4]+(1/3)P_0-(1/5)[35P_2+77P_4+143P_6]$

magnetic parameters, some apparent improvement must be expected even if three arbitrary independent operators are chosen.) We therefore attempted an analysis for Pr IV in which P^2, P^4, and P^6 were independently varied and the M^k omitted. The best fit gave a mean error of 18 cm^{-1} compared with 36 cm^{-1} found without either M^k or P^k, and 11 cm^{-1} found when M^k alone was used. However, only P^6 appeared to be significant, P^2 and P^4 being indeterminate in their signs. Bearing in mind this result, we made a further analysis, varying P^6 and all three M^k freely. Although this calculation uses 12 parameters (including E^0) to fit 13 levels, the result—that all errors are reduced to less than 1 cm^{-1}—appears to be significant, particularly since the M^k ratios are now found to be very close to those of the Hartree-Fock calculations. The resulting parameters are given in column 6 of Table V. However, it would be premature to assume that the value of -926 cm^{-1} for P^6 can be ascribed solely to the mechanism under study. With the aid of Rajnak's eigenfunctions,[24] the single term $f'\equiv 5f$ in the summation of Eq. (6) can be shown to yield $P^6=40$ cm^{-1}, and it is difficult to see how negative contributions could arise until f' functions that are well into the continuum are reached. The fact that P^2 and P^4 are not required makes one suspicious. Perhaps P^6 is reproducing other effects—for example, the expansion of the $4f$ eigenfunction as the energy is increased. Such possibilities must remain speculative for the moment.

An interesting aspect of the type of configuration interaction that produces the P^k is that the admixing of f' states into a particular f state is spin-dependent. The radial eigenfunction of an f electron is thus altered in a different way for the two possibilities $j=l\pm\frac{1}{2}$. The existence of different radial functions for $f_{5/2}$ and $f_{7/2}$ electrons is a feature of the Dirac theory of an electron in a central field, and evidently the introduction of the P^k is a way of taking this property into account by means of perturbation theory. Since $5f$ electrons in the actinides are more susceptible to relativistic effects than $4f$ electrons in the rare earths, we would expect the parameters P^k to be relatively more important in the former case than the latter.

V. GROUP THEORY

The evaluation of matrix elements, as described in Sec. II, becomes a tedious affair for configurations f^N in which $N\geq 3$. In an effort to simplify matters, it is natural to follow the lines laid down by Racah[1] for the Coulomb interaction. We have to break up H_{ss}, H_{soo}, and H_{ci} into parts having well-defined properties with respect to the groups used to define the states ψ. Apart from S and L, which can be regarded as specifying irreducible representations of the group R_3, the states ψ are described by the representations (σ), W, and U of the respective groups Sp_{14}, R_7, and G_2. A method to proceed for d electrons has already been elaborated,[7] as has the decomposition of H_{ss} for f electrons.[25] Furthermore, the representations (σ), W, and U needed to define the various decomposed parts of H_{soo} have recently been obtained by the method of plethysms.[26] In view of these accounts, it only seems necessary to summarize results. To treat H_{ci} simultaneously with H_{soo}, we write, for f^2,

$$(\psi\|T^{(11)}+t^{(11)}\|\psi')=\sum a_i(\psi\|z_i\|\psi')\,, \qquad (7)$$

where $i=5,\ 6,\ \cdots,\ 14$. (The operators z_i with $1\leq i\leq 4$ have already been used for H_{ss}.[25]) The group-theoretical descriptions of the z_i are given in Table VIII, as are also the coefficients a_i. Prefixes to (σ) denote the quasispin multiplicites, $2K+1$. The ranks κ and k of the operators in the spin and orbital spaces are unity in all cases. The operators z_i are defined in terms of their matrix elements for f^2 in Table IX. To construct operators described by $(1100000)(110)(11)^3P$ that have well-defined quasispin rank K, it is necessary to use one-particle as well as two-particle operators.[7,27] The con-

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[24] K. Rajnak, J. Chem. Phys. 37, 2440 (1962).

[25] B. R. Judd and H. T. Wadzinski, J. Math. Phys. 8, 2125 (1967). A factor was inadvertently omitted from Eq. (10) of this reference; the correct form is the special case for which $t=2$ of Eq. (4) above.

[26] P. R. Smith and B. G. Wybourne, J. Math. Phys. (to be published).

[27] B. R. Judd, *Second Quantization and Atomic Spectroscopy* (The Johns Hopkins Press, Baltimore, Md., 1967).

TABLE IX. Decomposition of matrix elements of H_{soo} for f^2.

ψ	ψ'	F[a]	$(\|z_5\|)$	$(\|z_6\|)$	$(\|z_7\|)$	$(\|z_8\|)$	$(\|z_9\|)$	$(\|z_{10}\|)$	$(\|z_{11}\|)$	$(\|z_{12}\|)$	$(\|z_{13}\|)$	$(\|z_{14}\|)$
${}^1S$	${}^3P$	1	0	0	0	0	0	0	0	$16-16$	2	$20+10$
${}^3P$	${}^3P$	1	1	1	1	1	1	0	0	$8-1$	1	$10-2$
${}^3P$	${}^1D$	$(1080)^{-1/2}$	210	-6	-105	3	70	6	12	$-90(8-1)$	-90	$-180(5-1)$
${}^1D$	${}^3F$	$(2/405)^{1/2}$	120	-6	-60	3	-35	-12	0	$45(8-1)$	45	$90(5-1)$
${}^3F$	${}^3F$	$(14)^{1/2}$	-4	0	-4	0	1	0	0	$8-1$	1	$10-2$
${}^3F$	${}^1G$	$(891)^{-1/2}$	-264	-12	132	6	77	-24	0	$-99(8-1)$	-99	$-198(5-1)$
${}^1G$	${}^3H$	$(98010)^{-1/2}$	-2310	-186	1155	93	-770	186	36	$990(8-1)$	990	$1980(5-1)$
${}^3H$	${}^3H$	$(55)^{-1/2}$	55	-1	55	-1	55	0	0	$55(8-1)$	55	$110(5-1)$
${}^3H$	${}^1I$	$(1019304)^{-1/2}$	6006	-546	-3003	273	2002	546	-252	$-2574(8-1)$	-2574	$-2574(10-2)$

[a] The numbers F are multiplying factors common to all entries in a row.

tributions to z_{12} and z_{14} from these two sources are given explicitly (the one-particle part first) in Table IX; the operator z_{13} is a pure one-particle operator, and is proportional to the ordinary spin-orbit interaction. Since $\mathbf{t}^{(11)}$ corresponds to the pure two-particle operator H_{ci}', the one-particle parts in Table IX cancel out when the sum of Eq. (7) is performed; but it is necessary to introduce them into z_{12}, z_{13}, and z_{14} if we are to take advantage of the properties of operators with well-defined K.

The matrix elements of the operators z_i can be calculated for any configuration f^N by using Eq. (4) with $t=1$ and $\mathbf{T}^{(tt)}$ replaced by z_i; the starting point is f^2, whose matrix elements are given in Table IX. The whole point of this approach is to take advantage of the group-theoretical properties that the operators z_i possess. Powerful selection rules abound, and the use of the Wigner-Eckart theorem for the groups Sp_{14}, R_7, or G_2 yields striking relations between sets of matrix elements. Racah's motivation for introducing continuous groups for his analysis of the Coulomb interaction was to obtain simplifications of precisely these kinds.

As an example of the use of Tables VIII and IX, we calculate

$$(f^3\,{}_1{}^2F\|T^{(11)}+t^{(11)}\|f^3\,{}_1{}^2F),$$

where ${}_1{}^2F$ denotes the term ${}^2F$ of f^3 for which the seniority is unity. This corresponds to a quasispin Q [defined[27] as $\frac{1}{2}(2l+1-v)$] of 3, and an M_Q [given by $-\frac{1}{2}(2l+1-N)$] of -2. All operators of Table VIII possess unique quasispin ranks, so we have only to know their values for the state $|QM_Q\rangle\equiv|3,-3\rangle$, and their dependence on M_Q follows at once from the Wigner-Eckart theorem. Now, the state $|3,-3\rangle$ is simply $|f\,{}_1{}^2F\rangle$, which is a single-electron state. For this, all pure two-electron operators $z_i(5\leq i\leq 11)$ have vanishing matrix elements; and for the rest, we need only consider their one-particle parts in Table IX. To give the entries 16, 2, and 20 in the first row of this table, the reduced matrix elements for $|f\,{}_1{}^2F\rangle$ must be $8(14)^{1/2}$, $(14)^{1/2}$, and $10(14)^{1/2}$, respectively. Since

$$-\begin{pmatrix}3 & K & 3\\ 2 & 0 & -2\end{pmatrix}\Big/\begin{pmatrix}3 & K & 3\\ 3 & 0 & -3\end{pmatrix}=1,\ \tfrac{2}{3},\ 0$$

for $K=0$, 1, and 2, respectively, we conclude that

$$\begin{aligned}(f^3\,{}_1{}^2F\|T^{(11)}+t^{(11)}\|f^3\,{}_1{}^2F)&=8(14)^{1/2}a_{12}+\tfrac{2}{3}(14)^{1/2}a_{13}\\ &=(14)^{1/2}[-13M^0+\tfrac{1}{3}M^2+(5/33)M^4-\tfrac{4}{3}P_0\\ &\qquad+\tfrac{3}{2}(35P_2+77P_4+143P_6)].\end{aligned}$$

VI. STRUCTURE OF COEFFICIENTS

The coefficients a_i of Table VIII exhibit a number of striking features. Perhaps the most obvious is the frequent recurrence of the linear combination $5P_2+6P_4-91P_6$. One immediately recalls Racah's parameter E^3, which is proportional to $5F_2+6F_4-91F_6$. However, whereas E^3 is associated with an operator that belongs to the representation (220) of R_7, the quantity $5P_2+6P_4-91P_6$ appears in those a_i that are associated with (221). To understand this, we first note that the entries of Table VII are products of Coulomb and spin-orbit matrix elements. These elements differ from those taken entirely within the f shell only in their radial parts. Consequently, we can form the products of the representations (000), (220), and (400) (to which the Coulomb interaction corresponds[1]), with the representation (110), which characterizes the spin-orbit interaction.[28] When this is done, it is found that only (220)×(110) contains (221) in its reduction; thus the combination of parameters P_k associated with (221) must parallel the integrals F_k associated with (220).

Analogous structures in the coefficients for the M^k can be treated in a similar way. The operators $\mathbf{W}^{(\kappa k)}$, from which H_{soo} is constructed, transform like (110) if k is odd, like (000) if $k=0$, and like (200) if k is even (and nonzero).[28] From Eq. (2) is it clear that odd and even orbital ranks are combined, so the transformation properties of H_{soo} must be characterized by the products (200)×(110) and (000)×(110). Since (211) can be formed only from the first product, the combination of parameters M^k associated with a given component [$(30)P$ or $(11)P$] must be fixed to within a multiplicative factor. This is why the combination $M^0+(8/21)M^2-(5/33)M^4$ occurs in both a_5 and a_7, for example.

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[28] B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Co., New York, 1963).

A further point to note is that a tensor $\mathbf{W}^{(\kappa k)}$ with odd k is associated in Eq. (2) only with M^{k-1} (and not with M^{k+1}). Thus $(000)\times(110)$ can only contribute to the coefficient of M^0. Hence, even in those cases (a_9, a_{12}, a_{13}, and a_{14}) that correspond to (110), the ratio of the coefficient of M^2 to those of M^4 must be invariant (and, in fact, equal to 11/5).

Arguments of these kinds can be extended to the subgroup G_2 or R_7. The main differences stem from the fact that (110) decomposes into the two representations (10) and (11) of G_2. The first is spanned by the single tensor $\mathbf{W}^{(\kappa 3)}$, which is associated with M^2. It can now be seen why the coefficient of M^2 vanishes for a_{11}: The U designation of a_{11} is (31), and this representation does not occur in the decompositions of either $(10)\times(20)$ or $(10)\times(00)$. Again, the ratio of the coefficients of M^0 and M^4 must be the same in a_6, a_8, and a_{10} since there is only one product of representations, namely, $(11)\times(20)$, that can both give rise to M^0 and M^4 and also produce (30)—to which a_6, a_8, and a_{10} correspond—in its reduction. Other connections can be established by similar arguments.

Group theory is useful in supplying a number of checks. For example, every coefficient of M^2 in Table VIII corresponding to an operator z_i that is not designated by the representation (11) of G_2 is a multiple of 37. Since such a high prime number is unlikely to appear in the denominators of the 6-j symbols or coefficients of fractional parentage, we expect every coefficient of M^2 in any matrix element of H_{soo} to be an exact multiple of 37 when the operators labeled by (11) have vanishing matrix elements. An example of this occurs in f^3 when matrix elements of H_{soo} are taken between states labeled by (11) and (21).

Finally, it should be remarked that the ten parameters a_i are not linearly independent. This is to be expected, since there are only nine matrix elements in f^2 in Tables II and VII. The additional degree of freedom is required to permit precise quasispin ranks to be assigned to all operators. The linear dependence of the a_i is expressed by the equation

$$8a_{12}+a_{13}+10a_{14}=0,$$

which automatically insures that the one-particle parts of the operators z_{12}, z_{13}, and z_{14} vanish when summed.

VII. CONCLUSION

The purpose of this paper is to demonstrate the importance of magnetic interactions between f electrons and to prepare the ground for more detailed and elaborate analyses. The approximation of equal M^k values should be the first to be lifted, but it would probably be unrealistic to do so until it is possible to include the parameters P^k. The seven parameters ζ_f, M^k, and P^k are only two fewer than the number of linearly independent coefficients a_i of Table VIII. This makes it attractive to work entirely within the group-theoretical scheme, using the a_i as parameters and only passing to the ζ_f, M^k, and P^k after the fitting procedure has been carried out. Such an approach would permit us to take into account many perturbation mechanisms that have not been considered here. For example, all perturbation mechanisms involving the spin-orbit interaction just once could be treated. The configuration f^3 possesses 17 multiplets which, being much greater than the nine magnetic parameters, is an attractive choice for further study. At the moment, there is considerable interest in this kind of work. Some results for f^2, essentially consistent with ours, have been recently reported; and some preliminary work on Pr III $4f^3$ has already been done.[29]

The inclusion of new parameters into term analyses of the f^N configurations should greatly improve the fits between experiment and theory. This should aid the prediction of unknown levels and the elimination of spurious ones. In addition, then, to deepening our understanding of the electronic structure of the f shell, the analysis should yield results of considerable practical importance.

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[29] Z. B. Goldschmidt and Z. H. Goldschmidt, results presented at the Atomic Spectroscopy Symposium, National Bureau of Standards, Gaithersburg, Maryland, 1967 (unpublished); and private communication.