curve is 67.2 G which is 2 G larger than the one where hyperfine structure is neglected.

In Fig. 5 the scattering intensity of Lyman-α radiation is shown near the (d-f) crossing point. The polar angles of the incident and scattered photon about the magnetic field direction are $\pi/4$ while their azimuthal angles differ by $n\pi$ where n is an integer. For $\Delta m_J=1$ crossings this geometry gives maximum coherent signal. Due to the anticrossing of the $m_F=-1$ levels there are four coherent contributions to the total signal. Using the notation $(\mathcal{J},\mathfrak{M}_J,m_F)$, let us examine the coherence produced by the two levels $(\frac{3}{2},-\frac{3}{2},-1)$ and $(\frac{1}{2},-\frac{1}{2},0)$. The state $(\frac{3}{2},-\frac{3}{2},-1)$ is a linear combination of three states, two of which are states with $m_I=-\frac{1}{2}$ and one a state with $m_I=\frac{1}{2}$. The state $(\frac{1}{2},-\frac{1}{2},0)$ is a linear combination of four states; two with $m_I=\frac{1}{2}$ while the other two have a $m_I=-\frac{1}{2}$. When the anticrossing is approached from the low-field side, the state $(\frac{3}{2},-\frac{3}{2},-1)$ has a large probability amplitude for the state $m_I=\frac{1}{2}$. The other amplitudes are of order $1/M$ smaller. On the other side of the anticrossing, the state $(\frac{3}{2},-\frac{3}{2},-1)$ has large amplitudes for the states with $m_I=-\frac{1}{2}$, and the other amplitude is much smaller. On the other hand, the state $(\frac{1}{2},-\frac{1}{2},0)$ always has large amplitudes for the $m_I=\frac{1}{2}$ states while the amplitudes for the $m_I=-\frac{1}{2}$ states are small. Since $\mathfrak{M}^{(-)}$ and $\mathfrak{M}^{(+)}$ contain the selection rule $m_I=m_I'$, there are large contributions to the coherent signal on the low-field side of the anticrossing from the terms with $m_I=\frac{1}{2}$. On the high-field side, however, all contributions are of order $1/M$ smaller. The features of the curves describing the other coherent contributions can be analyzed in a similar way.

The half-width of the total coherent-scattering intensity is 110.1 G which is 3.1 G larger than the curve obtained when hyperfine structure is neglected.

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Atomic Shell Theory Recast*

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Conventional shell theory for the electronic configurations l^N rests on the separation of the spin and orbital spaces according to the scheme $U(4l+2)\supset U(2)\times U(2l+1)$. If we are prepared to abandon the total spin quantum number S, the more symmetrical reduction $U(4l+2)\supset U(2l+1)\times U(2l+1)$ can be adopted, corresponding to the separation of electrons whose spins point up from those whose spins point down. The orbital structure of a representation $[\lambda]$ of $U(2l+1)$ can be carried over from ordinary shell theory; but the quantum numbers L_A and L_B in a typical coupled state $|([\lambda_A]L_A\times[\lambda_B]L_B)LM_LM_S\rangle$ are only pseudo-orbital. The existence of two distinct spaces, each of dimension $(2l+1)$, leads to many simplifications in the theory. States of the f shell can be classified unambiguously. The spin-orbit splitting of terms near the Russell–Saunders limit is easy to calculate; no fractional parentage coefficients are necessary. What is especially remarkable is that L_A and L_B are sometimes quite good quantum numbers, and this makes it possible to give simple explanations for many regularities in the energy-level patterns for configurations of the type f^N.

I. INTRODUCTION

THE separation of the spin and orbital spaces is a characteristic feature of atomic shell theory. There is, of course, a good reason for this. Spin-independent forces (such as the Coulomb interaction between the electrons) are often much larger than those that couple the spin and orbital spaces. It is thus natural to introduce the total spin **S** and the total orbital angular momentum **L**, the corresponding quantum numbers S and L being available for defining states. This structural division of the total space of an atom into spin and orbital parts has a serious disadvantage when configurations of the type l^N are considered. For all but the smallest values of l, there is a grave imbalance in the complexity of the spin and orbital spaces; the spin space remains simple and easy to handle, but the orbital space is often so intricate that even elaborate group-theoretical methods are insufficient to provide a complete scheme for classifying the states.[1]

The central idea of the present analysis is to introduce a new structural division of the total space. Instead of spin and orbital spaces, two distinct but essentially similar spaces are used. In the first (the A space), the spins of the electrons all point up (i.e., all $m_s=+\frac{1}{2}$); in the second (the B space), the spins of the electrons all

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

point down (all $m_s=-\frac{1}{2}$). Owing to the similarity between the A and B spaces, the complexities of the total space, to put it crudely, become equally divided between the A and B spaces instead of being almost entirely concentrated in the orbital space. The eigenfunctions of the configurations $(nl)^N$ are obtained by coupling together the A and B spaces, just as in conventional shell theory the spin and orbital spaces are combined. There are, however, important differences between these two cases, the main one being that it is now considerably easier to ensure that the Pauli exclusion principle is satisfied. In fact, the opposition of the spins in the A space compared to the B space means that it is enough that the principle is satisfied in each space separately.

When work was started, it was thought that this approach would have certain mathematical advantages, but that the various quantum numbers introduced to define eigenfunctions in the A and B spaces would not have any useful physical significance. Surprisingly enough, it turns out that these quantum numbers are sometimes quite good. This enables us to give simple explanations for many of the regularities in term schemes and multiplet structures for configurations of equivalent electrons.

II. GENERATORS

The spin and orbital angular momentum of a single electron are denoted by **s** and **l**. The eigenvalues m_s and m_l of their respective z components s_z and l_z characterize the single-electron eigenfunctions. The most general linear transformations of these $4l+2$ eigenfunctions that preserve their orthonormality form the unitary group $U(4l+2)$. Generators for this group are provided by the double tensors $\mathbf{w}^{(\kappa k)}$, whose amplitudes are determined by the equation

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

When treating configurations $(nl)^N$ with $N>1$, it is convenient to take for the generators the many-electron tensors $\mathbf{W}^{(\kappa k)}$, given by

$$\mathbf{W}^{(\kappa k)}=\sum_i \mathbf{w}_i^{(\kappa k)}, \tag{2}$$

where the sum runs over the electrons i. The traditional separation of the spin and orbital spaces is obtained by limiting the tensors $\mathbf{W}^{(\kappa k)}$ to those for which either $k=0$ or $\kappa=0$. The tensors $\mathbf{W}^{(00)}$ (the complete scalar) and $\mathbf{W}^{(10)}$ (a vector proportional to the total spin $\mathbf{S}$) form the generators for the group $U(2)$. On the other hand, the tensors for which $\kappa=0$ act solely within the orbital space, and, if we include the scalar $k=0$, form the generators for $U(2l+1)$. Together, the tensors constitute the generators of the subgroup $U(2)\times U(2l+1)$ of $U(4l+2)$. This expresses the separation of the spin and orbital spaces in the language of group theory.

Suppose we consider instead the tensors $\mathbf{A}^{(k)}$ and $\mathbf{B}^{(k')}$, defined by the equations

$$A_q^{(k)}=(W_{0q}^{(0k)}+W_{0q}^{(1k)})/\sqrt{2},$$
$$B_{q'}^{(k')}=(W_{0q'}^{(0k')}-W_{0q'}^{(1k')})/\sqrt{2}.$$

The commutators of the tensors $\mathbf{W}^{(\kappa k)}$ are known,[2] and hence those for $\mathbf{A}^{(k)}$ and $\mathbf{B}^{(k')}$ may be readily deduced. It is found that

$$[A_q^{(k)},B_{q'}^{(k')}]=0 \tag{3}$$

for all k, k', q, and q'. Furthermore, it can be shown that

$$[A_q^{(k)},A_{q'}^{(k')}]=\sum_{k''q''} c(kqk'q',k''q'')A_{q''}^{(k'')},$$
$$[B_q^{(k)},B_{q'}^{(k')}]=\sum_{k''q''} c(kqk'q',k''q'')B_{q''}^{(k'')},$$

in which the coefficients $c(kqk'q',k''q'')$ are precisely the same as those that occur in the commutators of the familiar tensors $\mathbf{V}^{(k)}$. In analogy with Eqs. (1) and (2), these are defined in terms of their single-electron components $\mathbf{v}_i^{(k)}$, for which

$$(nl\|v^{(k)}\|nl)=(2k+1)^{1/2}.$$

Since the tensors $\mathbf{V}^{(k)}$ are known to be the generators for the group $U(2l+1)$,[2] it follows that $\mathbf{A}^{(k)}$ and $\mathbf{B}^{(k)}$ must separately form the generators for this group. To distinguish the transformations composing this group, it is convenient to write $U_A(2l+1)$ and $U_B(2l+1)$. In view of Eq. (3), the transformations of $U_A(2l+1)$ and those of $U_B(2l+1)$ can be regarded as taking place in two different spaces—the A and B spaces—and we can write

$$U(4l+2)\supset U_A(2l+1)\times U_B(2l+1). \tag{4}$$

This represents our fundamental structural decomposition.

Subgroups of $U_A(2l+1)$ and $U_B(2l+1)$ are easy to find. We have only to refer to the group $U(2l+1)$ whose generators are the tensors $\mathbf{V}^{(k)}$ and use the fact that the commutation relations satisfied by these tensors are identical to those satisfied by either the $\mathbf{A}^{(k)}$ or the $\mathbf{B}^{(k)}$. Racah's decomposition

$$U(2l+1)\supset R(2l+1)\supset R(3),$$

which is described by limiting the tensors $\mathbf{V}^{(k)}$ to those with odd rank [for the rotation group $R(2l+1)$ in $2l+1$ dimensions] and then to just $\mathbf{V}^{(1)}$ [for $R(3)$], generalizes to

$$U_A(2l+1)\times U_B(2l+1)\supset R_A(2l+1)\times R_B(2l+1)\supset R_A(3)\times R_B(3). \tag{5}$$

For f electrons (i.e., when $l=3$), the product $(G_2)_A\times(G_2)_B$ can be inserted in the sequence (5), but this refinement has no practical value.

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

TABLE I. Classification of the states of f^N.

f^N	M_S	$[\lambda_A]\times[\lambda_B]$	$W_A \times W_B$
f^0	0	[0]×[0]	(000)×(000)
f^1	$\frac{1}{2}$	[1]×[0]	(100)×(000)
	$-\frac{1}{2}$	[0]×[1]	(000)×(100)
f^2	1	[11]×[0]	(110)×(000)
	0	[1]×[1]	(100)×(100)
	−1	[0]×[11]	(000)×(110)
f^3	$\frac{3}{2}$	[111]×[0]	(111)×(000)
	$\frac{1}{2}$	[11]×[1]	(110)×(100)
	$-\frac{1}{2}$	[1]×[11]	(100)×(110)
	$-\frac{3}{2}$	[0]×[111]	(000)×(111)
f^4	2	[1111]×[0]	(111)×(000)
	1	[111]×[1]	(111)×(100)
	0	[11]×[11]	(110)×(110)
	−1	[1]×[111]	(100)×(111)
	−2	[0]×[1111]	(000)×(111)
f^5	$\frac{5}{2}$	[11111]×[0]	(110)×(000)
	$\frac{3}{2}$	[1111]×[1]	(111)×(100)
	$\frac{1}{2}$	[111]×[11]	(111)×(110)
	$-\frac{1}{2}$	[11]×[111]	(110)×(111)
	$-\frac{3}{2}$	[1]×[1111]	(100)×(111)
	$-\frac{5}{2}$	[0]×[11111]	(000)×(110)
f^6	3	[111111]×[0]	(100)×(000)
	2	[11111]×[1]	(110)×(100)
	1	[1111]×[11]	(111)×(110)
	0	[111]×[111]	(111)×(111)
	−1	[11]×[1111]	(110)×(111)
	−2	[1]×[11111]	(100)×(110)
	−3	[0]×[111111]	(000)×(100)
f^7	$\frac{7}{2}$	[1111111]×[0]	(000)×(000)
	$\frac{5}{2}$	[111111]×[1]	(100)×(100)
	$\frac{3}{2}$	[11111]×[11]	(110)×(110)
	$\frac{1}{2}$	[1111]×[111]	(111)×(111)
f^7	$-\frac{1}{2}$	[111]×[1111]	(111)×(111)
	$-\frac{3}{2}$	[11]×[11111]	(110)×(110)
	$-\frac{5}{2}$	[1]×[111111]	(100)×(100)
	$-\frac{7}{2}$	[0]×[1111111]	(000)×(000)
f^8	3	[1111111]×[1]	(000)×(100)
	2	[111111]×[11]	(100)×(110)
	1	[11111]×[111]	(110)×(111)
	0	[1111]×[1111]	(111)×(111)
	−1	[111]×[11111]	(111)×(110)
	−2	[11]×[111111]	(110)×(100)
	−3	[1]×[1111111]	(100)×(000)
f^9	$\frac{5}{2}$	[1111111]×[11]	(000)×(110)
	$\frac{3}{2}$	[111111]×[111]	(100)×(111)
	$\frac{1}{2}$	[11111]×[1111]	(110)×(111)
	$-\frac{1}{2}$	[1111]×[11111]	(111)×(110)
	$-\frac{3}{2}$	[111]×[111111]	(111)×(100)
	$-\frac{5}{2}$	[11]×[1111111]	(110)×(000)
f^{10}	2	[1111111]×[111]	(000)×(111)
	1	[111111]×[1111]	(100)×(111)
	0	[11111]×[11111]	(110)×(110)
	−1	[1111]×[111111]	(111)×(100)
	−2	[111]×[1111111]	(111)×(000)
f^{11}	$\frac{3}{2}$	[1111111]×[1111]	(000)×(111)
	$\frac{1}{2}$	[111111]×[11111]	(100)×(110)
	$-\frac{1}{2}$	[11111]×[111111]	(110)×(100)
	$-\frac{3}{2}$	[1111]×[1111111]	(111)×(000)
f^{12}	1	[1111111]×[11111]	(000)×(110)
	0	[111111]×[111111]	(100)×(100)
	−1	[11111]×[1111111]	(110)×(000)
f^{13}	$\frac{1}{2}$	[1111111]×[111111]	(000)×(100)
	$-\frac{1}{2}$	[111111]×[1111111]	(100)×(000)
f^{14}	0	[1111111]×[1111111]	(000)×(000)

III. EIGENFUNCTIONS

The irreducible representations of the groups appearing in the decompositions (4) and (5) are available for classifying the eigenfunctions of the many-electron configurations. Irreducible representations of $U(2l+1)$ are denoted by the corresponding Young partition $[\lambda]$, and those of $R(2l+1)$ by W. For $R(3)$, we use the spectroscopic symbol $(S,P,D,\cdots)$ whose multiplicity $2L+1$ reproduces the dimension of the irreducible representation in question. The subscripts A and B distinguish the spaces. A state of l^N can thus be described by writing

$$|l^N([\lambda_A]W_A\tau_A L_A \times [\lambda_B]W_B\tau_B L_B)LM_L\rangle. \qquad (6)$$

The symbol τ_A is required to make the classification unambiguous when an irreducible representation of $R_A(3)$ occurs more than once in the decomposition of W_A. The symbol τ_B has an analogous significance. The quantum numbers L_A and L_B are coupled to give L, rather than left uncoupled and assigned additional quantum numbers M_{LA} and M_{LB}. This is because the generators for $R_A(3)\times R_B(3)$ can evidently be combined to give the generators for the group $R(3)$ for ordinary 3-dimensional space; hence L and M_L have their usual spectroscopic significance. Although the quantum number S cannot in general be included in the ket(6), yet we can, if we wish, assign a value of M_S, since $W_{00}^{(10)}$ commutes with all $\mathbf{A}^{(k)}$ and $\mathbf{B}^{(k)}$.

The Pauli exclusion principle imposes certain restrictions on the possible representations $[\lambda_A]$ and $[\lambda_B]$. The commuting operators of $U(4l+2)$ are the $4l+2$ products $\eta_\alpha^\dagger\eta_\alpha$, where $\eta_\alpha^\dagger$ is the creation operator for an electron in the state $\alpha(\equiv nlm_sm_l)$, and η_α the corresponding annihilation operator.[3] Acting on a determinantal product state of $(nl)^N$, they give eigenvalues of the type 1 or 0, depending on whether or not a state α is occupied. This sequence of eigenvalues, or *weight*, has $[11\cdots10\cdots0]$ as its highest component, and it is this component that defines the partition of $U(4l+2)$. The Young diagram simply consists of N cells arranged in a

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[3] B. R. Judd, in *Group Theory and its Applications*, edited by E. M. Loebl [Academic Press Inc., New York (to be published)].

vertical line. In terms of creation and annihilation operators, the separation of the total space into the A and B spaces is trivial to carry out. The operator $\eta_\alpha{}^\dagger$ is written as $a_\alpha{}^\dagger$ when $m_s=+\frac{1}{2}$ and as $b_\alpha{}^\dagger$ when $m_s=-\frac{1}{2}$. An analogous substitution is made for the annihilation operators. The eigenvalues of the $2l+1$ operators $a_\alpha{}^\dagger a_\alpha$ are either 0 or 1; and the same is true for the $2l+1$ operators $b_\alpha{}^\dagger b_\alpha$. The permitted representations of $U_A(2l+1)\times U_B(2l+1)$ are thus all of the type

$$[11\cdots10\cdots0]\times[11\cdots10\cdots0],$$

in which the number of symbols 1 in the first partition (say N_A) and the number of symbols 1 in the second partition (say N_B) satisfy

$$N_A+N_B=N.$$

Since the operators $a_\alpha{}^\dagger a_\alpha$ count the number of states for which $m_s=+\frac{1}{2}$, and the operators $b_\alpha{}^\dagger b_\alpha$ do the same for the $m_s=-\frac{1}{2}$ states, it is obvious that we can write

$$N_A-N_B=2M_S.$$

The states of the configuration f^N, which we shall draw on to illustrate the theory, are classified according to the schemes (4) and (5) in Table I. To avoid a great deal of repetition, the decomposition

$$R_A(7)\times R_B(7)\rightarrow R_A(3)\times R_B(3)$$

is omitted; the relevant branching rules are set out in Table II for not only f but also p, d, and g electrons.

Correspondence with the traditional classification of Racah[1] can be made by actually decomposing the Kronecker products $W_A\times W_B$. For example, we see from Table I that the states of f^3 with $M_S=\frac{1}{2}$ belong to $(110)\times(100)$. Nutter's tables[4] give at once

$$(110)\times(100)=(100)+(111)+(210),$$

and it is immediately verified by a glance at Table 2-1 of Wybourne[5] that the three representations on the right are just the ones that arise in Racah's classification for the states of f^3 with $M_S=\frac{1}{2}$. However, the whole point of the present approach is not to make such decompositions. It can be seen from Table I that every $[\lambda_A]$ and $[\lambda_B]$ decomposes into a single representation W_A or W_B; and Table II indicates that for p, d, and f electrons the symbols τ_A and τ_B of the ket(6) are not required. In these cases the scheme

$$|l^N([\lambda_A]L_A\times[\lambda_B]L_B)LM_L\rangle \tag{7}$$

gives a complete group-theoretical classification of the states. In contrast, Racah's method leaves some ambiguities for f^N when $5\leq N\leq 9$. The g shell fares much worse. In the conventional method, no fewer than 26 ^2K terms exist in g^9 with the same group-theoretical description.[6] On the other hand, it can be seen from Table II that even in the most unfavorable cases we have at most only two like representations to separate.

TABLE II. Branching rules for the reduction $R(2l+1)\rightarrow R(3)$.

l	W	L
p	(0)	S
	(1)	P
d	(00)	S
	(10)	D
	(11)	PF
f	(000)	S
	(100)	F
	(110)	PFH
	(111)	$SDFGI$
g	(0000)	S
	(1000)	G
	(1100)	$PFHK$
	(1110)	PF^2GHIKM
	(1111)	$SD^2FG^2HI^2KLN$

IV. MATRIX ELEMENTS

The simplicity of the designations of the eigenfunctions would count for little if the calculation of the matrix elements of operators of physical significance were not straightforward to perform. The procedure that we must evidently follow is to express an operator as a linear combination of tensors of the type

$$\{\mathbf{T}_A{}^{(k)}\mathbf{U}_B{}^{(k')}\}^{(K)},$$

where $\mathbf{T}_A{}^{(k)}$ and $\mathbf{U}_B{}^{(k')}$ act only in the spaces A and B, respectively. Equation (7.1.5) of Edmonds[7] immediately yields

$$\begin{aligned}(l^N([\lambda_A]\tau_AL_A\times[\lambda_B]\tau_BL_B)L\|\{\mathbf{T}_A{}^{(k)}\mathbf{U}_B{}^{(k')}\}^{(K)}\|l^N([\lambda_A']\tau_A'L_A'\times[\lambda_B']\tau_B'L_B')L')\\ =([\lambda_A]\tau_AL_A\|T_A{}^{(k)}\|[\lambda_A']\tau_A'L_A')([\lambda_B]\tau_BL_B\|U_B{}^{(k')}\|[\lambda_B']\tau_B'L_B')\\ \times\{(2L+1)(2K+1)(2L'+1)\}^{1/2}\begin{Bmatrix}L_A & L_A' & k\\ L_B & L_B' & k'\\ L & L' & K\end{Bmatrix}.\end{aligned} \tag{8}$$

This is our basic equation for the calculation of matrix elements. Its advantage over the standard approach lies chiefly in the fact that the reduced matrix elements of $\mathbf{T}_A{}^{(k)}$ and $\mathbf{U}_B{}^{(k')}$ involve representations $[\lambda_A]$, $[\lambda_A']$, $[\lambda_B]$, and $[\lambda_B']$ that are all of the type $[11\cdots10\cdots0]$.

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[4] P. B. Nutter, Raytheon Technical Memorandum No. T-544, 1964 (unpublished).

[5] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (John Wiley & Sons, Inc., New York, 1965).

[6] B. G. Wybourne, J. Chem. Phys. **45**, 1100 (1966).

[7] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

Conventionally, such a partition describes the terms of l^N with maximum multiplicity (maximum S) which are particularly simple to treat. The actual evaluation of the reduced matrix elements is greatly simplified by this correspondence. For a single electron, for example,

$$(l_A\|a^{(k)}\|l_A)=(l_B\|b^{(k)}\|l_B)=(l\|v^{(k)}\|l)=(2k+1)^{1/2}, \qquad (9)$$

where $\mathbf{a}^{(k)}$ and $\mathbf{b}^{(k)}$ are single-electron components of $\mathbf{A}^{(k)}$ and $\mathbf{B}^{(k)}$, respectively. The quantum numbers l_A and l_B correspond to the vectors

$$\mathbf{l}_A=(1/2+s_z)\mathbf{l}, \quad \mathbf{l}_B=(1/2-s_z)\mathbf{l}.$$

The generalization of Eqs. (9) to the many-electron case is straightforward. A particular matrix element

$$([\lambda_A]\tau_A L_A\|A^{(k)}\|[\lambda_A']\tau_A' L_A')$$

can be immediately found for $l\leq 3$ by interpreting $[\lambda_A]$ and $[\lambda_A']$ as representations of the group $U(2l+1)$ whose generators are the tensors $\mathbf{V}^{(k)}$. We have only to replace $\mathbf{A}^{(k)}$ by $(2k+1)^{1/2}\mathbf{U}^{(k)}$ (which is identical to $\mathbf{V}^{(k)}$) and refer to the tables of Nielson and Koster[8] for the reduced matrix elements of $\mathbf{U}^{(k)}$. Owing to the selection rule $\Delta M_S=0$ on $\mathbf{A}^{(k)}$, all matrix elements vanish unless $[\lambda_A]\equiv[\lambda_A']$.

Another property of the reduced matrix elements is of considerable interest. Suppose $[\lambda_A]$ comprises N_A symbols 1 and $2l+1-N_A$ symbols 0. We denote the representation comprising $2l+1-N_A$ symbols 1 and N_A symbols 0 by $[\tilde{\lambda}_A]$; both $[\lambda_A]$ and $[\tilde{\lambda}_A]$ decompose into the same irreducible representation W_A of $R_A(2l+1)$. The interchange $[\lambda_A]\leftrightarrow[\tilde{\lambda}_A]$ is equivalent to particle-hole conjugation for spin-free particles, from which we deduce

$$\begin{aligned}([\lambda_A]\tau_A L_A\|A^{(k)}\|[\lambda_A]\tau_A' L_A')&\\ =(-1)^{k+1}([\tilde{\lambda}_A]\tau_A L_A\|A^{(k)}\|[\tilde{\lambda}_A]\tau_A' L_A')&\\ +\delta(k,0)\delta(\tau_A,\tau_A')\delta(L_A,L_A')&\\ \times(2l+1)^{1/2}(2L_A+1)^{1/2}.& \qquad (10)\end{aligned}$$

This may be readily checked for special cases by using the tables of Koster and Nielson.[8] An identical equation holds when A is everywhere replaced by B.

In contrast to the creation operators $\eta_\alpha^\dagger$, which form the components of a double-rank tensor,[9] the operators $a_\alpha^\dagger$ and $b_\alpha^\dagger$ are single-rank tensors. As a consequence of this, we find that the equation relating a reduced matrix element of $\mathbf{a}^\dagger$ to a fractional parentage coefficient is

$$\begin{aligned}([\lambda_A]\tau_A L_A\|a^\dagger\|[\bar{\lambda}_A]\bar{\tau}_A\bar{\Gamma}_A)=(-1)^{N_A}\{N_A(2L_A+1)\}^{1/2}&\\ \times([\lambda_A]\tau_A L_A\{|[\bar{\lambda}_A]\bar{\tau}_A\bar{\Gamma}_A),& \qquad (11)\end{aligned}$$

whereas the corresponding formula for a reduced matrix element of $\eta^\dagger$ [Eq. (31) of Ref. 9] contains the additional factor $(2S+1)^{1/2}$ on the right. The reduced matrix elements of $\mathbf{b}^\dagger$ are given by replacing the subscripts A by B in Eq. (11).

V. COULOMB INTERACTION

As a first example of the theory, we consider the Coulomb interaction between the electrons of an atom. We write

$$e^2/r_{ij}=\sum_k e^2(r_<^k/r_>^{k+1})(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)}).$$

The tensors $\mathbf{C}^{(k)}$ are related to the $\mathbf{v}^{(k)}$ by the equation[2]

$$\mathbf{C}^{(k)}=\mathbf{v}^{(k)}(-1)^l(2l+1)(2k+1)^{-1/2}\begin{pmatrix} l & k & l \\ 0 & 0 & 0\end{pmatrix},$$

so that our central problem is to evaluate the scalar products

$$\sum_{i>j}(\mathbf{v}_i^{(k)}\cdot\mathbf{v}_j^{(k)}).$$

In terms of tensors acting in the A and B spaces, we readily find

$$\sum_{i>j}(\mathbf{v}_i^{(k)}\cdot\mathbf{v}_j^{(k)})=\sum_{i>j}(\mathbf{a}_i^{(k)}\cdot\mathbf{a}_j^{(k)})+\sum_{i>j}(\mathbf{b}_i^{(k)}\cdot\mathbf{b}_j^{(k)})+\mathbf{A}^{(k)}\cdot\mathbf{B}^{(k)}, \qquad (12)$$

since products of the type $(\mathbf{a}_i^{(k)}\cdot\mathbf{b}_i^{(k)})$ that occur in the last scalar product are identically zero. The two sums on the right of Eq. (12) correspond to putting $k=k'=K=0$ in Eq. (8), and are trivially simple to evaluate. The product $\mathbf{A}^{(k)}\cdot\mathbf{B}^{(k)}$ is only slightly more difficult to handle; it is found by putting $k'=k$ and $K=0$. In this way the matrix elements of the Coulomb interaction are found as linear combinations of the radial integrals

$$F^{(k)}=e^2\langle(nl)^2|(r_<^k/r_>^{k+1})|(nl)^2\rangle.$$

To illustrate this method in detail, we take the three terms of f^6 for which $M_S=2$, $L=2$; and the three terms of f^3 for which $M_S=\frac{1}{2}$, $L=2$. From Table I we see that the first three correspond to

$$[\lambda_A]\times[\lambda_B]\equiv[11111]\times[1],$$

and the second three to the product $[11]\times[1]$. Since both $[11111]$ and $[11]$ decompose into (110) of $R_A(7)$, and since (110) → PFH (see Table II), our basic eigenfunctions are

$$|([11111]P\times[1]F)D\rangle, \quad |([11111]F\times[1]F)D\rangle, \quad |([11111]H\times[1]F)D\rangle \qquad (13)$$

for f^6, and

$$|([11]P\times[1]F)D\rangle, \quad |([11]F\times[1]F)D\rangle, \quad |([11]H\times[1]F)D\rangle \qquad (14)$$

for f^3. The matrix elements of the Coulomb interaction that arise from the two sums on the right of Eq. (12) are diagonal in L_A and L_B, and can be readily obtained—

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[8] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^N, d^N, and f^N Configurations* (Massachusetts Institute of Technology Press, Cambridge, Massachusetts, 1963).

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

together with their associated factors—simply by referring to the energies of $[\lambda_A]L_A$ and $[\lambda_B]L_B$ in the tables of Nielson and Koster,[8] and adding the two parts. Thus we find that the energies of $[11111]P$, $[11111]F$, $[11111]H$, $[1]F$, $[11]P$, $[11]F$, and $[11]H$ are $10E^0+33E^3$, $10E^0$, $10E^0-9E^3$, 0, E^0+33E^3, E^0, and E^0-9E^3, respectively, where the parameters E^k are Racah's linear combinations of the radial integrals $F^{(k)}$. For the term in $\mathbf{A}^{(k)}\cdot\mathbf{B}^{(k)}$, we use Eq. (8) in the form

$$\begin{aligned}\langle f^6([11111]L_A\times[1]F)D|(\mathbf{A}^{(k)}\cdot\mathbf{B}^{(k)})&\\ \times|f^6([11111]L_B\times[1]F)D\rangle&\\ =\begin{Bmatrix}L_A & k & L_B\\ 3 & 2 & 3\end{Bmatrix}([11111]L_A\|A^{(k)}\|[11111]L_B)&\\ \times([1]F\|B^{(k)}\|[1]F)&\end{aligned}\tag{15}$$

for the D terms of f^6 with $M_S=2$. The reduced matrix elements are found by using Nielson and Koster's tables[8] for $\mathbf{U}^{(k)}$ and multiplying their entries by $(2k+1)^{1/2}$. Owing to Eq. (10), an almost identical result holds for f^3. In fact, we can write down both energy matrices in the form $[d_{ij}]$, the individual matrix elements d_{ij} being given by the following equations:

$$\begin{aligned}d_{11}&=9E^0+(9/2)E^1+33E^3\\&\qquad\pm(84E^0+39E^1+1716E^2+132E^3)/14,\\ d_{12}&=d_{21}=\pm(E^1-286E^2)(6/7)^{1/2},\\ d_{13}&=d_{31}=\pm(E^1+65E^2-9E^3)(66)^{1/2}/7,\\ d_{22}&=9E^0+(9/2)E^1\pm(36E^0+13E^1+572E^2-22E^3)/6,\\ d_{23}&=d_{32}=\pm(E^1+260E^2-28E^3)(44/63)^{1/2},\\ d_{33}&=9E^0+(9/2)E^1-9E^3\\&\qquad\pm(252E^0+107E^1-10790E^2-494E^3)/42.\end{aligned}$$

The upper sign corresponds to the D terms of f^6 with $M_S=2$; the lower sign to the D terms of f^3 with $M_S=\frac{1}{2}$. The states from which the matrix elements d_{ij} are constructed are ordered as in (13) and (14). The energy eigenvalues ϵ can be found by solving the secular equation

$$|d_{ij}-\epsilon\delta(i,j)|=0\tag{16}$$

in the usual way.

VI. *LL* COUPLING

It is clear that the solutions to Eq. (16) must be identical to the term energies obtained by the conventional approach. The terms of f^6 with $M_S=2$ are all of the type ^5D; those of f^3 with $M_S=\frac{1}{2}$ are ^4D and two terms of the type ^2D. In contrast with the energy matrices obtained by the standard methods, the two matrices $[d_{ij}]$ are in a form that displays their close connection. Indeed, if $33E^3$ were deleted from d_{11} and $-9E^3$ from d_{33}, the spacings of the three ^5D terms of f^6 could be obtained from those of the D terms of f^3 simply by inverting the energy-level scheme. This remarkable result (which can be extended to include all terms of f^6 with $M_S=2$ and all terms of f^3 with $M_S=\frac{1}{2}$) throws new light on a familar connection between the terms of l^2 and those of the half-filled shell l^{2l+1} with maximum and next-to-maximum multiplicity: One energy-level scheme can be obtained from the other by a simple inversion. This is illustrated in Fig. 1 for f^2 and f^7. For $M_S=0$ of f^2 and $M_S=\frac{5}{2}$ of f^7, we find from Table I that

$$[\lambda_A]\times[\lambda_B]\equiv[1]\times[1],\quad[111111]\times[1],$$

and only $\mathbf{A}^{(k)}\cdot\mathbf{B}^{(k)}$ of the three terms on the right-hand side of Eq. (12) has nonvanishing matrix elements. This is precisely the scalar product that gives rise to the alternating signs in the d_{ij}. Our method thus provides a simple explanation for the inversion represented in Fig. 1, and at the same time shows why other sets of terms do not show similar properties.

A more spectacular success of the theory is the comparative purity of the eigenstates produced by diagonalizing the energy matrices. That is, a term occurring in nature can sometimes be labeled quite accurately by just one product $[\lambda_A]L_A\times[\lambda_B]L_B$. A good example of *LL* coupling, as this situation may be called, is provided by the ^5D terms of f^6. For $4f$ hydrogenic functions, which are a good approximation for rare-earth ions, we have[10]

$$\begin{aligned}E^0&=-18.87F_2,\quad &E^1&=14.68F_2,\\ E^2&=0.077F_2,\quad &E^3&=1.49F_2.\end{aligned}\tag{17}$$

These parameters lead to energies $-102.4F_2$, $-183.3F_2$, and $-231.3F_2$ with respective eigenfunctions

$$\begin{aligned}&-0.996|(P\times F)D\rangle+0.078|(F\times F)D\rangle\\&\qquad-0.053|(H\times F)D\rangle,\\ &0.094|(P\times F)D\rangle+0.990|(F\times F)D\rangle\\&\qquad-0.109|(H\times F)D\rangle,\\ &-0.050|(P\times F)D\rangle+0.114|(F\times F)D\rangle\\&\qquad+0.992|(H\times F)D\rangle.\end{aligned}\tag{18}$$

The symbols $[\lambda_A]$ and $[\lambda_B]$ have been omitted from the kets for the sake of clarity. In all cases $[\lambda_A]=[11111]$ and $[\lambda_B]=[1]$. It is at once seen that *LL* coupling is extremely well obeyed, the eigenfunctions above being pure states of the type $|(L_A\times L_B)L\rangle$ to within 98%. This is in contrast with Racah's classification scheme, where no single state makes a dominant contribution.

Of course, *LL* coupling works better for some terms than for others. The situation for the D terms of f^3 is quite poor, though even there *LL* coupling turns out to be useful in predicting certain properties of the levels (for example, the small spin-orbit splitting of the lowest D term).

To conclude this section, we give another example of good *LL* coupling, the four ^4G terms of f^5. The result of a complete diagonalization for the hydrogenic parameters (17) is shown in the central part of Fig. 2. On the

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[10] J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) **A240**, 509 (1957).

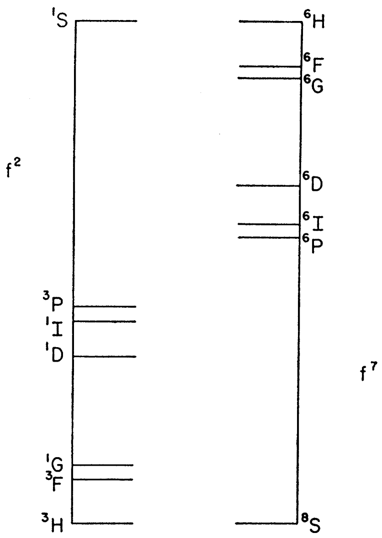

FIG. 1. The terms of f^2 (with $M_S=0$), when inverted, coincide with the terms of f^7 (with $M_S=\frac{5}{2}$), provided the same set of Slater integrals are used in both configurations. This familiar result is related to the alternation in sign of the matrix elements of $\mathbf{A}^{(k)}\cdot\mathbf{B}^{(k)}$.

left are Racah's diagonal matrix elements, on the right the diagonal matrix elements for the four states $|([1111]L_A\times[1]F)G\rangle$, where $L_A\equiv D$, F, G, and I. The latter are much closer to the actual energies.

VII. *g* ELECTRONS

The process of classifying states according to irreducible representations of groups can be extended to operators. The method consists in studying the commutators of the operators with respect to the generators of the relevant groups.[3] The results for several operators of interest are summarized in Table III. They are given in a form that is valid for all l. As an example of the usefulness of such classifications, we consider the energies of the terms of l^N of maximum multiplicity. Owing to the symmetry about the half-filled shell, attention may be restricted to those configurations for which $N\leq 2l+1$. From Table I, we deduce that all states with $M_S=S$ belong to the representations $[11\cdots 1]\times[0]$ of $U_A(2l+1)\times U_B(2l+1)$. It can also be seen that all representations $W_A\times W_B$ into which these product representations decompose are of the type $W_A=(11\cdots 10\cdots 0)$ and $W_B=(00\cdots 0)$. The fact that the states are completely scalar in the B space, when combined with the result (given in Table III) that the tensors $\mathbf{B}^{(k)}$ (with $k>0$) possess no scalar components in the B space, means that all matrix elements of $\mathbf{B}^{(k)}$ (with $k>0$) taken between states of maximum S and M_S are zero. This in turn implies that the scalar product $\mathbf{A}^{(k)}\cdot\mathbf{B}^{(k)}$ in Eq. (12) has null matrix elements when $k>0$. The relative energies of the terms of maximum multiplicity of l^N are thus determined solely by

$$\sum_{i>j}(\mathbf{a}_i^{(k)}\cdot\mathbf{a}_j^{(k)})\quad(k\text{ even}).$$

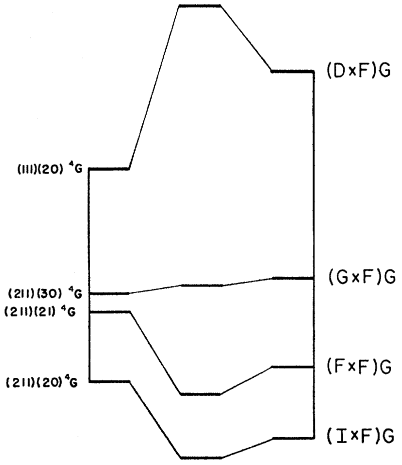

FIG. 2. Diagonal matrix elements for the ^5G terms of f^5 in LL coupling (on the right) are closer to the exact energies (in the center) than the diagonal matrix elements in Racah's scheme (on the left).

TABLE III. Transformation properties of operators for l^N.

Operator	$[W_AL_A\times W_BL_B]^{(L)}$
$\mathbf{a}^{(k)}$ or $\mathbf{A}^{(k)}$ (odd k)	$[(110\cdots 0)k\times(00\cdots 0)0]^{(k)}$
$\mathbf{a}^{(k)}$ or $\mathbf{A}^{(k)}$ (even nonzero k)	$[(20\cdots 0)k\times(00\cdots 0)0]^{(k)}$
$\mathbf{b}^{(k)}$ or $\mathbf{B}^{(k)}$ (odd k)	$[(00\cdots 0)0\times(110\cdots 0)k]^{(k)}$
$\mathbf{b}^{(k)}$ or $\mathbf{B}^{(k)}$ (even nonzero k)	$[(00\cdots 0)0\times(20\cdots 0)k]^{(k)}$
$\mathbf{a}^\dagger$	$[(10\cdots 0)l\times(00\cdots 0)0]^{(l)}$
$\mathbf{b}^\dagger$	$[(00\cdots 0)0\times(10\cdots 0)l]^{(l)}$
$W_{1q}^{(1k)}$ or $W_{-1q}^{(1k)}$	$[(10\cdots 0)l\times(10\cdots 0)l]_q^{(k)}$

From Table III, we see that the transformation properties in the A space are determined by the product $(20\cdots 0)\times(20\cdots 0)$, which decomposes into

$$(00\cdots 0)+(220\cdots 0)+(40\cdots 0)$$
$$+(110\cdots 0)+(20\cdots 0)+(310\cdots 0).$$

Of these representations, only the first three possess $R_A(3)$ scalars in their decomposition. Furthermore, the operator $(00\cdots 0)S$ displaces all terms equally; while any operator classified as $(40\cdots 0)S$ must have zero matrix elements, since $(40\cdots 0)$ does not occur in the reduction of

$$(11\cdots 10\cdots 0)\times(11\cdots 10\cdots 0).$$

The conclusion is striking: The relative energies of the terms of maximum multiplicity can only involve as many radial parameters (i.e., linear combinations of the integrals $F^{(k)}$) as there are S states in the decomposition of $(220\cdots 0)$ of $R_A(2l+1)$. For f electrons, only one S state occurs; as is well known, all relative energies of the terms of maximum multiplicity can be expressed as multiples of the one parameter E^3.

For g electrons, it is found that (2200) contains in its decomposition two S states.[6] This means that two parameters are required here. The results of Shortley and Fried[11] for g^2, which were established almost thirty years ago, must thus be expressible in a simple form for terms of maximum multiplicity. Indeed, we find that the term energies $E(^{2S+1}L)$ can be written as follows:

$$
\begin{aligned}
E(^3P)&=X+98Y+11Z,\\
E(^3F)&=X+33Y+11Z,\\
E(^3H)&=X-13Z,\\
E(^3K)&=X,
\end{aligned}
$$

where

$$
\begin{aligned}
X&=F_0-392F_2-784F_4-152F_6-17F_8,\\
Y&=3(5F_2+10F_4-3F_6-68F_8),\\
Z&=3(7F_2-35F_4+27F_6+17F_8).
\end{aligned}
$$

The quantities F_k are related through numerical factors[11] to the integrals $F^{(k)}$. Unless the co-ordinates of the g electrons fluctuate only slightly from a constant radius—which is most unlikely—the parameter Z is positive. This implies $E(^3H)<E(^3K)$. Thus g^2 is a simple configuration for which Hund's rule is not obeyed.[12] The relative energies of all terms of maximum multiplicity of other configurations g^N must be expressible in terms of Y and Z of course, but preliminary calculations indicate that further deviations from Hund's rule are not to be expected.

VIII. SPIN-ORBIT INTERACTION

The splittings of terms near the Russell-Saunders limit are calculated by making use of the equivalence

$$\zeta\sum_i(\mathbf{s}_i\cdot\mathbf{l}_i)\equiv\lambda\mathbf{S}\cdot\mathbf{L},\tag{19}$$

which is valid for a manifold of states of constant S and L. The relation between λ and the spin-orbit parameter ζ is established by setting the right- and left-hand sides of Eq. (19) between suitable states and evaluating the two matrix elements. When the terms are described by basis states of the type (6) above, the procedure can again be followed. It is convenient to assign the same value of M_S to both bra and ket, for then we get at once

$$
\begin{aligned}
\lambda M_SM_L=\zeta\langle([\lambda_A]\tau_AL_A\times[\lambda_B]\tau_BL_B)LM_LM_S\\
\times|\sum_i(s_{zi}l_{zi})|([\lambda_A]\tau_A'L_A'\times[\lambda_B]\tau_B'L_B')LM_LM_S\rangle.
\end{aligned}
$$

Now

$$
\begin{aligned}
\sum_i s_{zi}l_{zi}&=W_{00}{}^{(11)}\{l(l+1)(2l+1)/6\}^{1/2}\\
&=(A_0{}^{(1)}-B_0{}^{(1)})\{l(l+1)(2l+1)/12\}^{1/2},
\end{aligned}
$$

and

$$
\begin{aligned}
&([\lambda_A]\tau_AL_A\|A^{(1)}\|[\lambda_A]\tau_A'L_A')\\
&\quad=\{3/l(l+1)(2l+1)\}^{1/2}([\lambda_A]\tau_AL_A\|L_A\|[\lambda_A]\tau_A'L_A')\\
&\quad=\zeta(\tau_A,\tau_A')\zeta(L_A,L_A')\{3L_A(L_A+1)(2L_A+1)/\\
&\qquad\qquad l(l+1)(2l+1)\}^{1/2}.
\end{aligned}
$$

The equation for the reduced matrix element of $\mathbf{B}^{(1)}$ can be obtained at once by replacing the subscript A everywhere by B. The 9-j symbol of Eq. (8) can be explicitly evaluated, and we arrive at the result

$$
\begin{aligned}
\lambda=\zeta\delta(\tau_A,\tau_A')\delta(\tau_B,\tau_B')\delta(L_A,L_A')\delta(L_B,L_B')\\
\times[L_A(L_A+1)-L_B(L_B+1)]/[2M_SL(L+1)].
\end{aligned}\tag{20}
$$

The simplicity of this result is remarkable. Unlike the conventional expression,[10] no sum over products of coefficients of fractional parentage appears; and, being diagonal in all quantum numbers, no cross terms occur when λ is evaluated for states of the type (18). The three pure states (13) lead to $\lambda=-5\zeta/12$, 0, and $3\zeta/4$, respectively; these numbers agree well with the complete calculation,[10] which yielded $\lambda=-0.409\zeta$, 0.004ζ, and 0.737ζ. The fact that the spin-orbit splitting for the lowest ^5D term of f^6 came out two orders of magnitude larger than the next highest ^5D term can now be readily understood.

Occasionally a term can be described by a single value of L_A and a single value of L_B. We see at once from Eq. (20) that when $L_A=L_B$, the spin-orbit splitting is zero. The ^2P term of f^3 is a case in point. Its description in LL coupling is simply

$$|f^3([11]F\times[1]F)PM_LM_S\rangle,$$

since neither $[11]P$ nor $[11]H$ can be coupled with $[1]F$ to give a P state. So $L_A=L_B=3$ and $\lambda=0$. This resolves the long-standing problem of why the spin-orbit splitting of ^2P of f^3 should be zero.

Of course, Eq. (20) reproduces all the standard properties of multiplet splittings. As can be seen from Table I, the operation of conjugation (interchanging holes and electrons) corresponds to the interchange $W_A\leftrightarrow W_B$, which implies $L_A\leftrightarrow L_B$ and hence $\lambda\leftrightarrow-\lambda$. This accounts for the familiar opposition of multiplet splittings of conjugate terms in a shell.

A special case of Eq. (20) is of some interest. For a given term of maximum multiplicity, we can always make the choice $M_S=S$. It is evident from Table I that either $L_B=0$ (for the first half of a shell) or $L_A=0$ (for the second half). In the first case, $L_A=L$; in the second, $L_B=L$. Substitution in Eq. (20) yields the well-known result $\lambda=\pm\zeta/2S$, where the upper and lower signs refer, respectively, to the first and second halves of a shell.

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[11] G. H. Shortley and B. Fried, Phys. Rev. **54**, 739 (1938).

[12] This agrees with the semiclassical argument of N. Karayianis [Am. J. Phys. 33, 201 (1965)]. An explicit demonstration that $E(^3H)<E(^3K)$ has been made for hydrogenic 5g electrons by J. Bauche (private communication).

IX. SPIN-OTHER-ORBIT COUPLING

The power of the methods based on the use of the A and B spaces is illustrated by considering the magnetic interaction between the spin of one electron and the orbit of another. As a specific example, it is convenient to study the effect of this interaction on the sextet levels of f^7. Since f^7 is a half-filled shell, all diagonal matrix elements of the spin-orbit interaction vanish[9]; consequently, the spin-other-orbit interaction H_{soo} plays a more important role than it does for other configurations of f electrons.

Conventional theory provides two avenues for treating this problem. The first is to construct all the relevant two-particle fractional parentage coefficients connecting the sextets of f^7 with the sextets and quartets of f^5. Each matrix element of H_{soo} is then expressed as a sum over matrix elements of H_{soo} for the two separated electrons f^2. Once the last have been calculated, the sum can be performed. The second approach is to set up a chain calculation in which the available tables of fractional parentage coefficients are used to relate the matrix elements of H_{soo} or f^N to those of f^{N-1}. Starting then with f^2, we eventually arrive at the required results for f^7. Either method is extremely tedious, not least because H_{soo} is perhaps the most complex operator commonly encountered in atomic spectroscopy. (A third method,[5] in which the two-particle operator is converted into a product of sums of single-particle operators, suffers from its complexity and the need for subsidiary tables of reduced matrix elements.)

If we restrict our attention to matrix elements of H_{soo} that are diagonal in M_S, we may write H_{soo} (for equivalent l electrons) as follows[13]:

$$\begin{aligned}H_{\mathrm{soo}}=-\sum_{i\neq j}\sum_{k}\,&[(k+1)(2l+k+2)(2l-k)/3]^{1/2}\\&\times[\{\mathbf{w}_i^{(0\,k+1)}\mathbf{w}_j^{(1k)}\}_{00}{}^{(11)}\{M^{(k-1)}(l\|C^{(k+1)}\|l)^2\\&+2M^{(k)}(l\|C^{(k)}\|l)^2\}+\{\mathbf{w}_i^{(0k)}\mathbf{w}_j^{(1\,k+1)}\}_{00}{}^{(11)}\\&\times\{M^{(k)}(l\|C^{(k)}\|l)^2+2M^{(k-1)}(l\|C^{(k+1)}\|l)^2\}],\end{aligned}$$

where the radial integrals $M^{(k)}$ are defined by[14]

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

The first step in treating H_{soo} by the methods described in the previous sections is to replace the tensors $\mathbf{w}^{(\kappa k)}$ by the appropriate combinations of the tensors $\mathbf{a}^{(k)}$ and $\mathbf{b}^{(k)}$. Having done this, we make an analogous statement to Eq. (19):

$$H_{\mathrm{soo}}\equiv\lambda'\mathbf{S}\cdot\mathbf{L}. \tag{21}$$

Once λ' is known, the contribution to multiplet structure coming from spin-other-orbit interactions can be readily calculated. Setting both sides of Eq. (21) between states of l^N, and then passing to reduced matrix elements, we find

$$\begin{aligned}\lambda'=-(M_S)^{-1}\sum_{k}&[(k+1)(2l+k+2)(2l-k)/3L(L+1)(2L+1)]^{1/2}\\&\times[\tfrac{3}{2}\{M^{(k)}(l\|C^{(k)}\|l)^2+M^{(k-1)}(l\|C^{(k+1)}\|l)^2\}(\psi\|\sum_{i\neq j}\{\mathbf{a}_i^{(k)}\mathbf{a}_j^{(k+1)}\}^{(1)}-\{\mathbf{b}_i^{(k)}\mathbf{b}_j^{(k+1)}\}^{(1)}\|\psi')\\&+\tfrac{1}{2}\{M^{(k)}(l\|C^{(k)}\|l)^2-M^{(k-1)}(l\|C^{(k+1)}\|l)^2\}(\psi\|\{\mathbf{A}^{(k)}\mathbf{B}^{(k+1)}\}^{(1)}-\{\mathbf{A}^{(k+1)}\mathbf{B}^{(k)}\}^{(1)}\|\psi')],\end{aligned}$$

in which

$$\psi\equiv([\lambda_A]\tau_AL_A\times[\lambda_B]\tau_BL_B)L,$$

and

$$\psi'\equiv([\lambda_A]\tau_A'L_A'\times[\lambda_B]\tau_B'L_B')L.$$

We now make the specific substitutions $[\lambda_A]=[11\cdots1]$ (in which $2l$ symbols 1 appear),

$$[\lambda_B]=[1],\quad L_A=L_B=L_A'=L_B'=l,$$

corresponding to the terms of next-to-maximum multiplicity of the half-filled shell l^{2l+1}. Equations (8) and (10) are used to simplify the matrix elements, and the final result is

$$\begin{aligned}\lambda'=-4M^{(0)}\left(\frac{2l+1}{2l-1}\right)+\sum_{k}&\frac{(2l+k+2)(2l-k)(k+1)}{(2l-1)L(L+1)(k+2)}(l\|C^{(k)}\|l)^2M^{(k)}(-1)^L\\&\times\left[\frac{3L(L+1)}{2l(2l+1)(l+1)}(-1)^L+(k+2)\begin{Bmatrix}l&l&k\\l&l&L\end{Bmatrix}+\begin{Bmatrix}l&l&k+1\\l&l&L\end{Bmatrix}-(k+1)\begin{Bmatrix}l&l&k+2\\l&l&L\end{Bmatrix}\right].\end{aligned}\tag{22}$$

For our purposes, we have only to set $l=3$ and run over the values of L satisfying $6\geq L\geq1$. However, the general form of Eq. (22) is convenient, because we can set in turn $l=1$ and $l=2$, thus checking our results against the known results[15] for p^3 and d^5. The calculations for f electrons are summarized in Table IV.

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

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

[15] H. Horie, Progr. Theoret. Phys. (Kyoto) 10, 296 (1953); T. M. Dunn and Wai-Kee Li, J. Chem. Phys. 46, 2907 (1967).

The importance of spin-other-orbit effects can be gauged by taking the values of the integrals $M^{(k)}$ as tabulated by Blume, Freeman, and Watson[16] for the configuration f^7 in Gd^{3+}. They give (in cm^{-1}) $M^{(0)}=3.70$, $M^{(2)}=1.71$, and $M^{(4)}=1.16$, from which we calculate (using Table IV) $\lambda'(^6I)=-17\ \mathrm{cm}^{-1}$. This produces an energy separation between $^6I_{7/2}$ and $^6I_{15/2}$ of $24\lambda'$, namely 408 cm^{-1}. Since the observed[17] multiplet structure (which is regular, not inverted) extends over only 827 cm^{-1}, it is clear that spin-other-orbit effects must play an important role. Wybourne[18] recently diagonalized the complete f^7 energy matrix, including in it Coulombic and spin-orbit effects, but neglecting contributions from spin-other-orbit interactions. He found that an interpolated spin-orbit coupling constant ζ predicts multiplet splittings that are too large, and it is probable that this result is due, at least in part, to the neglected effects of H_{soo}. However, it would be necessary to carry out a further complete diagonalization, allowing also for spin-spin interactions and relativistic effects, before a conclusive answer could be given. A detailed treatment of this kind is beyond the scope of the present article.

X. CONCLUSION

Having stressed the advantages of the present classification scheme, a word should be added about its deficiencies. These stem from the abandonment of S. The fact that S is a good quantum number for electrostatic interactions means that the Coulombic energy matrix for a given M_S includes among its eigenvalues all those that arise from energy matrices corresponding to higher M_S values. The duplication that this leads to may not be too troublesome with present computing techniques, especially since the matrix elements themselves may be easier to compute than by conventional methods. Indeed, the independent checks that this duplication affords may be a positive advantage, provided the energy matrices do not become too large. The problem becomes more acute when the spin-orbit interaction is considered; for, unless we are only interested in the Russell-Saunders limit, we must consider the mixing of M_S values, and we are left only with M_J to characterize the matrices. The duplication of eigenvalues occurs much more frequently, and probably makes this extension uneconomic, except for a few special cases.

TABLE IV. Spin-other-orbit coupling constants for the sextets of f^7.

Term	λ'
^6P	$-(21/5)M^{(0)}+(9/5)M^{(2)}+(21/11)M^{(4)}$
^6D	$-(319/75)M^{(0)}+(221/225)M^{(2)}-(47/99)M^{(4)}$
^6F	$-(13/3)M^{(0)}+(11/45)M^{(2)}+(5/99)M^{(4)}$
^6G	$-(111/25)M^{(0)}-(53/825)M^{(2)}+(361/1815)M^{(4)}$
^6H	$-(343/75)M^{(0)}+(311/5445)M^{(2)}+(287/5445)M^{(4)}$
^6I	$-(71/15)M^{(0)}+(131/495)M^{(2)}+(1355/14157)M^{(4)}$

The value of the approach based on the A and B spaces lies chiefly in the insight it gives into shell structure, and in the ease with which certain calculations can be performed. Although the applications described above have been restricted to equivalent electrons, it is clear that it would be straightforward to extend the method to inequivalent electrons: It is only necessary to separate the electrons with spin up from those with spin down and put them in the A and B spaces.

The reason for the frequent occurrence of remarkably good LL coupling is not clear. A naive interpretation would be to conclude that the Coulomb interactions between electrons with all their spins up, and those between electrons with all their spins down, are more important than the interactions between electrons with their spins opposed. This is by no means the case, particularly since electrons with opposed spins are not restricted to nonoverlapping orbits by the Pauli exclusion principle. The difficulty of giving a physical basis for LL coupling is accentuated by the fact that, apart from a few trivial cases, no single choice of Slater integrals can ensure perfect coupling for all terms in a configuration l^N. A possible line of attack on this problem is to examine in detail the coupling between L_A and L_B. This plays a crucial role in determining whether or not LL coupling is obeyed.

Note added in proof. Dr. M. Wilson has kindly drawn my attention to an article by Shudeman,[19] in which electrons with spin up are separated from those with spin down in order to count the number of terms with a given S and L in the configurations l^N, where $l\leq 6$.

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