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ABSTRACT

To every irreducible representation W of the rotation group in $2\ell+1$ dimensions that is used to classify states of the electronic configurations ℓ^n, there correspond two couples (v,S), where v and S stand for the seniority number and total spin, respectively. Determinantal product states are introduced to examine this correspondence in detail. It is shown that for two double tensors $\underset{\sim}{W}^{(\kappa k)}$ and $\underset{\sim}{W}^{(\kappa' k)}$, the set of reduced matrix elements

$$(\ell^n\, v_1\, W\, \xi\, S_1\, L \,\|\, W^{(\kappa k)} \,\|\, \ell^n\, v_1'\, W'\, \xi'\, S_1'\, L'),$$

for fixed n, v_1, v_1' W, and W', is proportional to the set

$$(\ell^m\, v_2\, W\, \xi\, S_2\, L \,\|\, W^{(\kappa' k)} \,\|\, \ell^m\, v_2'\, W'\, \xi'\, S_2'\, L'),$$

where ξ and ξ' are additional labels that may be required to define the states uniquely, provided (a) the two couples (v_1,S_1) and (v_2,S_2) are distinct, (b) the two couples (v_1',S_1') and (v_2',S_2') are distinct, and (c) the sum $\kappa+\kappa'+k$ is odd. The amplitudes of the double tensors are chosen so that the constant of proportionality is equal to the ratio of two 3-j symbols, multiplied by a phase factor. An explicit expression for this factor is given for f electrons, and a number of applications are discussed.

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I. SYMMETRY

Conjugate electronic configurations of the type ℓ^n and $\ell^{4\ell+2-n}$ share many properties. Perhaps the most familiar is the occurrence of identical term schemes; as a consequence of this, a table of the terms occurring in the configurations ℓ^0, ℓ^1, ℓ^2, $\cdots$, $\ell^{4\ell+2}$ exhibits a symmetry about the half-filled shell, $\ell^{2\ell+1}$. A glance at Table I [7] of Condon and Shortley,[1] which lists the terms of all configurations of the type p^n, d^n, and f^n, makes it obvious that other kinds of symmetry exist. The most striking is the symmetry with respect to L (the quantum number of the total orbital angular momentum) of the terms of maximum multiplicity about the quarter- and three-quarter–filled shells. For example, the terms of f^5 with S (the quantum number of the total spin angular momentum) equal to 5/2 are ^6P, ^6F, and ^6H; while those of f^2 with S equal to 1 are ^3P, ^3F, and ^3H. At first sight, it appears difficult to find similar types of symmetry for terms possessing less than the maximum value of S. However, this is because the quantum number that should be associated with a sequence of L values is not S, but M_S. With this clue, we can uncover a large number of symmetries of a rather spectacular kind in Condon and Shortley's table; for example, the L values of the terms of f^5 that can produce components with $M_S=\pm3/2$, namely

$$S\ P^3\ D^3\ F^5\ G^4\ H^4\ I^3\ K^2\ L\ M, \tag{1}$$

are precisely the same as the L values of the terms of f^4 that can produce components with $M_S=\pm1$. [The superscript to a letter of the Sequence (1) indicates the number of times the corresponding L value occurs.]

We can gain some understanding of the recurrence of a sequence of L values by listing the irreducible representations W of $R_{2\ell+1}$, the rotation group in $2\ell+1$ dimensions, to which the representations $\mathcal{D}_L$ of R_3 belong. From Table II of Elliott et al.,[2] we find, for example, that Sequence (1) corresponds to the irreducible representations (110), (211), and(111) of R_7, both for f^4 and f^5. The problem of explaining why certain sequences of L values recur in different configurations can thus be made equivalent to the problem of explaining why certain sequences of W values recur. In the latter form, the problem is seen to be closely connected to an observation of Racah,[3] namely, that to every representation W of the type used in classifying states of ℓ^n, there correspond two values of the couple (v,S), where v stands for the seniority. If we denote two such couples by (v_1,S_1) and (v_2,S_2), then, according to Eq. (54) of Racah,[3]

$$v_1+2S_2 = v_2+2S_1 = 2\ell+1. \tag{2}$$

For the representations (110), (211), and (111) of our example, we find, from Table 2 of Elliott et al.,[2] that the couples (v,S) are (5,5/2), (5,3/2), and (3,3/2) for f^5, and (2,1), (4,1), and (4,2) for f^4.

In themselves, the symmetries with respect to L possess little more than a curiosity value. Our reason for introducing them lies in the hope that they will lead to symmetries with respect to matrix elements. It is well known that the matrix elements of most operators exhibit simple symmetry properties about the half-filled shell, and for states of maximum multiplicity it is usually not difficult to derive relations between matrix elements in symmetrical positions on either side of the quarter- or three-quarter-filled shell [see, for example, Eq. (15) of Judd[4]]. It therefore seems reasonable to anticipate analogous relations for other types of symmetry. This expectation is strengthened by Eq. (73) of Racah,[3] which relates matrix elements of the part e_2 of the Coulomb interaction between states defined by one couple (v_1,S_1) to those between states defined by the corresponding couple (v_2,S_2). Furthermore, Wybourne[5] has shown that many matrix elements of the spin-orbit interaction between states belonging to the two representations W and W' of R_7 are proportional to similar matrix elements in other configurations. Some of his results are examples of Eqs. (67) and (69b) of Racah,[6] and are of no interest here; of the others, in each case the pair of couples (v_1,S_1) and (v_2,S_2) corresponding to W, and also the pair (v_1',S_1') and (v_2',S_2') corresponding to W', separately satisfy Eqs. (2).

The first aim of this paper is to explore the symmetries within configurations of the type ℓ^n. Most single-particle interactions of atomic spectroscopy can be concisely expressed as the components of double tensors, and the second objective is to derive relations between the matrix elements of such operators. Since the spin-orbit interaction is the scalar part of a double tensor of rank one with respect to spin, and of similar rank with respect to orbit, the second part of the program can be regarded as a generalization of Wybourne's[5] work to arbitrary double tensors.

II. DOUBLE TENSORS

In order to define the operators with which we shall be concerned, we first introduce the tensors $\underset{\sim}{t}^{(\kappa)}$ and $\underset{\sim}{v}^{(k)}$ that act in the spin and orbital spaces respectively of a single electron, and for which

$$(s \| t^{(\kappa)} \| s) = (2\kappa+1)^{1/2}$$

and

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

The $(2\kappa+1)(2k+1)$ products

$$w_{\pi q}^{(\kappa k)} = t_{\pi}^{(\kappa)} v_{q}^{(k)} \qquad (-\kappa \leq \pi \leq \kappa;\ -k \leq q \leq k)$$

form the components of the double tensor $\underset{\sim}{w}^{(\kappa k)}$, for which

$$(s\ \ell \| w^{(\kappa k)} \| s\ \ell) = (2\kappa+1)^{1/2}(2k+1)^{1/2}. \tag{3}$$

Many-electron tensor operators for the configuration ℓ^n can be easily constructed by summing the operators for the n individual electrons; thus

$$\underset{\sim}{W}^{(\kappa k)} = \sum_i (\underset{\sim}{w}^{(\kappa k)})_i$$

and

$$\underset{\sim}{V}^{(k)} = \sum_i (\underset{\sim}{v}^{(k)})_i .$$

We note

$$\underset{\sim}{V}^{(k)} = \underset{\sim}{W}^{(0k)}\sqrt{2}.$$

The set of quantum numbers $WSLM_SM_L$ is not always sufficient to specify a state of ℓ^n completely. We therefore include the additional symbol ξ; for f electrons this can often be replaced by an irreducible representation

U of the group G_2.[3] All reduced matrix elements of $\underset{\sim}{W}^{(\kappa k)}$ can be calculated by means of the formula

$$(\ell^n W \xi S L \| W^{(\kappa k)} \| \ell^n W' \xi' S' L')$$

$$= n[(2S+1)(2\kappa+1)(2S'+1)(2L+1)(2k+1)(2L'+1)]^{1/2}$$

$$\times \sum_{\overline{\psi}} (\psi\{|\overline{\psi})(\psi'\{|\overline{\psi})(-1)^{\overline{S}+s+S+\kappa+\overline{L}+\ell+L+k} \qquad (4)$$

$$\times \begin{Bmatrix} S & \kappa & S' \\ s & \overline{S} & s \end{Bmatrix} \begin{Bmatrix} L & k & L' \\ \ell & \overline{L} & \ell \end{Bmatrix}$$

where ψ, ψ' and $\overline{\psi}$ are abbreviations for $W\xi SL$, $W'\xi'S'L'$, and $\overline{W}\overline{\xi}\overline{S}\overline{L}$, respectively. However the construction of the fractional parentage coefficients $(\psi\{|\overline{\psi})$ and $(\psi'\{|\overline{\psi})$, and the summation over the parent terms $\overline{\psi}$, are often extremely tedious to perform. In seeking to establish relations between different reduced matrix elements, we aim to circumvent this procedure as much as possible.

III. DETERMINANTAL PRODUCT STATES

In Section I we mentioned the correspondence between the states f^5 with $M_S=\pm 3/2$, and those of f^4 with $M_S=\pm 1$. For both configurations, the state for which $M_L=L=9$ can be expressed as a single determinantal product state. However, without examining the phases of our states in detail, we cannot be sure whether, for example, we should identify

$$|f^5, {}^4M, M_S=-3/2, M_L=9)$$

with

$$\{3^+, 3^-, 2^-, 1^-, 0^-\}$$

or with

$$-\{3^+, 3^-, 2^-, 1^-, 0^-\}.$$

We shall return to questions of phase later for the moment, we avoid the difficulty by introducing the new states

$$|\ell^n\, W\, \xi\, S\, L\, M_S\, M_L\rangle$$

characterized by angular brackets, whose phases are at our disposal. We can therefore write

$$|f^5,\ ^4M,\ M_S=-3/2,\ M_L=9\rangle \equiv \{3^+,\ 0^-,\ 1^-, 2^-, 3^-\} \qquad (5)$$

and

$$|f^4,\ ^3M,\ M_S=-1,\ M_L=9\rangle \equiv \{3^+, 1^-, 2^-, 3^-\}. \qquad (6)$$

Operating on Eq. (5) with $W^{(12)}_{0-2}$, and using Eq. (3), we find

$$W^{(12)}_{0-2}\ |f^5,\ ^4M,\ M_S=-3/2,\ M_L=9\rangle$$

$$\equiv (5/84)^{1/2}\{1^+,\ 0^-,\ 1^-,\ 2^-,\ 3^-\} + (5/42)^{1/2}\{3^+,\ -2^-,\ 1^-,\ 2^-,\ 3^-\}$$

$$+ (1/7)^{1/2}\{3^+,\ -1^-,\ 0^-,\ 2^-,\ 3^-\}. \qquad (7)$$

Similarly, from Eq. (6), we get

$$W^{(02)}_{0-2}\ |f^4,\ ^3M,\ M_S=-1,\ M_L=9\rangle$$

$$\equiv (5/84)^{1/2}\{1^+,\ 1^-,\ 2^-,\ 3^-\} + (5/42)^{1/2}\{3^+,\ 1^-,\ 0^-,\ 3^-\}$$

$$+ (1/7)^{1/2}\{3^+,\ -1^-,\ 2^-,\ 3^-\}. \qquad (8)$$

The striking similarity between Eqs. (7) and (8) prompts us to ask the following questions:

(i) Can the determinantal product states of f^5 for which $M_S=-3/2$ be put into a one-to-one correspondence with the determinatal product states of f^4 for which $M_S=-1$?

(ii) If (i) is true, what is its generalization?

(iii) If it can be established that the determinantal product state $\{a_\gamma\}$ of ℓ^{n_a} corresponds to the unique determinantal product state $\{b_\gamma\}$ of ℓ^{n_b}, and vice versa, what are the conditions on κ, k, q, κ', k', and q' if $c_{\gamma\rho}$ and $d_{\gamma\rho}$ in the expansions

$$W_{0q}^{(\kappa k)}\{a_\gamma\} = \sum_\rho c_{\gamma\rho}\{a_\rho\} \tag{9}$$

and

$$W_{0q'}^{(\kappa' k')}\{b_\gamma\} = \sum_\rho d_{\gamma\rho}\{b_\rho\} \tag{10}$$

are to satisfy

$$c_{\gamma\rho} = d_{\gamma\rho} \tag{11}$$

for all γ and ρ?

Questions (i) and (ii) can be taken together. Suppose that the g integers $m_i (i = 1, 2, \cdots, g)$, constituting the set P_α, satisfy the inequalities

$$\ell \geq m_1 > m_2 > \cdots > m_i > \cdots > m_g \geq -\ell \tag{12}$$

and that the h integers m_j' $(j=1, 2, \cdots, h)$, constituting the set P_β', satisfy the inequalities

$$\ell \geq m_1' > m_2' > \cdots > m_j' > \cdots > m_h' \geq -\ell. \tag{13}$$

We denote the combined set of g+h integers by Q_γ. We can construct two determinantal product states, corresponding to any such set Q_γ, according to the following rules:

(a) Delete from

$$\{\ell^+, (\ell-1)^+, \cdots, (-\ell)^+, \ell^-, (\ell-1)^-, \cdots, (-\ell)^-\},$$

the state corresponding to a completely filled shell, those entries $(m_\ell)^+$ for which m_ℓ coincides with a member of P_β, and also those entries $(m_\ell)^-$ for which m_ℓ coincides with a member of P_β'.

(b) Delete from

$$\{\ell^+, (\ell-1)^+, \cdots, (-\ell)^+\},$$

the state corresponding to a half-filled shell with maximum M_S, those entries $(m_\ell)^+$ for which m_ℓ is a member of P_α, and insert the sequence

$$(-m_1')^-, (-m_2')^-, \cdots, (-m_h')^-$$

between $(-\ell)^+$ and the final bracket.

The resulting quantities, which we denote by $\{a_\gamma\}$ and $\{b_\gamma\}$, respectively, are

$$\{a_\gamma\} \equiv \{\ell^+, \cdots, (m_i+1)^+, (m_i-1)^+, \cdots (-\ell)^+, \ell^-, \cdots, (m_j'+1)^-,$$

$$(m_j'-1)^-, \cdots, (-\ell)^-\} \qquad (14)$$

and

$$\{b_\gamma\} \equiv \{\ell^+, \cdots, (m_i+1)^+, (m_i-1)^+, \cdots, (-\ell)^+,$$

$$(-m_1')^-, (-m_2')^-, \cdots, (-m_j')^-, \cdots, (-m_h')^-\}. \qquad (15)$$

The first, $\{a_\gamma\}$, is a determinantal product state of $\ell^{4\ell+2-g-h}$; the second $\{b_\gamma\}$, of $\ell^{2\ell+1-g+h}$. The values of M_S for these two states, which we write as M_{Sa} and M_{Sb}, are given by

$$M_{Sa} = \frac{1}{2}(h-g)$$

and

$$M_{Sb} = \frac{1}{2}(2\ell+1-g-h).$$

Upon writing

$$4\ell+2-g-h = n_a$$

and

$$2\ell+1-g+h = n_b,$$

we see

$$M_{Sa} = -\frac{1}{2}(2\ell+1-n_b) \qquad (16)$$

and

$$M_{Sb} = -\frac{1}{2}(2\ell+1-n_a). \qquad (17)$$

If two entries of a determinantal product state are interchanged, the state becomes multiplied by -1. Two determinantal product states, whose entries can be perfectly matched by a process of rearrangement, are equivalent.

The Inequalities (12) and (13) impose a standard ordering on the entries of the states (14) and (15), and guarantee that no two determinantal product states $\{a_\gamma\}$ and $\{a_\delta\}$, deriving from two distinct sets Q_γ and Q_δ, are equivalent. Similar remarks apply to states of the type $\{b_\gamma\}$. If we suppose ℓ, g, and h to be fixed, it follows that to each state $\{a_\gamma\}$ of ℓ^{n_a} there corresponds a unique state $\{b_\gamma\}$ of ℓ^{n_b}, and vice versa. From Inequalities (12) and (13), g and h are nonnegative integers, not exceeding $2\ell+1$. Provided we restrict our attention to configurations ℓ^n for which $n \leq 2\ell+1$— and, in view of the familiar symmetry with respect to the half-filled shell, nothing is gained by considering configurations in the second half of the shell— these conditions imply only that n_a+n_b must be an odd integer greater than or equal to $2\ell+1$. Given, then, two configurations ℓ^{n_a} and ℓ^{n_b} comprising an odd and an even number of electrons, the total number being at least $2\ell+1$, the states of ℓ^{n_a} for which M_S is determined by Eq. (16) can be put into a one-to-one correspondence with those of ℓ^{n_b}, for which M_S is determined by Eq. (17). This statement answers Questions (i) and (ii) above.

Having established a method for drawing correspondences between states of the types $\{a_\gamma\}$ and $\{b_\gamma\}$, it is straightforward to construct the right-hand sides of Eqs. (9) and (10) in detail, and to pick out corresponding coefficients $c_{\gamma\rho}$ and $d_{\gamma\rho}$. For Eq. (11) to be valid for arbitrary ℓ, the conditions on κ, k, q, κ', k', and q' turn out to be

$$\begin{aligned} q' &= q, \\ k' &= k, \\ (-1)^{\kappa+\kappa'+k} &= -1. \end{aligned} \tag{18}$$

The last equation holds if $\kappa+\kappa'+k$ is odd. These equations provide the answers to Question (iii).

IV. MATRIX ELEMENTS

The infinitesimal operators of the group $R_{2\ell+1}$ can be taken to be $W_{0q}^{(\dot{0}k)}$, where k is odd.[3] Any one of these operators, acting on a member $\{a_\gamma\}$ of the collection of determinantal product states of ℓ^{n_a} with $M_S = M_{Sa}$, generates a linear combination of states of the collection. It follows that the collection of states $\{a_\gamma\}$ for all possible Q_γ forms a basis for a representation of $R_{2\ell+1}$. Now for every operation with $W_{0q}^{(0k)}$ on a state $\{a_\gamma\}$ of ℓ^{n_a}, we can construct a corresponding operation on the state $\{b_\gamma\}$ of ℓ^{n_b}. According to Eqs. (18), the appropriate operator is again the infinitesimal operator $W_{0q}^{(0k)}$ of $R_{2\ell+1}$. Hence the transformation properties of the basis functions $\{a_\gamma\}$ are identical to those of the basis functions $\{b_\gamma\}$. We conclude that the irreducible representations W, into which the two representations with these bases decompose, are also identical. This accounts for the recurrence of sequences of W values, the existence of which was mentioned in Section I.

The correspondence between the transformation properties of the two sets of basis functions $\{a_\gamma\}$ and $\{b_\gamma\}$ holds not only for $R_{2\ell+1}$, but also for any of its subgroups, since the infinitesimal operators of the latter can be chosen from those operators $W_{0q}^{(0k)}$ for which k is odd. The labels L and M_L can be interpreted as irreducible representations of R_3 and R_2; hence, given a particular expansion

$$|\ell^{n_a} v_1 W \xi S_1 L M_{Sa} M_L\rangle = \sum_\rho \lambda_\rho \{a_\rho\} \tag{19}$$

for ℓ^{n_a}, we can be sure that the linear combination

$$\sum_\rho \lambda_\rho \{b_\rho\} \tag{20}$$

corresponds to the same set of quantum numbers W, L, and M_L. The symbol ξ can also be carried over if its choice influences the properties of the linear combination of determinantal product states with respect to the tensors $W_{0q}^{(0k)}$ for which k is odd. However, since either n_a or n_b is odd and the other even, the couple (v_2,S_2) associated with the Expression (20) cannot be the same as (v_1,S_1). We may therefore write

$$|\ell^{n_b}\ v_2\ W\ \xi\ S_2\ L\ M_{Sb}\ M_L\rangle = \sum_\rho \lambda_\rho\ \{b_\rho\}, \tag{21}$$

with the understanding the v_1, v_2, S_1, and S_2 satisfy Eqs. (2).

The construction of the matrix elements follows easily. If we operate on the right-hand sides of Eqs. (19) and (20) with $W_{0q}^{(\kappa k)}$ and $W_{0q}^{(\kappa' k)}$, respectively, where $\kappa+\kappa'+k$ is odd, the resultant linear combinations of determinantal product states correspond perfectly. The matrix elements are readily completed in a quite general fashion, and we obtain the result

$$\langle\ell^{n_a}\ v_1'\ W'\ \xi'\ S_1'\ L'\ M_{Sa}\ M_{L'}\ |\ W_{0q}^{(\kappa k)}\ |\ \ell^{n_a}\ v_1\ W\ \xi\ S_1\ L\ M_{Sa}\ M_L\rangle$$
$$= \langle\ell^{n_b}\ v_2'\ W'\ \xi'\ S_2'\ L'\ M_{Sb}\ M_{L'}\ |\ W_{0q}^{(\kappa' k)}\ |\ \ell^{n_b}\ v_2\ W\ \xi\ S_2\ L\ M_{Sb}\ M_L\rangle.$$

To bring the notation into line with that of Eq. (4), we reverse the labelings of the states, and replace the angular brackets by regular ones. The latter operation introduces a phase factor $(-1)^x$, where x is independent of κ,κ', and k. Passing to reduced matrix elements, we obtain

$$\frac{(\ell^{n_a}\ v_1\ W\ \xi\ S_1\ L\ \|\ W^{(\kappa k)}\ \|\ \ell^{n_a}\ v_1'\ W'\ \xi'\ S_1'\ L')}{(\ell^{n_b}\ v_2\ W\ \xi\ S_2\ L\ \|\ W^{(\kappa' k)}\ \|\ \ell^{n_b}\ v_2'\ W'\ \xi'\ S_2'\ L')}$$

$$= (-1)^{S_2-S_1-M_{Sb}+M_{Sa}+x} \begin{pmatrix} S_2 & \kappa' & S_2' \\ -M_{Sb} & 0 & M_{Sb} \end{pmatrix} \begin{pmatrix} S_1 & \kappa & S_1' \\ -M_{Sa} & 0 & M_{Sa} \end{pmatrix}^{-1}$$

$$= (-1)^{x+(n_b+v_2-v_1-n_a)/2} \begin{pmatrix} \frac{1}{2}(2\ell+1-v_1) & \kappa' & \frac{1}{2}(2\ell+1-v_1') \\ \frac{1}{2}(2\ell+1-n_a) & 0 & -\frac{1}{2}(2\ell+1-n_a) \end{pmatrix}$$

$$\times \begin{pmatrix} \frac{1}{2}(2\ell+1-v_2) & \kappa' & \frac{1}{2}(2\ell+1-v_2') \\ \frac{1}{2}(2\ell+1-n_b) & 0 & -\frac{1}{2}(2\ell+1-n_b) \end{pmatrix}^{-1}$$

The last line of the above equation follows from Eqs. (2), (17), and (18). To complete the program outlined in the last paragraph of Section I we have but to determine x.

V. PHASE

Racah[3] has shown that the fractional parentage coefficients can be factorized according to

$$\begin{aligned}(\psi\{|\overline{\psi}) &\equiv (\ell^n\ v\ W\ \xi\ S\ L\ \{|\ell^{n-1}\ \overline{v}\ \overline{W}\ \overline{\xi}\ \overline{S}\ \overline{L}) \\ &= (\ell^n\ v\ S\ \{|\ell^{n-1}\ \overline{v}\ \overline{S} + \ell)\ (W\ \xi\ L\ |\ \overline{W}\ \overline{\xi}\ \overline{L} + \ell).\end{aligned}$$

If the fractional parentage coefficients are always constructed as a product of these two parts, we can be sure that the second factor does not contain any hidden phase factors dependent on n. Under these conditions, we can often use Eq. (4) to gain information about x.

Suppose, for example, that we make the substitutions $\kappa=k=\kappa'=1$, $v_1'=v_1-2$, and $S_1'=S_1-1$ in the reduced matrix elements of Eq. (22). Equations (2) must be satisfied by the primed quantities, and we deduce that $v_2'=v_2+2$, $S_2'=S_2+1$. The ratio of the reduced matrix elements can be related by Eq. (67) of Racah[6] to a ratio for which n_a and n_b assume the special values v_1 and v_2+2, respectively. The couple $(\overline{v}, \overline{S})$ for the matrix element of the numerator can now be only

$(v_1-1,\ S_1-1/2)$; that for the matrix element of the denominator, only $(v_2+1,\ S_2+1/2)$. Both of these couples correspond to the same $\overline{W}$; hence, if Eq. (4) is used to compute the ratio, the sum

$$\sum_{\overline{L}\,\overline{\xi}} (W\ \xi\ L\ |\ \overline{W}\ \overline{\xi}\ \overline{L} + \ell)\ (W'\ \xi'\ L'\ |\ \overline{W}\ \overline{\xi}\ \overline{L} + \ell)$$

$$\times\ (-1)^{\overline{L}+\ell+L+1} \begin{Bmatrix} L & 1 & L' \\ \ell & \overline{L} & \ell \end{Bmatrix} \tag{23}$$

occurs in both numerator and denominator, and therefore cancels. Equations (52) of Racah[3] give the magnitudes of the coefficients of the type

$$(\ell^n\ v\ S\ \{|\ \ell^{n-1}\ \overline{v}\ \overline{S} + \ell).$$

The phase of such a quantity is independent of n,[3] and, following Racah, we denote it by $\epsilon(v\ S\ \{|\ \overline{v}\ \overline{S})$. The result of the calculation is

$$\frac{(\ell^{n_a}\ v_1\ W\ \xi\ S_1\ L\ \|\ W^{(11)}\ \|\ \ell^{n_a}\ v_1-2\ W'\ \xi'\ S_1+1\ L')}{(\ell^{n_b}\ v_2\ W\ \xi\ S_2\ L\ \|\ W^{(11)}\ \|\ \ell^{n_b}\ v_2+2\ W'\ \xi'\ S_2-1\ L')}$$

$$= -\ \frac{\epsilon(v_1\ S_1\ \{|\ v_1-1,\ S_1-1/2)\,\epsilon(v_1-2,\ S_1+1\ \{|\ v_1-1,\ S_1-1/2)}{\epsilon(v_2\ S_2\ \{|\ v_2+1,\ S_2+1/2)\,\epsilon(v_2+2,\ S_2-1\ \{|\ v_2+1,\ S_2+1/2)}\ \Xi \tag{24}$$

where

$$\Xi\ =\ \left[\frac{(n_a+2-v_1)(4\ell+4-n_a-v_1)(2S_1-1)2S_1(2S_1+1)}{(n_b-v_2)(4\ell+2-n_b-v_2)(2S_2+1)(2S_2+2)(2S_2+3)}\right]^{1/2}.$$

So much for the left-hand side of Eq. (22). The right-hand side, involving the ratio of two 3-j symbols, evaluates to

$$(-1)^{x+1}\Xi\ . \tag{25}$$

The immediate conclusion, independent of the choice made for the phases

$\epsilon(v\ S\ \{|\ \bar{v}\ \bar{S})$, is that x is independent of ξ, ξ', L, and L', and depends solely on the spins and seniorities of the states involved in the matrix elements. Equations (2) permit us to narrow down the dependence simply to the seniorities.

The above analysis can be repeated for other special cases. There are not many to consider, since the seniorities and spins with common subscripts can differ by, at most, 2 and 1, respectively, if the matrix elements are not to vanish. If $S_1'=S_1$, however, $\bar{S}$ can sometimes assume two values, and we cannot be sure that the simple factorization that allowed us to cancel the summations (23) still prevails. This difficulty can be circumvented, if the matrix elements are not completely diagonal with respect to v, W, ξ, and L, by making use of the fact that the corresponding reduced matrix elements of $\underset{\sim}{W}^{(01)}$, being proportional to those of $\underset{\sim}{L}$, must vanish. The sum over $\bar{L}$ and $\bar{\xi}$ for $\bar{S}=S_1-1/2$ can now be related to the similar sum for $\bar{S}=S_1+1/2$, and, with a little manipulation, the dependence of the ratio of the reduced matrix elements on ξ, L, ξ' and L' can again be removed. This method, which has been previously used by Elliott et al.,[2] breaks down if one of the matrix elements is completely diagonal in all quantum numbers; but in this case it is easy to see that the other matrix element must also be completely diagonal, and hence $(-1)^x=1$. The result of working through the various special cases is that the conclusions of the preceding paragraph are true in general: x is always independent of ξ, ξ', L, and L', and depends only on the seniorities.

Thus

$$x = x(v_1, v_2, v_1', v_2'). \tag{26}$$

The precise form of x depends on the phases $\epsilon(v\ S\ \{|\ \bar{v}\ \bar{S})$. If these are still at our disposal, then we can go no further in our determination of x. However, for some values of ℓ a particular choice has been made; for example, Eqs. (56) of Racah[3] determine the phases of $\epsilon(v\,S\,\{|\,\bar{v}\,\bar{S})$ for f electrons. We may therefore compare expressions, such as (24) and (25), for all the various types of couples (v,S); the resulting values of x required to lead to agreement as to phase for f electrons can be summarized in the equation

$$x = v_1\delta(v_1,v_1') + v_2\delta(v_2,v_2') + 1.$$

Upon putting this value of x into Eq. (22) the ratio of the two reduced matrix elements is made unambiguous.

VI. APPLICATIONS

We may specialize Eq. (22) in several ways. A prudent step is to check that it reproduces those special cases that are already known. Wybourne[5] expresses his results for the matrices of the spin-orbit coupling in terms of the matrix elements of a quantity Λ defined by

$$(\ell^n\, W\, \xi\, S\, L\, J\, M_J \mid \sum_i (\underset{\sim}{s}_i \cdot \underset{\sim}{\ell}_i) \mid \ell^n\, W'\, \xi'\, S'\, L'\, J\, M_J)$$

$$= (-1)^{J+y} \begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix} (\ell^n\, W\, \xi\, S\, L\, |\Lambda|\, \ell^n\, W'\, \xi'\, S'\, L'),$$

where $y = 0$ or $-1/2$ according as n is even or odd. From Eq. (25) of Racah,[6] we may easily prove

$$\frac{(\psi_1\, |\Lambda|\, \psi_1')}{(\psi_2\, |\Lambda|\, \psi_2')} = (-1)^{S_1'-S_2'+y_2-y_1} \frac{(\psi_1 \,\|\, W^{(11)} \,\|\, \psi_1')}{(\psi_2 \,\|\, W^{(11)} \,\|\, \psi_2')} , \qquad (27)$$

where

$$\psi_1 \equiv \ell^{n_a}\, v_1\, W\, \xi\, S_1\, L,$$

$$\psi_1' \equiv \ell^{n_a}\, v_1'\, W'\, \xi'\, S_1'\, L',$$

$$\psi_2 \equiv \ell^{n_b}\, v_2\, W\, \xi\, S_2\, L,$$

and

$$\psi_2' \equiv \ell^{n_b}\, v_2'\, W'\, \xi'\, S_2'\, L' .$$

By combining Eqs. (22) and (27), the ratio of the matrix elements of Λ for any set of states ψ_1, ψ_1', ψ_2, and ψ_2' can readily be found. Of the 31 entries in Table III of Wybourne,[5] 20 are special cases of this kind; the remainder are examples of Eqs. (67) and (69b) of Racah.[6] We obtain complete agreement with Wybourne for 16 of the 20, but the signs of the right hand sides of the sixth, ninth, tenth, and eleventh equations of his Table IIIb are incorrect, and should be reversed. In a private communication, Wybourne has confirmed these four corrections.[7]

Although we have distinguished between Eq. (22) (for which $v_1 \neq v_2$ and $v_1' \neq v_2'$) and Eqs. (67) and (69b) of Racah[6] (for which $v_1 = v_2$ and $v_1' = v_2'$), it should be pointed out that Racah's equations can be derived from Eq. (22). It is only necessary to compare Eq. (22), as it stands, to a similar equation in which n_a possesses its minimum value, namely the larger of v_1 and v_1'. Suppose, for example, we take $v_1 = v_1' = v$ and choose $\kappa + k$ to be even. For Eq. (22) to be valid, we must have $\kappa' = 1$. We set $n_a = v$ in Eq. (22) and then $n_a = n$. The matrix elements

$$(\psi_2' \,\|\, W^{(1k)} \,\|\, \psi_2)$$

can be easily eliminated, and we get

$$\frac{(\ell^n \; v \; W \; \xi \; S \; L \,\|\, W^{(\kappa k)} \,\|\, \ell^n \; v \; W' \; \xi' \; S' \; L')}{(\ell^v \; v \; W \; \xi \; S \; L \,\|\, W^{(\kappa k)} \,\|\, \ell^v \; v \; W' \; \xi' \; S' \; L')}$$

$$= (-1)^{(v-n)/2} \begin{pmatrix} \frac{1}{2}(2\ell+1-v) & 1 & \frac{1}{2}(2\ell+1-v) \\ \frac{1}{2}(2\ell+1-n) & 0 & -\frac{1}{2}(2\ell+1-n) \end{pmatrix}$$

$$\times \begin{pmatrix} \frac{1}{2}(2\ell+1-v) & 1 & \frac{1}{2}(2\ell+1-v) \\ \frac{1}{2}(2\ell+1-v) & 0 & -\frac{1}{2}(2\ell+1-v) \end{pmatrix}^{-1}$$

$$= (2\ell+1-n)/(2\ell+1-v),$$

which agrees with Eq. (69b) of Racah.[6]

The applications of Eq. (22) that have been considered so far simply reproduce established results. However, it is only necessary to take k to be even to obtain a large number of new equations. This is because $\kappa+\kappa'$ must be odd, and so κ cannot equal κ'. We may therefore relate the matrix elements of $\underset{\sim}{W}^{(12)}$ in one configuration to those of $\underset{\sim}{W}^{(02)}$ in another; in fact, for any matrix element of $\underset{\sim}{W}^{(12)}$, a matrix element of $\underset{\sim}{W}^{(02)}$ in another configuration can be found to which it is related by Eq. (22). Since tensors of the type $\underset{\sim}{W}^{(12)}$ and $\underset{\sim}{W}^{(02)}$ are used in the study of hyperfine structure and crystalline field effects, respectively, a considerable amount of labor can be saved by taking advantage of this relation. For example, on setting $v_1=v_1'$, $S_1=S'$, $v_2=v_2'$, and $S_2=S_2'$ in Eq. (22), we obtain, for the even k,

$$\frac{(\ell^{n_a} v_1 W \xi S_1 L \| W^{(1k)} \| \ell^{n_a} v_1 W \xi' S_1 L')}{(\ell^{n_b} v_2 W \xi S_2 L \| V^{(k)} \| \ell^{n_b} v_2 W \xi' S_2 L')}$$

$$= - \left[\frac{(2\ell+1-v_2)(2\ell+2-v_2)(2\ell+3-v_2)}{2(2\ell+1-n_b)^2} \right]^{1/2} . \qquad (28)$$

This result is independent of v_1 and S_2, and relates, for example, the matrix elements of part of the hyperfine interaction for the quartets of f^5 to the matrix elements of $\underset{\sim}{V}^{(2)}$ for the terms of f^4 with a seniority of 4. Matrix elements of the latter kind are the easier to evaluate, since fewer parents are involved. Equation (28) should therefore be useful in calculating, for example, the contribution to the hyperfine structure of PmI $4f^5\ {}^6H_J$ coming from admixtures of quartet states.

FOOTNOTE AND REFERENCES

* Work done under the auspices of the U. S. Atomic Energy Commission.

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7. Table III of Wybourne contains other errors that are more obviously typographical. Of these, three possess a mathematical significance: In the second equation of Table III a, the representation (110) on the extreme right should be (111); in the fifth equation of this Table, the seniority number 4 should be replaced by 3; and in the last equation of Table III c, the factor $-[2(2)/3]^{1/2}$ should read $-[2(2)^{1/2}/3]$.