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Technical Report

EVALUATION OF MATRIX ELEMENTS IN CRYSTALLINE FIELD THEORY

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INTRODUCTION

In the interpretation of optical and microwave absorption spectra of crystalline solids, the so-called crystalline field theory, which is based on the ionic approximation, has been proved to be a remarkably successful one. The essential problem is to diagonalize the free ion Hamiltonian plus the perturbation due to ligand field. Two equivalent approaches are in use, namely, the strong-field scheme and the weak-field scheme. In the former approach the full use of the symmetry of ligand field from the beginning leads to simplified expressions for the matrix elements (see Sugano and Tanabe). In the latter approach the advantages are that one can make use of the results of the corresponding free-ion calculations and, as a result of the spherical symmetry, one can get a general formula for the reduced matrix element. In this report, we use the weak-field scheme for the evaluation of matrix elements in L-S coupling scheme. The interest is mainly on the iron-group (3d-group) elements so that Racah's results in the free atom case are still largely applicable. Racah's method combines the tensor algebra, which is the extension of vector algebra in Condon and Shortley, and the method of constructing the wave function for equivalent electrons using the vector-coupling formula and fractional-parentage coefficients. We shall find that the application of this powerful technique will not only give a systematic way of evaluating matrix elements of all terms that appeared in our Hamiltonian, but will also greatly simplify the computations of seemingly very complex problems of evaluating matrix elements between many electron wave functions.

References to the use of this technique to atomic and nuclear physics are scattered in various literatures and monographs. A variety of notations has been used, so that considerable care is needed in applying the indicated formulas. For this reason, we shall present a summary of relevant formulas in a manner convenient for application to solid-state physics. Also, the reference to tabulations of requisite numerical constants will be given.

In Part I, we first introduce the concept of irreducible tensors and some of its algebra. The extended Wigner-Eckart theorem which is applicable to irreducible tensors of any rank is then stated. Using the Wigner-Eckart theorem,* we then evaluate the most general form of matrix elements involving spin-free (space-free) tensors, tensor product of two commuting tensors, scalar product of two commuting tensors, and double tensors between eigenfunctions in the L-S coupling scheme in terms of various recoupling-coefficients (3-j, 6-j and 9-j symbols) of angular momenta and certain types of reduced matrices.

In Part II, then, we try to reduce each term of the Hamiltonian to these standard forms. We shall find that if we fix our attention on only a single configuration, evaluation of all the matrix elements can be reduced to the calculations of two types of reduced matrices, i.e., $(\alpha SL\|\overline{U}^{(k)}\|\alpha'S'L')$ and $(\alpha SL\|\overline{V}^{qp}\|\alpha'S'L')$. For each of them, we then give formulas in terms of the fractional-parentage coefficients and Racah coefficients so that our problem of evaluating matrix elements is completely solved.

The type of terms we consider in the Hamiltonian are:

1. electrostatic interation between equivalent electrons
2. crystalline field potential

*And the vector-coupling formula.

3. spin-orbit coupling energy

4. spin-spin interaction energy

5. hyperfine interaction

6. quadrupole interaction.

As supplements to the text we give:

Appendix A: Rotation of coordinate system and rotation of field;

Appendix B: Proof of Wigner-Eckart thorem;

Appendix C: Definitions and properties of 3-j, 6-j and 9-j symbols;

Appendix D: Numerical tables for: $(d^n \alpha SL \| \bar{U}^{(k)} \| d^n \alpha' S' L')$, k = 2,4, n = 2,5 and $(d^n \alpha SL \| \bar{V}^{1k} \| d^n \alpha' S' L')$, n = 2,4, k = 1,2 which should be enough for evaluation of matrix elements of the six kinds of interaction considered above.

PART I

1.1 DEFINITION OF IRREDUCIBLE TENSOR OPERATORS

A set of 2k+1 operators T^k_q(k integer, q = -k, -k+1 ..., k-1, k) which transform irreducibly according to the k-th irreducible representation of the rotation group, under rotations of the frame of reference, is called an irreducible tensor of rank k.

A rotation $R(\alpha\beta\gamma)$ where $(\alpha\beta\gamma)$ are the Euler angles corresponds to a rotation matrix $R(\alpha\beta\gamma)$ such that the components of a vector in unprimed (original) coordinate system S and the primed (rotated) coordinate system S' are related by

$$\mathbb{r}' = \mathbb{R}(\alpha\beta\gamma)\,\mathbb{r} \quad . \tag{1.1}$$

This rotation $R(\alpha\beta\gamma)$ gives rise to an unitary operator O_R by which the set of components of an irreducible tensor is transformed according to

$$O_R\, T^k_q\, O_R^{-1} = \sum_{q'=-k}^{k} T^k_{q'}\, D^{(k)}_{q'q}(R) \quad , \tag{1.2}$$

and also by which a wave function $|\alpha SLJM>$ is rotated into (see Appendix A)

$$O_R\, |\alpha SLJM> = \sum_{M'} |\alpha SLJM'>\, D^{(J)}_{M'M}(R) \tag{1.3}$$

where $D^{(j)}_{m'm}(R)$ is defined by

$$D^{(j)}_{m'm}(R) = < jm' \mid O_R \mid jm > \tag{1.4}$$

and $|jm>$ is the simultaneous eigenfunction of total angular momentum J^2 and Z-component of it J_z. (Edmonds 4.1.10).*

It is well known that the operator O_R can be written in terms of the total

*See References.

angular momentum operator as

$$O_{R\xi}(\theta) = \exp(i\theta J_\xi) \qquad (1.5)$$

where ξ is the axis of rotation and θ is the angle of rotation (Edmonds, 4.1.9). For an infinitesimal rotation $\delta\theta$ about axis ξ,

$$O_{R\xi}(\delta\theta) \simeq 1 + i\delta\theta J_\xi$$

$$O_{R\xi}^{-1}(\delta\theta) \simeq 1 - i\delta\theta J_\xi$$

$$D^{(k)}_{q'q}(\delta\theta) = < kq' | 1 + i\delta\theta J_\xi | kq > = \delta_{q'q} + i\delta\theta < kq' | J_\xi | kq >$$

therefore Eq. (1.2) becomes

$$(1 + i\ \theta J_\xi)\ T^k_q\ (1 - i\delta\theta J_\xi) = \sum_{q'=-k}^{k} T^k_{q'} \left\{ \delta_{q'q} + i\delta\theta < kq' | J_\xi | kq > \right\}$$

or

$$[J_\xi, T^k_q] = \sum_{q'} T^k_{q'} < kq' | J_\xi | kq > \qquad (1.6)$$

which is valid for any arbitrary $\delta\theta$. From Eq. (1.6) it easily follows the following three commutation relations of T^k_q with respect to the angular momentum J,

$$[J_\pm, T^k_q] = [(k \mp q)(k \pm q + 1)]^{1/2}\ T^k_{q \pm 1} \qquad (1.7)$$

$$[Jo, T^k_q] = q\ T^k_q \qquad (1.8)$$

where

$$J_\pm = J_X \pm iJy\ ; \qquad J_o = J_Z .$$

Equations (1.7) and (1.8) are the alternative way of defining an irreducible tensor which is useful when one prefers an algebraic way of proving theorems about T^k_q (see Racah II).

Examples of irreducible tensors:

A. For $k = q = 0$, $D^0_{00}(R) = 1$ therefore Eq. (1.2) gives

$$O_R\ T^0_0\ O_R^{-1} = T^0_0$$

which shows that T^0_0 is invariant under rotations and hence is a scalar.

B. For k = 1, q = -1, 0 1 Equ. (1.7) and (1.8) give

$$[J_+, T^1_1] = 0 \qquad [J_-, T^1_1] = \sqrt{2}\, T^1_0 \qquad [J_0, T^1_1] = T^1_1 \tag{1.9}$$

$$[J_+, T^1_0] = \sqrt{2}\, T^1_1 \quad [J_-, T^1_0] = \sqrt{2}\, T^1_{-1} \qquad [J_0, T^1_0] = 0$$

$$[J_+, T^1_{-1}] = \sqrt{2}\, T^1_0 \quad [J_-, T^1_{-1}] = 0 \qquad [J_0, T^1_{-1}] = -T^1_{-1} \quad .$$

Let

$$T^1_1 = -\frac{1}{\sqrt{2}}(T_x + i\,T_y)\ ; \quad T^1_{-1} = \frac{1}{\sqrt{2}}(T_x - i\,T_y)\ ; \quad T^1_0 = T_z \quad .$$

Then Eq. (1.9) leads to the following set of commutator relations,

$$[J_x, T_x] = 0 \qquad [J_y, T_y] = 0 \qquad [J_z, T_z] = 0$$

$$[J_x, T_y] = iT_z \qquad [J_y, T_z] = iT_x \qquad [J_z, T_x] = iT_y \tag{1.10}$$

$$[J_x, T_z] = -iT_y \qquad [J_y, T_x] = -iT_z \qquad [J_z, T_y] = -iT_x \quad .$$

It is immediately seen that (T_x, T_y, T_z) defined this way is just the T type of vector defined in TAS.* Since J, L, and S are all T type vectors with respect to J, the following type of combinations of components of J, L, and S

$$L_{\pm 1} = \mp\frac{1}{\sqrt{2}}(L_x \pm iL_y) = \mp\frac{1}{\sqrt{2}} L_\pm \quad ; \quad L_0 = L_z \tag{1.11}$$

are examples of first rank irreducible tensors.

C. In general, let us define

$$C_{\ell m}(\hat{r}) = \left(\frac{4\pi}{2\ell + 1}\right)^{1/2} Y_{\ell m}(\hat{r})$$

$$= (-1)^{\frac{(m+|m|)}{2}} \left(\frac{(\ell-|m|)!}{(\ell+|m|)!}\right)^{1/2} P_\ell^{|m|}(\cos\theta) e^{im\phi} \tag{1.12}$$

and remember

$$L_\pm\ C_{\ell m}(\theta,\phi) = [(\ell \mp m)(\ell \pm m + 1)]^{1/2}\ C_{\ell,\ m\pm 1}(\theta,\phi)$$

$$L_z\ C_{\ell m}(\theta,\phi) = m\ C_{\ell m}(\theta,\phi)\ ,$$

*See References.

regarding then $C_{\ell m}(\hat{r})$ as an operator and noting that both $L_{\pm}$ and L_z are first order linear differential operators, we obtain immediately

$$[L_{\pm}, C_{\ell m}(\hat{r})] = [(\ell \mp m)(\ell \pm m + 1)]^{1/2} C_{\ell, m\pm 1}(\hat{r})$$

$$[L_0, C_{\ell m}(\hat{r})] = m C_{\ell m}(\hat{r})$$

which shows that $C_{\ell m}(\hat{r})$ $(m = -\ell, \ldots, +\ell)$ is an ℓ-th rank irreducible tensor operator with respect to orbital angular momentum $\underline{L}$, which are sometimes called "spherical tensors." For example,

$$\begin{aligned} C_{11} &= -\frac{1}{\sqrt{2}} \frac{1}{r} (x + iy) \\ C_{10} &= \frac{1}{r} z \\ C_{1\bar{1}} &= \frac{1}{\sqrt{2}} \frac{1}{r} (x - iy) \end{aligned} \qquad (1.13)$$

and $\underset{\sim}{r} = (x,y,z)$ is an T type vector with respect to $\underline{L}$.

1.2 TENSOR-PRODUCT AND SCALAR PRODUCT OF TWO TENSORS

There is a general method of constructing irreducible tensors of higher (lower) ranks from two irreducible tensors analogous to the vector-coupling method. Let the two tensors be $T^{k_1}_{q_1}(A_1)$ and $T^{k_2}_{q_2}(A_2)$ where A_1 and A_2 indicate that the two tensors do not necessarily act on the same part of the system.

Then

$$\begin{aligned} \left\{T^{k_1}(A_1) \times T^{k_2}(A_2)\right\}^K_Q &= \sum_{q_1 q_2} T^{k_1}_{q_1}(A_1)\, T^{k_2}_{q_2}(A_1)\, T^{k_2}_{q_2}(A_2) < k_1 q_1 k_2 q_2 | KQ > \\ &= \sum_{q_1} T^{k_1}_{q_1}(A_1)\, T^{k_2}_{Q-q_1}(A_2) < k_1 q_1 k_2 Q\text{-}q_1 | KQ > \end{aligned} \qquad (1.14)$$

where $< k_1 q_1 k_2 q_2 | KQ >$ is the vector-coupling coefficient and vanishes unless $|k_1 - k_2| \leqslant K \leqslant k_1 + k_2$, (this condition will be denoted as $\Delta(k_1 k_2 K)$ hereafter), and $Q = q_1 + q_2$. Thus from two tensors of rank k_1 and k_2, we can build up irreducible tensors of rank ranging from $|k_1 - k_2|$ to $k_1 + k_2$. In a particular case, when $k_1 = k_2 = k$, it is possible to have $K = 0 = Q$ corresponding to contraction of tensors, i.e.

$$\left\{T^k(A_1) \times T^k(A_2)\right\}^0_0 = \sum_q T^k_q(A_1)\, T^k_{-q}(A_2) \langle kqk\bar{q}|00\rangle$$

$$= (-1)^k (2k+1)^{-1/2} \sum_q (-1)^q T^k_q(A_1) T^k_{-q}(A_2)$$

since $\langle kqk\bar{q}|00\rangle = (-1)^{k-q}(2k+1)^{-1/2}$.

Let us define the scalar product of tensors $T^k_q(A_1)$ and $T^k_q(A_2)$ as

$$T^k(A_1)\cdot T^k(A_2) = (-1)^k(2k+1)^{1/2}\left\{T^k(A_1) \times T^k(A_2)\right\}^0_0 = \sum_q (-1)^q T^k_q(A_1)T^k_{-q}(A_2)\,. \tag{1.15}$$

Examples of tensor product and scalar product:

A. Consider the spin-orbit interaction energy $\lambda L \cdot S$.

From Eq. (1.11)

$$L_x = \frac{1}{\sqrt{2}}(L_{-1} - L_{+1}); \quad L_y = \frac{i}{\sqrt{2}}(L_{-1} + L_{+1}); \quad L_z = L_0$$

similarly for S_x, S_y, and S_z. We have then

$$\begin{aligned}\lambda S\cdot L &= \lambda(-S_1 L_{-1} - S_{-1} L_1 + S_0 L_0) \\ &= \lambda \sum_q (-1)^q S_q L_{-q}\end{aligned} \tag{1.16}$$

which is the scalar product of S_μ and L_ν.

B. Consider the nuclear-electron dipole-dipole interaction

$$H_{ne} = -a\underline{I}\cdot\left\{\underline{S} - \frac{3(\underline{S}\cdot\underline{r})\underline{R}}{r^2}\right\}$$

where I_μ is a rank one tensor; therefore the expression in the bracket must be a rank one tensor too. We can construct it from a rank one tensor S_μ and rank two tensor $C_\nu^{(2)}(\hat{r})$, i.e.

$$X_Q^{(1)} = A \sum_q S_q C_{Q-q}^{(2)}(\hat{r}) < 1q\, 2\, Q-q | 1Q >$$

$$= \left\{ \underline{S} - \frac{3(S\cdot r)r}{r^2} \right\}_Q$$

by evaluating the Z-component (Q = 0) of both sides, one can determine the constant A to be $\sqrt{10}$. Therefore

$$H_{ne} = -a \sum_\mu (-1)^\mu I_\mu X_{-\mu}$$

$$= -a\sqrt{10} \sum_{\mu,q} (-1)^\mu I_\mu S_q C_{-\mu-q}^{(2)}(\hat{r}) < 1q 2 -\mu-q | 1\ \mu > , \quad (1.17)$$

C. Another important example of the scalar product is given by the addition theorem of spherical harmonics, which says

$$P_\ell(\cos\theta_{12}) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} (-1)^m Y_{\ell m}(\theta,\phi)\, Y_{\ell\bar{m}}(\theta_2\phi_2)$$

in terms of $C_{\ell m}$, we have

$$P_\ell(\cos\theta_{12}) = \sum_{m=-\ell}^{\ell} (-1)^m C_{\ell m}(\theta_1\phi_1)\, C_{\ell\bar{m}}(\theta_2\phi_2) \quad (1.18)$$

which is just the scalar product of $C_{\ell m}(1)$ and $C_{\ell m}(2)$.

1.3 DOUBLE TENSORS (TWO-SIDED TENSORS) (See Wigner, p. 273)

When an operator in the Hamiltonian is made up of a sum of one-electron operators, each of which is the product of operators acting on spin part and orbital part of the wave function respectively, it is convenient to introduce the concept of double tensor. The definition of a double tensor operator has an intimate connection with the separability of the unitary operator O_R into the spin part and the space part. In Pauli's theory of electron spin, the one electron wave function is assumed to be a product of a space part and a spin part. Consequently, it is possible to split O_R into product of two unitary and mutually commuting operators P_R and Q_R acting on orbital part and spin part of the wave function respectively (Wigner, section 20), namely

$$O_R \doteq P_R Q_R = Q_R P_R \tag{1.19}$$

and

$$P_R |\alpha S M_S L M_L > = \sum_{M_L'} |\alpha S M_S L M_L' > D^{(L)}_{M_L' M_L}(R) \tag{1.20}$$

$$Q_R |\alpha S M_S L M_L > = \sum_{M_S'} |\alpha S M_S' L M_L > D^{(S)}_{M_S' M_S}(R) \tag{1.21}$$

(See Appendix A).

With this understanding, we can define a double tensor T^{qp} which is of degree q with regard to Q_R and of degree p with regard to P_R and irreducible with regard to each of them, i.e.

$$Q_R\, T^{qp}_{\nu\mu}\, Q_R^{-1} = \sum_{\nu'} T^{qp}_{\nu'\mu}\, D^{(q)}_{\nu'\nu}(R) \tag{1.22}$$

$$P_R\, T^{qp}_{\nu\mu}\, P_R^{-1} = \sum_{\mu'} T^{qp}_{\nu\mu'}\, D^{(p)}_{\mu'\mu}(R) \tag{1.23}$$

With respect to O_R, the T^{qp} is not irreducible but transforms according to the direct product of $D^{(q)}$ and $D^{(p)}$:

$$O_R\, T^{qp}_{\nu\mu}\, O_R^{-1} = \sum_{\nu'\mu'} T^{qp}_{\nu'\mu'}\, D^{(q)}_{\nu'\nu}(R)\, D^{(p)}_{\mu'\mu}(R) \tag{1.24}$$

However, one can form a linear combination of $T^{qp}_{\nu\mu}$ using vector-coupling coefficient to get an irreducible tensor T^{K}_{Q} analogous to the tensor product mentioned in Section 1.2 (Wigner, p. 284), namely

$$T^{K}_{Q} = \sum_{\nu,\mu} T^{qp}_{\nu\mu} < q\nu p\mu | KQ > \tag{1.25}$$

It is evident that the simplest example of $T^{qp}_{\nu\mu}$ is just the product $T^q_\nu(S)T^p_\mu(\ell)$. A more familiar one is the spin-orbit coupling energy of n equivalent electrons:

$$\zeta \sum_{i=1}^{n} \underset{\sim}{s}(i) \cdot \underset{\sim}{\ell}(i) = \zeta \sum_{i=1}^{n} \sum_{\nu} (-1)^{\nu} s_{\nu}(i) \ell_{-\nu}(i)$$

$$= \zeta \sum_{\nu} (-1)^{\nu} \, T^{11}_{\nu\bar{\nu}} \qquad (1.26)$$

where

$$T^{11}_{\nu\bar{\nu}} = \sum_{i=1} s_{\nu}(i) \ell_{-\nu}(i)$$

$$= \sum_{i=1}^{n} t^{11}_{\nu\bar{\nu}}(i) \quad * \qquad ,$$

1.4 WIGNER-ECKART THEOREM (See Appendix B)

The first simplification in calculation of matrix elements of tensor operators comes from application of the well-known theorem (Edmonds, p. 75) which states that if:

(1) state $|\alpha JM\rangle$ rotates irredicibly according to $D^{(J)}$

(2) state $|\alpha' J' M'\rangle$ rotates irredicibly according to $D^{(J')}$.

(3) T^k_q rotates irreducibly according to $D^{(k)}$

then the matrix element of T^k_q between the two states can be separated into product of two factors: a vector-coupling coefficient which specifies the angular dependence (M, q and M') of the matrix element, and a reduced matrix which depends on the magnitude of J, J', k and the physical nature of the operator T^k_q, namely

*It is easy to see that when a one-electron operator $t^k(i)$ is an irreducible tensor of rank k, the sum of such operators over any finite number of electrons is also an irredicible tensor of the same rank. The similar thing holds for one electron double tensors.

$$< \alpha JM \mid T^k_q \mid \alpha' J' M' > \; = \; < J'M'kq|JM > \frac{(\alpha J \| T^k \| \alpha' J')}{(2J+1)^{1/2}} \qquad (1.27)$$

$$= (-1)^{J-M} \begin{pmatrix} J & k & J' \\ \overline{M} & q & M' \end{pmatrix} (\alpha J \| T^k \| \alpha' J') \qquad (1.28)$$

(see Appendix B)

where

$$\begin{pmatrix} J & k & J' \\ \overline{M} & q & M' \end{pmatrix} = \frac{< J'M'kq|JM >}{(2J+1)^{1/2}} (-1)^{-J+M}$$

is the symmetrized V-C coefficient or the 3-j symbol of Wigner.

The following points about the theorem should be noted:

A. α denotes all the necessary quantum number besides J and M to specify completely the state. It can be, for example, the principal quantum number, L, S, parity and seniority number.

B. The selection rules are built in the V-C coefficient, i.e., the matrix element is zero unless $\Delta(JkJ')$ and $M = q + M'$ and the parities satisfy the relation $\Pi_i \; \Pi_k \; \Pi_f = 1$.

C. The reduced (or double bar) matrix element is not a matrix element in the real sense. It is essentially defined by Eq. (1.27) or Eq. (1.28); the symbol in it merely indicates the dependence of its value on them.

D. When T^k_q does not act on the spin (or space) part of the wave function, that is, when $[Q_R, T^k_q] = [Q^{-1}_R, T^k_q] = 0$, we have

$$O_R \, T^k_q \, O^{-1}_R = P_R \, Q_R \, T^k_q \, Q^{-1}_R \, P^{-1}_R = P_R \, T^k_q \, P^{-1}_R = \sum_{q'} T^k_{q'} \, D^{(k)}_{q'q} \qquad (1.29)$$

that is, we have wave functions in the S^2, L^2, S_z, L_z representation which rotate irreducibly with respect to P_R and Q_R separately,

$$P_R |\alpha S M_S L M_L > = \sum_{M'_L} |\alpha S M_S L M'_L > D^{(L)}_{M'_L M_L}(R) \qquad (1.30)$$

$$Q_R |\alpha S M_S L M_L > = \sum_{M_S'} |\alpha S M_S' L M_L > D^{(S)}_{M_S' M_S}(R) \qquad (1.31)$$

and we have the W-E theorem for $T^k_q(2)$ which act on space part only,

$$< \alpha S M_S L M_L \mid T^k_q(2) \mid \alpha' S' M_S' L' M_L' >$$

$$= (-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ M_L & q & M_L' \end{pmatrix} (\alpha SL \| T^k(2) \| \alpha' SL') \, \delta_{SS'} \delta_{M_S M_S'} \qquad (1.32)$$

(notice that the reduced matric element is M_S and M_S' independent)

and similarly for $T^k_q(1)$ we have

$$< \alpha S M_S L M_L \mid T^k_q(1) | \alpha' S' M_S' L' M_L' >$$

$$= (-1)^{S-M_S} \begin{pmatrix} S & k & S' \\ M_S & q & M_S' \end{pmatrix} (\alpha SL \parallel T^k(1) \| \alpha' S' L) \, \delta_{LL'} \delta_{M_L M_L'} \quad . \qquad (1.33)$$

E. Equation (1.27) shows that for two tensors of the same rank k, their matrix elements between states of same αJ are proportional:*

$$\frac{< \alpha L M_L | T^k_q(2) | \alpha L M_L' >}{< \alpha L M_L | U^k_q(2) | \alpha L M_L' >} = \frac{(\alpha L \| T^k(2) \| \alpha L)}{(\alpha L \| U^k(2) \| \alpha L)}$$

(for nonvanishing denominators)

the special case is when $k = 1$, $q = \mu (\mu = 0, 1, -1)$.

$$T^1_\mu = r C_{1\mu}(\hat{r})$$

$$U^1_\mu = L_\mu$$

then

$$< \alpha L M_L | r C_{1\mu}(\hat{r}) | \alpha L M_L' > = \frac{(\alpha L \| r C_1 \| \alpha L)}{(\alpha L \| L \| \alpha L)} < \alpha L M_L | L_\mu | \alpha L M_L' > \quad ,$$

*Note: It is necessary that $(\alpha L \| L \| \alpha L) \neq 0$, but $(\alpha L \| L \| \alpha L') = 0$ for $L \neq L'$.

From Eq. (1.11) and (1.13) this becomes

$$< \alpha LM_L | \mp \frac{1}{\sqrt{2}} (x \pm iy) |\alpha LM_L' > \; = \; \frac{(\alpha L\|rC_1\|\alpha L)}{(\alpha L\|L\|\alpha L)} \; < \alpha LM_L | \mp \frac{1}{\sqrt{2}} (L_x \pm iL_y) |\alpha LM'_L >$$

$$< \alpha LM_L | \; z \; |\alpha LM_L' > \; = \; \frac{(\alpha L\|rC_1\|\alpha L)}{(\alpha L\|L\|\alpha L)} < \alpha LM_L |L_z |\alpha LM_L' >$$

Thus

$$< \alpha LM_L | \; x \; | \; \alpha LM_L' > \; = \; \beta < \alpha LM_L |L_x |\alpha LM_L' >$$

$$< \alpha LM_L | \; y \; | \; \alpha LM_L' > \; = \; \beta < \alpha LM_L |L_y |\alpha LM_L' >$$

$$< \alpha LM_L | \; z \; | \; \alpha LM_L' > \; = \; \beta < \alpha LM_L |L_z |\alpha LM_L' > \qquad (1.34)$$

where $\beta = \frac{(\alpha L\|rC_1\|\alpha L)}{(\alpha L\|L\|\alpha L)}$ which is constant for a fixed $^{2s+1}$ L term. Equation (1.34) is sometimes called the operator equivalence by the spin resonance worker, which says that in calculating the matrix element of x, y, z and their powers between states of a fixed $^{2s+1}$ L term (usually the ground terms of the paramagnetic ion) one can replace them by the corresponding powers of the angular momentum operators, provided that one pays proper attention to the non-commuting property of angular momentum operators. (See Bleaney and Stevens).

1.5 MATRIX ELEMENTS OF SPIN-FREE OPERATORS $T_q^k(2)$

If

$$[T_q^k(2), Q_R] \; = \; [T_q^k(2), Q_R^{-1}] \; = \; 0$$

and

$$O_R T_q^k(2) O_R^{-1} \; = \; P_R T_q^k(2) P_R^{-1} \; = \; \sum_{q'} T_{q'}^k D_{q'q}^{(k)}(R) \quad ,$$

A. In S^2, L^2, S_z, L_z representation.

Since $[S^2, T_q^k(2)] \; = \; 0 \; = \; [S_z, T_q^k(2)]$ there are no non-diagonal matrix elements with respect to S^2 and S_z. So by Eq. (1.32) the W-E theorem

$$< \alpha SM_S LM_L |T_q^k(2) |\alpha' S' M_S' L' M_L' >$$

$$= \; \delta_{SS'} \delta_{M_S M_S'} (-1)^{L-M_L} \begin{pmatrix} L & k & L' \\ M_L & q & M_L' \end{pmatrix} (\alpha SL\|T^k\|\alpha' S' L') \quad . \qquad (1.32)$$

The fact that the reduced matrix element is independent of M_S is shown in Appendix B.

B. In S^2, L^2, J^2, J_z representation.

$$< \alpha SLJM \mid T_q^k(2) \mid \alpha'S'L'J'M' >$$

$$= \delta_{SS'} < \alpha SLJM \mid T_q^k(2) \mid \alpha'S'L'J'M' >$$

since

$$O_R \mid \alpha SLJM > = \sum_{M'} \mid \alpha SLJM' > D^{(J)}_{M'M}(R) \quad .$$

By the W-E theorem Eq. (1.28)

$$< \alpha SLJM \mid T_q^k(2) \mid \alpha'S'L'J'M' >$$

$$= \delta_{SS'} \begin{pmatrix} J & k & J' \\ \bar{M} & q & M' \end{pmatrix} (\alpha SLJ \| T^k(2) \| \alpha'S'L'J')(-1)^{J-M} . \quad (1.35)$$

In (Edmonds, 7.1.8), it is shown that the reduced matrix in Eq. (1.35) is related to that of Eq. (1.32) by

$$(\alpha SLJ \| T^k(2) \| \alpha'SL'J')$$

$$= \sqrt{(2J+1)(2J'+1)}\ W\ (JSkL';LJ')(\alpha SL \| T^k(2) \| \alpha'SL') \quad (1.36)$$

$$= (-1)^{J+S+L'+k} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & L & S \\ L' & J' & k \end{Bmatrix} (\alpha SL \| T^k(2) \| \alpha'SL') \quad (1.37)$$

where $\begin{Bmatrix} J & L & S \\ L' & J' & k \end{Bmatrix}$ is the 6-j symbol of Wigner which is related to the Racah coefficient by

$$\begin{Bmatrix} J & L & S \\ L' & J' & k \end{Bmatrix} = (-1)^{J+L+J'+L'}\ W(JLJ'L' ; Sk) \quad (1.38)$$

(See Appendix C).

Equations (1.32), (1.35), and (1.37) show that the evaluation of matrix elements of a spin-free operator in both S^2, L^2, S_z, L_z and S^2, L^2, J^2, J_z representations are reduced to the evaluation of single reduced matrix element $(\alpha SL \| T^k(2) \| \alpha'SL')$.

Similarly, when $T^k_q(1)$ is space-free, the analogous equation to Equ. (1.37) is

$$(\alpha SLJ\|T^k(1)\|\alpha'S'LJ') = (-1)^{J'+S+L+k}\sqrt{(2J+1)(2J'+1)}\begin{Bmatrix} S & J & L \\ J' & S' & k \end{Bmatrix}(\alpha SL\|T^k(1)\|\alpha'S'L) \quad (1.39)$$

1.6 MATRIX ELEMENTS OF TENSOR PRODUCT OF TWO COMMUTING TENSORS

$$T^k_Q = \sum T^{k_1}_{q_1} T^{k_2}_{q_2} < k_1q_1k_2q_2|K_Q > \quad (1.14)$$

and

$$[T^{k_1}_{q_1}, \underline{L}] = 0\ , \quad [T^{k_2}_{q_2}, \underline{S}] = 0$$

$$O_R T^{k_1}_{q_1} O_R^{-1} = Q_R T^{k_1}_{q_1} Q_R^{-1} = \sum_{q_1'} T^{k_1}_{q_1'} D^{(k_1)}_{q_1'q_1}(R) \quad (1.40)$$

$$O_R T^{k_2}_{q_2} O_R^{-1} = P_R T^{k_2}_{q_2} P_k^{-1} = \sum_{q_2'} T^{k_2}_{q_2'} D^{(k_2)}_{q_2'q_2}(R)$$

$$O_R|\alpha SLJM> = \sum_{M'} |\alpha SLJM'> D^{(J)}_{M'M}(R)\ .$$

In S^2, L^2, J^2, J_z representation, the W-E theorem gives

$$< \alpha SLJM \mid T^k_Q \mid \alpha''S'L'J'M' > = (-1)^{J-M}\begin{pmatrix} J & L & J' \\ M & Q & M' \end{pmatrix}(\alpha SLJ\|T^k\|\alpha'S'L'J')\ . \quad (1.27)$$

On the other hand (Edmonds, 7.1.5) shows that

$$< \alpha SLJM \mid T^k_Q \mid \alpha'S'L'J'M' >$$

$$= (-1)^{J-M}\begin{pmatrix} J & K & J' \\ M & Q & M' \end{pmatrix}\sqrt{(2K+1)(2J+1)(2J'+1)}\begin{Bmatrix} S & L & J \\ S' & L' & J' \\ k_1 & k_2 & k \end{Bmatrix}(\alpha SL\|T^{k_1}T^{k_2}\|\alpha'S'L') \quad (1.41)$$

where the last factor is the 9-j symbol of Wigner. (See Appendix C). Comparison of Eq. (1.27) and (1.41) shows that

$$(\alpha SLJ\|T^k\|\alpha'S'L'J') = \sqrt{(2k+1)(2J+1)(2J'+1)}\begin{Bmatrix} S & L & J \\ S' & L' & J' \\ k_1 & k_2 & K \end{Bmatrix} \times (\alpha SL\|T^{k_1}T^{k_2}\|\alpha'S'L') \quad (1.42)$$

where

$$(\alpha SL\|T^{k_1}T^{k_2}\|\alpha'S'L') = \sum_{\alpha''} (\alpha S\|T^{k_1}\|\alpha''S')(\alpha''L\|T^{k_2}\|\alpha'L') \quad . \tag{1.43}$$

1.7 MATRIX ELEMENTS OF SCALAR PRODUCT OF TWO COMMUTING TENSORS

In Eq. (1.27) of the last section, if we put K = 0 = Q, $k_1 = k_2 = k$,

$$< \alpha SLM|T_0^0|\alpha'S'L'J'M' > = (-1)^{J-M} \begin{pmatrix} J & 0 & J' \\ \overline{M} & 0 & M' \end{pmatrix} (\alpha SLJ\|T^0\|\alpha'S'L'J') \quad .$$

But from Eq. (1.15)

$$T_0^0 = (-1)^k(2k+1)^{-1/2} \sum_q (-1)^q T_q^k(1)T_{-q}^k(2)$$

and further [from Appendix C (C-7)]

$$\begin{pmatrix} J & 0 & J' \\ \overline{M} & 0 & M' \end{pmatrix} = (-1)^{J-M}(2J+1)^{-1/2} \delta_{JJ'}\delta_{MM'} \quad . \tag{1.44}$$

Therefore

$$< \alpha SLJM| \sum_q (-1)^q T_q^k(1)T_{-q}^k(2) |\alpha'S'L'J'M' >$$

$$= (-1)^{-k}(2k+1)^{1/2}(2J+1)^{-1/2} \delta_{JJ'}\delta_{MM'}(\alpha SLJ\|T^0\|\alpha'S'L'J') \tag{1.45}$$

Now from Eq. (1.42),

$$(\alpha SLJ\|T^0\|\alpha'S'L'J) = (\alpha SL\|T^kT^k\|\alpha'S'L') \quad \times$$

$$(2J+1) \begin{Bmatrix} S & L & J \\ S' & L' & J \\ k & k & 0 \end{Bmatrix}$$

where

$$\begin{Bmatrix} S & L & J \\ S' & L' & J \\ k & k & 0 \end{Bmatrix} = \frac{(-1)^{J+L+S'+k}}{\sqrt{(2J+1)(2k+1)}} \begin{Bmatrix} S & L & J \\ L' & S' & k \end{Bmatrix} \tag{1.46}$$

[Appendix C (Eq. C-19)]

Therefore

$$(\alpha SLJ\|T^0\|\alpha'S'L'J)$$

$$= (-1)^{J+L+S'+k} (2J+1)^{1/2}(2k+1)^{-1/2} \begin{Bmatrix} S & L & J \\ L' & S' & k \end{Bmatrix}$$

$$\times \quad (\alpha SL\|T^kT^k\|\alpha'S'L') \tag{1.47}$$

Substituting Eq. (1.47) into Eq. (1.45), we get finally:

$$< \alpha SLJM|T^k(1) \cdot T^k(2)|\alpha' S' L' J' M' >$$

$$= \delta_{JJ'}\delta_{MM'}(-1)^{J+L+S'} \begin{Bmatrix} S & L & J \\ L' & S' & k \end{Bmatrix} (\alpha SL \| T^k(1) \cdot T^k(2) \| \alpha' S' L') \qquad (1.48)$$

$$= \delta_{JJ'}\delta_{MM'}(-1)^{J+L+S'} \begin{Bmatrix} S & L & J \\ L' & S' & k \end{Bmatrix} \sum_{\alpha''} (\alpha S \| T^k(1) \| \alpha'' S')(\alpha'' L \| T^k(2) \| \alpha' L') \ .$$

Equation (1.48) is the matrix element of two commuting operators in the S^2 L^2, J^2, J_z representation. It reduces to the same type of reduced matrix element appeared in (1.43). The matrix is diagonal in J^2 and J_z because it is a tensor of rank zero, scalar.

1.8 MATRIX ELEMENTS OF DOUBLE TENSORS

A. In S^2, L^2, S_z, L_z representation.

By the definition of a double tensor operator in Section 1.3, together with the W-E theorem in the form as in Section 1.4, D, we easily see that

$$< \alpha S M_S L M_L | T^{qp}_{\nu\mu} | \alpha' S' M'_S L' M'_L >$$

$$= (-1)^{L-M_L} \begin{pmatrix} L & p & L' \\ \bar{M}_L & \mu & M'_L \end{pmatrix} (\alpha S M_S L \| T^{qp} \| \alpha' S' M'_S L')$$

$$= (-1)^{S-M_S} \begin{pmatrix} S & q & S' \\ \bar{M}_S & \nu & M'_S \end{pmatrix} (\alpha S L M_L \| T^{qp} \| \alpha' S' L' M'_L) \ .$$

Hence

$$< \alpha S M_S L M_L | \ T^{qp}_{\nu\mu} \ | \alpha' S' M'_S L' M'_L >$$

$$= (-1)^{S-M_S+L-M_L} \begin{pmatrix} S & q & S' \\ \bar{M}_S & \nu & M'_S \end{pmatrix} \begin{pmatrix} L & p & L' \\ \bar{M}_L & \mu & M'_L \end{pmatrix} (\alpha SL \| T^{qp} \| \alpha' S' L') \ . \qquad (1.49)$$

B. In S^2, L^2, J, J_z representation.

As we have mentioned in Section 1,3, we can construct an irreducible tensor T^K_Q by (1.25)

$$T^K_Q = \sum T^{qp}_{\nu\mu} < q\nu p\mu \mid KQ > \quad . \qquad (1.25)$$

Therefore by W-E theorem

$$< \alpha SLJM \mid T^K_Q \mid \alpha' S' L' J' M' >$$

$$= (-1)^{J-M} \begin{pmatrix} J & K & J' \\ \overline{M} & Q & M' \end{pmatrix} (\alpha SLJ \| T^K \| \alpha' S' L' J')$$

analogous to Eq. (1.42), (see Trees, 1951)

$$(\alpha SLJ \| T^K \| \alpha' S' L' J')$$

$$= \sqrt{(2K+1)(2J+1)(2J'+1)} \begin{Bmatrix} S & L & J \\ S' & L' & J' \\ q & p & k \end{Bmatrix} (\alpha SL \| T^{qp} \| \alpha' S' L') \quad . \qquad (1.50)$$

Here we have a reduced matrix element $(\alpha SL \| T^{qp} \| \alpha' S' L')$ instead of $(\alpha SL \| T^{k_1}(1) T^{k_2}(2) \| \alpha' S' L')$ as in Eq. (1.42).

In fact the latter is the special case of the former, as was mentioned in the last paragraph of Section 1.3. Also analogous to Eq. (1.48), we have

$$< \alpha SLJM \mid \sum_\mu (-1)^\mu \, T^{pp}_{\overline{\mu}\mu} \mid \alpha' S' L' J' M' >$$

$$= (-1)^{L+S'+J} \begin{Bmatrix} S & L & J \\ L' & S' & p \end{Bmatrix} (\alpha SL \| T^{pp} \| \alpha' S' L') \delta_{JJ'} \delta_{MM'} \quad . \qquad (1.51)$$

Thus in all cases we have shown that the evaluation of matrices reduces to the evaluation of two types of reduced matrix elements, namely $(\alpha SL \| T^k \| \alpha' S' L')$ and $(\alpha SL \| T^{qp} \| \alpha' S' L')$.

PART II

2.1 EVALUATION OF THE REDUCED MATRIX ELEMENT $(\alpha SL\|T^{qp}\|\alpha'S'L')$ and $(\alpha SL\|T^{k}\|\alpha'S'L')$

In Part I, we have reduced the problem of evaluation of matrix elements of: (1) spin-free (or space-free) tensor operators; (2) tensor product and scalar product of two commuting tensors; and (3) double tensors between wave functions of equivalent electrons in both LSJM and LSM_LM_S representation to essentially the problem of evaluating two types of reduced matrix elements written above. In this section, our task is to reduce them further into one-electron integrals using Racah's method of constructing wave functions for equivalent electrons.

It is shown in Racah's paper (Racah III) that the vector-coupling formula does not lead to antisymmetric wave functions for equivalent electrons. However, suitable linear combinations of vector-coupled eigenfunctions would produce desired antisymmetric eigenfunctions. Racah called the coefficients of linear combination "coefficients of fractional parentage."

Suppose we know an antisymmetric eigenfunction for the ℓ^{n-1} configuration: $|\ell^{n-1}\alpha_1S_1M_{S_1}L_1M_{L_1}>$. We want to get an eigenfunction for configuration ℓ^n: $|\ell^n\alpha SM_SLM_L>$ by adding one electron ℓ_n. Therefore use the vector-coupling formula:

$$|\ell^{n-1}(\alpha_1S_1L_1)\ell_n\alpha SL> \sum_{\substack{M_{S_1}m_{s_n}\\ M_{L_1}m_{\ell_n}}} |\ell^{n-1}\alpha_1S_1M_{S_1}L_1M_{L_1}>|\beta s_nm_{s_n}>|\beta\ell_nm_{\ell_n}> \times <S_1M_{S_1}s_nm_{s_n}|SM_S><L_1M_{L_1}\ell_nm_{\ell_n}|LM_L> \quad (2.1)$$

However Eq. (2.1) is not antisymmetric with respect to the interchange of n^{th} electron with the rest of n-1 electrons. In order to get an antisymmetric eigenfunction including the n^{th} electron, a further linear combination of Eq. (2.1) using coefficient of fractional parentage has to be used, namely:

$$|\ell^n \alpha S M_S L M_L > = \sum_{\alpha_1 S_1 L_1} |\ell^{n-1}(\alpha_1 S_1 L_1)\ell_n \alpha SL > < \ell^{n-1}(\alpha_1 S_1 L_1)\ell\alpha SL |\} \ell^n \alpha SL > . \quad (2.2)$$

The fractional parentage coefficient $< \ell^{n-1}(\alpha_1 S_1 L_1)\ell\alpha SL |\} \ell^n \alpha SL >$ in which the parent term is indicated by bracket, is tabulated in Racah III for p^n and d^n configurations.

Now using Eq. (2.1) and (2.2), let us calculate the matrix element

$$I = < \ell^n \alpha S M_S L M_L | T^{qp}_{n\nu\mu} | \ell^n \alpha' S' M_S' L' M_L' > \quad (2.3)$$

in which $T^{qp}_{n\nu\mu}$ is made up of one electron operator:

$$T^{qp}_{n\nu\mu} = \sum_{i=1}^{n} t^{qp}_{\nu\mu}(i) \quad . \quad (2.4)$$

Since electrons are equivalent, the matrix element of every term in Eq. (2.4) is equal, i.e.

$$I = \sum_{i=1}^{n} < \ell^n \alpha S M_S L M_L | t^{qp}_{\nu\mu}(i) | \ell^n \alpha' S' M_S' L' M_L' >$$

$$= n < \ell^n \alpha S M_S L M_L | t^{qp}_{\nu\mu}(n) | \ell^n \alpha' S' M_S' L_L' > \quad .$$

Here we purposely retain the n^{th} term in the sum.

Now substituting Eq. (2.2) for the wave functions, we have

$$I = n \sum_{\substack{\alpha_1 S_1 L_1 \\ \alpha_2 S_2 L_2}} < \ell^n \alpha SL \{ |\ell^{n-1}(\alpha_1 S_1 L_1)\ell\alpha SL >$$

$$< \ell^{n-1}(\alpha_1 S_1 L_1)\ell_n \alpha SL | t^{qp}_{\nu\mu}(n) | \ell^{n-1}(\alpha_2 S_2 L_2)\ell_n \alpha' S' L' >$$

$$\times < \ell^{n-1}(\alpha_2 S_2 L_2)\ell\alpha' S' L' |\} \ell^n \alpha' S' L' >$$

Again using Eq. (2.1) and notice

$$< \ell^{n-1}\alpha_1 S_1 M_{S_1} | \ell^{n-1}\alpha_2 S_2 M_{S_2} > = \delta\alpha_1\alpha_2 \delta_{S_1 S_2} \delta_{M_{S_1} M_{S_2}} \quad (2.5)$$

$$< \ell^{n-1}\alpha_1 L_1 M_{L_1} | \ell^{n-1}\alpha_2 L_2 M_{L_2} > \;=\; \delta_{\alpha_1\alpha_2}\delta_{L_1L_2}\delta_{M_{L_1}M_{L_2}} \tag{2.6}$$

we obtain

$$I = n \sum_{\alpha_1 S_1 L_1} < \ell^n \alpha SL \{| \ell^{n-1}(\alpha_1 S_1 L_1)\ell\alpha SL > < \ell^{n-1}(\alpha_1 S_1 L_1)\ell\alpha' S' L' |\} \ell^n \alpha' S' L' >$$

$$\times \sum_{\substack{M_{S_1} M_{L_1} \\ m_{sn} m'_{sn} \\ m_{\ell n} m_{\ell n}}} < SM_S | S_1 M_{S_1} s_n m_{sn} > < LM_L | L_1 M_{L_1} \ell_n m_{\ell n} > < \beta s_n m_{sn} \ell_n m_{\ell n} | t^{qp}_{\nu\mu}(n) | \beta s_n m'_{sn} \ell_n m'_{\ell n} >$$

$$\times \; < S_1 M_{S_1} s_n m'_{sn} | S' M'_S > < L_1 M_{L_1} \ell_n m'_{\ell n} | L' M'_L > \; . \tag{2.7}$$

From now on we can drop the subscript n for the n-th electron and write (following Slater, II, p. 156)

$$a(\ell^n \alpha SL; \alpha_1 S_1 L_1) \;\equiv\; < \ell^n \alpha SL \{| \ell^{n-1}(\alpha_1 S_1 L_1)\ell\alpha SL > \; . \tag{2.8}$$

Further, for the one electron integral, we can use the W-E theorem in the form of Eq. (1.49), i.e.,

$$< \beta s m_s \ell m_\ell | t^{qp}_{\nu\mu} | \beta s m'_s m'_\ell > \;=\; (-1)^{s-m_s+\ell-m_\ell} \begin{pmatrix} s & q & s \\ m_s & \nu & m'_s \end{pmatrix} \begin{pmatrix} \ell & p & \ell \\ m_\ell & \mu & m'_\ell \end{pmatrix} (\beta s\ell \| t^{qp} \| \beta s\ell)$$

$$= \; < s m'_s q\nu | s m_s > < \ell m_\ell p\mu | \ell m_\ell > \frac{(\beta s\ell \| t^{qp} \| \beta s\ell)}{\sqrt{(2s+1)(2\ell+1)}} \; .$$

Therefore Eq. (2.7) becomes

$$I \;=\; n \sum_{\alpha_1 S_1 L_1} a(\ell^n \alpha SL; \alpha_1 S_1 L_1) a(\ell^n \alpha' S' L'; \alpha_1 S_1 L_1) \frac{(\beta s\ell \| t^{qp} \| \beta s\ell)}{\sqrt{(2s+1)(2\ell+1)}}$$

$$\sum_{\substack{M_{S_1} M_{L_1} \\ m_s m'_s \\ m_\ell m'_\ell}} < S_1 M_{S_1} s m_s | SM_S > < s m'_s q\nu | s m_s > < S_1 M_{S_1} s m'_s | S' M'_S >$$

$$< L_1 M_{L_1} \ell m_\ell | LM_L > < \ell m'_\ell p\mu | \ell m_\ell > < L_1 M_{L_1} \ell M'_\ell | L' M'_L > \tag{2.9}$$

The last summation in Eq. (2.9) can be done using the formula for product of three V-C coefficients [Appendix C(Eq. C.13)].

$$\sum_{\substack{m_2\\m_{12}\\m_{23}}} < j_1m_1j_2m_2|j_{12}m_{12} > < j_{12}m_{12}j_3m_3|j\,m > < j_2m_2j_3m_3|j_{23}m_{23} >$$

$$= \sqrt{(2j_{12}+1)(2j_{23}+1)}\; W(j_1j_2jj_3;j_{12}j_{13}) < j_1m_1j_{23}m-m_1|jm > \tag{2.10}$$

and get

$$\sum_{M_{S_1}m_sm_s'} < S_1M_{S_1}sm_s|SM_S > < sm_s'q\nu|sm_s > < S_1M_{S_1}sm_s | S'M_S' > \times \sum_{M_{L_1}M_\ell M_\ell'}$$

$$< L_1M_{L_1}\ell m_\ell|LM_L > < \ell m_\ell' p\mu|\ell m_\ell > < L_1M_{L_1}\ell M_\ell'|L'M_L' >$$

$$= (-1)^{q+s+S'+S_1}\sqrt{(2s+1)(2S'+1)}\; W(SsS's;S_1q) < S'M_S'q\nu|SM_S >$$

$$\times (-1)^{p+\ell+L'+L_1}\sqrt{(2\ell+1)(2L'+1)}\; W(L\ell L'\ell;L_1p) < L'M_L'p\mu|LM_L > . \tag{2.11}$$

Substituting back to Eq. (2.9), we finally obtain

$$I = n\sqrt{(2S'+1)(2L'+1)}\sum_{\alpha_1S_1L_1} a(\ell^n\alpha SL;\alpha_1S_1L_1)a(\ell^n\alpha'S'L';\alpha_1S_1L_1)(\beta s\ell\|t^{qp}\|\beta s\ell)$$

$$(-1)^{q+s+S'+S_1}W(SsS's;S_1q) < S'M_S'q\nu|SM_S >$$

$$(-1)^{p+\ell+L'+L_1}W(L\ell L'\ell;L_1p) < L'M_L'p\mu|LM_L > . \tag{2.12}$$

While from Eq. (1.49) we have another expression for I, i.e.

$$I = < S'M_S'q\nu|SM_S > < L'M_L'p\mu|LM_L > \frac{(\alpha SL\|T_n^{qp}\|\alpha'S'L')}{\sqrt{(2S+1)(2L+1)}} . \tag{1.49}$$

Hence the comparison of Eq. (2.12) and (1.49) gives the reduced matrix element $(\alpha SL\|T_n^{qp}\|\alpha'S'L')$ as

$$(\alpha SL\|T_n^{qp}\|\alpha'S'L') = n\sqrt{(2S+1)(2S'+1)(2L+1)(2L'+1)}\;(\beta\tfrac{1}{2}\ell\|t^{qp}\|\beta\tfrac{1}{2}\ell)$$

$$\times \sum_{\alpha_1S_1L_1} a(\ell^n\alpha SL;\alpha_1S_1L_1)a(\ell^n\alpha'S'L';\alpha_1S_1L_1)(-1)^{q+\frac{1}{2}+S'+S_1}(-1)^{p+\ell+L'+L_1}$$

$$W(S\tfrac{1}{2}S'\tfrac{1}{2};S_1q)W(L\ell L'\ell;L_1p) , \tag{2.13}$$

Since the special case of T_n^{qp} when q = 0, p = k is

$$T_n{}^k = \sum_{i=1}^{n} t^k(i) . \tag{2.14}$$

We easily get the reduced matrix element for this spin-free (or space-free) operator by the same procedure:

$$(\alpha SL\|T_n^k(2)\|\alpha'S'L') = \delta_{SS'} n\sqrt{(2L+1)(2L'+1)}$$
$$\times \sum_{\alpha_1 S_1 L_1}{}' (-1)^{k+\ell+L'+L_1} a(\ell^n\alpha SL;\alpha_1S_1L_1)a(\ell^n\alpha'S'L';\alpha_1S_1L_1)$$
$$W(L\ell L'\ell;L_1k)\ (\beta\ell\|t^k(2)\|\beta\ell) \tag{2.15}$$

and

$$(\alpha SL\|T_n^k(1)\|\alpha'S'L') = \delta_{LL'}\ n\sqrt{(2S+1)(2S'+1)}$$
$$\times \sum_{\alpha_1 S_1 L_1} (-1)^{k+\frac{1}{2}+S'+S_1} a(\ell^n\alpha SL;\alpha_1S_1L_1)a(\ell^n\alpha'S'L';\alpha_1S_1L_1)$$
$$W(S\tfrac{1}{2}S'\tfrac{1}{2};Sk_1)(\beta\tfrac{1}{2}\|t^k(1)\|\beta\tfrac{1}{2}) \tag{2.16}$$

Equations (2.13), (2.15) and (2.16) formally contain the final results we obtain for the task we set forth in this section. The one-electron reduced matrix elements in them can be evaluated by an ordinary method. It depends, of course, on the specific nature of the operator.

For the convenience of numerical tabulation, Racah (II,III) defined the so-called unit double tensor operator V^{qp} and the unit tensor operator $U^{(k)}$. As can be seen from Eq. (2.13) and (2.15), if we divide through both sides by the respective one-electron reduced matrices, we obtain:

$$(\ell^n\alpha SL\| \frac{T_n^{qp}}{(\beta\frac{1}{2}\ell\|t^{qp}\|\beta\frac{1}{2}\ell)} \|\ell^n\alpha'S'L') = n\sqrt{(2S+1)(2S'+1)(2L+1)(2L'+1)}(-1)^{q+p+\frac{1}{2}+\ell+S'+L'}$$
$$\times\sum_{\alpha_1 S_1 L_1}(-1)^{S_1+L_1}a(\ell^n\alpha SL;\alpha_1S_1L_1)a(\ell^n\alpha'S'L';\alpha_1S_1L_1)$$
$$\times\ W(S\tfrac{1}{2}S'\tfrac{1}{2};S_1q)W(L\ell L'\ell;L_1p) \tag{2.13}$$

$$(\ell^n\alpha SL\| \frac{T_n^{(k)}(2)}{(\beta\ell\|t^k(2)\|\beta\ell)} \|\ell^n\alpha'S'L')$$

$$= \delta_{SS'}\, n\sqrt{(2L+1)(2L'+1)}\, (-1)^{k+\ell+L'}$$

$$\times \sum_{\alpha_1 S_1 L_1} (-1)^{L_1} a(\ell^n\alpha SL;\alpha_1S_1L_1)a(\ell^n\alpha'S'L';\alpha_1S_1L_1)W(L\ell L'\ell;L_1k) \quad . \qquad (2.15')$$

Notice that the right hand sides of the formulas do not contain the specific nature of operators T_n^{qp} and $T_n^{(k)}(2)$ but only depend on their rank and the configuration ℓ^n. Therefore one can tabulate the value of them for various n, q, p and k thus define:

$$\frac{T_n^{qp}}{(\beta\frac{1}{2}\ell\|t^{qp}\|\beta\frac{1}{2}\ell)} \equiv \sqrt{\frac{2}{3}}\, V^{qp} \qquad (2.13a)$$

and

$$\frac{T_n^{(k)}(2)}{(\beta\ell\|t^k(2)\|\beta\ell)} \equiv U^{(k)}(2) \quad . \qquad (2.15a)$$

We list some values for the one-electron reduced matrices below for the latter references (Edmonds, p. 76):

$$(\beta\ell\|\ell\|\beta\ell) = \sqrt{\ell(\ell+1)(2\ell+1)} \qquad (2.15b)$$

$$(\beta\tfrac{1}{2}\|s\|\beta\tfrac{1}{2}) = \sqrt{\frac{3}{2}} \qquad (2.16b)$$

$$(\beta\ell\|C^{(k)}\|\beta\ell) = (-1)^{\ell}(2\ell+1)\begin{pmatrix}\ell & k & \ell\\ 0 & 0 & 0\end{pmatrix} \quad . \qquad (2.15c)$$

2.2 RECURSION FORMULA

So far our consideration has been confined to operators of the form

$T_n^k = \sum_{i=1}^{n} t^k(i)$ and $T_n^{qp} = \sum_{i=1}^{n} t^{qp}(i)$. But when we have the tensor interaction the operator of which contains coordinate of two electrons such as the spin-spin interaction or the electrostatic interaction, then evaluation of the general formulas for the reduced matrix element becomes very complicated. In this case, it is perhaps more convenient to use the recursion formula by which we derive all the matrix elements of d^n configurations starting from the knowledge of d^2 configuration.

Our tensor operator is of the form:

$$T_n^{qp} = \sum_{i>j}^{n} t^{qp}(ij) \tag{2.17}$$

$$I = \langle \ell^n \alpha S M_S L M_L | T_n^{qp} | \ell^n \alpha' S' M_S' L' M_L' \rangle \quad .$$

Since all the electrons are equivalent, each term in Eq. (2.17) contributes the equal amount to the matrix element. If we now remove one electron, the value of the matrix element will become (n-2)/n times the original one (since there is $\frac{1}{2}n(n-1)$ terms in Eq. (2.17), therefore

$$I = \frac{n}{n-2} \langle \ell^n \alpha S M_S L M_L | T_{n-1}^{qp} | \ell^n \alpha' S' M_S' L' M_L' \rangle \quad .$$

We substitute Eq. (2.2) for the wave function on both sides and get

$$I = \frac{n}{n-2} \sum_{\substack{\alpha_1 S_1 L_1 \\ \alpha_2 S_2 L_2}} a(\ell^n \alpha SL; \alpha_1 S_1 L_1) a(\ell^n \alpha' S' L'; \alpha_2 S_2 L_2) \langle \ell^{n-1}(\alpha_1 S_1 L_1)\ell_n SL | T_{n-1}^{qp} | \ell^{n-1}(\alpha_2 S_2 L_2)\ell n S' L' \rangle \quad . \tag{2.18}$$

Then use Eq. (2.1) to get the explicit dependence of wave functions on the n-th (removed) electron to evaluate the matrix element in Eq. (2.18), and remember Eq. (2.11), and Eq. (2.13), we get

$$(\ell^n\alpha SL\|T_n^{qp}\|\ell^n\alpha'S'L')$$
$$= (-1)^{L+S-\ell-\frac{1}{2}+p+q}\ \frac{n}{n-2}\ [(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2} \quad x$$

$$\sum_{\substack{\alpha_1 S_1 L_1 \\ \alpha_2 S_2 L_2}} (-1)^{L_2+S_2} a(\ell^n\alpha SL'\alpha_1 S_1 L_1)a(\ell^n\alpha'S'L';\alpha_2 S_2 L_2) \quad x$$

$$< \ell^{n-1}\alpha_1 S_1 L_1\|T_{n-1}^{qp}\|\ell^{n-1}\alpha_2 S_2 L_2 > \quad W(S_1 S S_2 S';\frac{1}{2}\ q)W(L_1 L L_2 L';\ell p) \quad .$$

2.3 MATRIX ELEMENTS OF ELECTROSTATIC INTERACTION

The operator under consideration is:

$$H_{e.s} = \sum_{i>j} \frac{e^2}{r_{ij}} \quad . \qquad (2.20)$$

It is evident that

$$Q_R\ H_{e.s.}\ Q_R^{-1} = H_{e.s.}$$
$$P_R\ H_{e.s.}\ P_R^{-1} = H_{e.s.}$$
$$O_R\ H_{e.s.}\ O_R^{-1} = H_{e.s.} \qquad (2.21)$$

Therefore both in SLJM and SM_SLM_L representations $H_{e.s.}$ is diagonal. However, if the state is not completely characterized by the angular momentum quantum numbers only, it can have a non-diagonal element between other quantum numbers (like α). Since

$$< d^n\alpha SLJM|H_{e.s.}|d^n\alpha'SLJM >$$

$$= \sum_{\substack{M_S M_L \\ M_S' M_L'}} < SM_SLM_L|JM > < d^n\alpha SM_SLM_L|H_{e.s.}|d^n\alpha'SM_S'LM_L' > < SM_S'LM_L'|JM > \qquad (2.22)$$

Consider

$$< d^n\alpha SM_SLM_L|H_{e.s.}|d^n\alpha'SM_S'LM_L' > \quad .$$

Equation (2.21) shows that $H_{e.s.}$ is scalar with respect to Q_R and P_R respectively. Therefore we have by W-E theorem

$$< d^n\alpha SM_S LM_L | H_{e.s.} | d^n\alpha' SM'_S LM'_L >$$

$$= (-1)^{S-M_S} \begin{pmatrix} S & 0 & S \\ M_S & 0 & M'_S \end{pmatrix} (d^n\alpha SLM_L \| H_{e.s.} \| d^n\alpha' SLM'_L)$$

$$= (2S+1)^{-1/2} \delta_{M_S M'_S} (d^n\alpha SLM_L \| H_{e.s.} \| d^n\alpha' SLM'_L)$$

and

$$= (-1)^{L-M_L} \begin{pmatrix} L & 0 & L \\ M_L & 0 & M'_L \end{pmatrix} (d^n\alpha SM_S L \| H_{e.s.} \| d^n\alpha' SM'_S L)$$

$$= (2L+1)^{-1/2} \delta_{M_L M'_L} (d^n\alpha SM_S L \| H_{e.s.} \| d^n\alpha' SM'_S L)$$

or

$$< d^n\alpha SM_S LM_L | H_{e.s.} | d^n\alpha' SM'_S LM'_L > = [(2S+1)(2L+1)]^{-1/2} \delta_{M_S M'_S} \delta_{M_L M'_L} \times (d^n\alpha SL \| H_{e.s.} \| d^n\alpha' SL) \quad . \tag{2.23}$$

Substituting Eq. (2.23) into Eq. (2.22)

$$< d^n\alpha SLJM | H_{e.s.} | d^n\alpha' SLJM >$$

$$= \sum_{M_S M_L} < SM_S LM_L | JM > < SM_S LM_L | JM > [(2S+1)(2L+1)]^{-1/2} (d^n\alpha SL \| H_{e.s.} \| d^n\alpha' SL)$$

$$= [(2S+1)(2L+1)]^{-1\ 2} (d^n\alpha SL \| H_{e.s.} \| d^n\alpha' SL) \tag{2.24}$$

Equations (2.23) and (2.24) show that the term values in both LSJM and $LM_L SM_S$ representations are exactly the same. This is just the familiar result that the term values are characterized only by S and L values and α which, in the case of d^n configuration, is just the "seniority number" v (see Racad III).

It is quite easy to see that the operator $H_{e.s.}$ is a particular case of the operator considered in Section 2.2. Therefore, the value of matrix elements for d^n configurations in general can be obtained from the recursion formula (2.18). In this special case, the same procedure as used in deriving (2.18) yields

$$< d^n\alpha S M_S L M_L | H_{e.s.} | d^n\alpha' S M_S L M_L > \;=\; < d^n\alpha SLJM | H_{e.s.} | d^n\alpha' SLJM >$$

$$= \; [(2S+1)(2L+1)]^{-1/2} (d^n\alpha SL \| H^n_{e.s.} \| d^n\alpha' SL)$$

$$= \frac{n}{n-2} \sum_{\substack{\alpha_1\alpha_1' \\ S_1L_1}} a(d^n\alpha SL;\alpha_1S_1L_1)a(d^n\alpha' SL;\alpha_1'S_1L_1) < d^{n-1}\alpha_1S_1L_1 | H^{n-1}_{e.s.} | d^{n-1}\alpha_1'S_1L_1 > \qquad (2.25)$$

Since the $< d^2\alpha SL | \frac{e^2}{r_{12}} | d^2\alpha SL >$ can be calculated by an ordinary method and the result is well known (Racah III):

TABLE I

αSL \ $\alpha' S' L'$	^1_0S	^3_2P	^1_2D	^3_3F	^1_2G
^1_0S	A+14B+7C				
^3_2P		A+7B			
^1_2D			A-3B+2C		
^3_2F				A-8B	
^1_2G					A+4B+2C

Table I, together with Eq. (2.25) can be used to obtain all the matrix elements of d^n configurations. Constants A, B, and C in the table, called Racah's parameters, are related to the Slater integral by

$$A \;=\; F_0 - 49F_4 \;=\; F^0 - \frac{F^4}{9}$$

$$B \;=\; F_2 - 5F_4 \;=\; \frac{1}{441}\,(9F^2 - 5F^4) \qquad (2.26)$$

$$C \;=\; 35F_4 \;=\; \frac{5}{63}\,F^4$$

It should be noted that in Table I the coefficients of A in every matrix element are the same. Therefore, in discussing the relative term values (as in the case of optical absorption spectra) only two parameters, B and C, need be considered. Further, the recursion formula (2.25) shows also that the relative term values in all d^n configurations can be characterized by two parameters, B and C alone.

2.4 MATRIX ELEMENTS OF CRYSTALLINE FIELD POTENTIAL

The crystalline field potential can be expressed as

$$V_{C.F.} = \sum_{i=1}^{n} \sum_{k} C_{kq} r^k \, Y_{kq}(\theta_i \phi_i) \qquad (2.27)$$

For the d-electron in the crystalline field of one of the 32-point groups, $k \leq 4$ and actually k can take two values, 2 and 4 only. Therefore, our basic matrix element is

$$< d^n \alpha SLJM | \sum_{i=1}^{n} C_{kq} r^k Y_{kq}(\theta_i \phi_i) | d^n \alpha' S' L' J' M' > \qquad \text{and}$$

$$< d^n \alpha S M_S L M_L | \sum_{i=1}^{n} C_{kq} r^k Y_{kq}(\theta_i \phi_i) | d^n \alpha' S' M_S' L' M_L' > \qquad (2.28)$$

If we notice

$$Y_{kq} \sim t_q^k(2) \quad \text{(acts on space part of wave function only)}$$

Then

$$\sum_{i=1}^{n} C_{kq} r^k Y_{kq}(\theta_i \phi_i) = T_{nq}^{(k)}(2) = \sum_{i=1}^{n} t_{iq}^k(2) \qquad (2.29)$$

We have shown in Part I that both matrix elements in (2.28) can be reduced to the problem of evaluating one-reduced matrix element.

$$(d^n \alpha SL \| T_n^{(k)}(2) \| d^n \alpha' S' L')$$

and we further showed that this reduced matrix element is given by Eq. (2.15), i.e.

$$(d^n\alpha SL\|T_n^k(2)\|d^n\alpha'S'L') = \delta_{SS'}\, n\sqrt{(2L+1)(2L'+1)} \times$$

$$\sum_{\alpha_1 S_1 L_1} (-1)^{k+\ell+L'+L_1} a(d^n\alpha SL;\alpha_1 S_1 L_1)a(d^n\alpha'S'L';\alpha_1 S_1 L_1) \times$$

$$W(L\ell L'\ell;L_1 k)(\beta\ell\|t^k(2)\|\beta\ell) \quad (2.15)$$

The summation over $\alpha_1 S_1 L_1$ is extended to all common parent terms for terms αSL and $\alpha'S'L'$

Now our problem is to evaluate the one-electron matrix element $(\beta\ell\|t^k(2)\|\beta\ell)$.

$$t_q^k(2) = C_{kq} r^k Y_{kq}$$

$$(\beta\ell\|t^k\|\beta\ell) = (\beta\|C_{kq}r^k\|\beta)(\ell\|Y_{kq}\|\ell) \quad (2.30)$$

But

$$(\ell\|Y_k\|\ell) = (-1)^\ell\sqrt{\frac{2k+1}{4\pi}}\,(2\ell+1)\begin{pmatrix}\ell & k & \ell\\ 0 & 0 & 0\end{pmatrix} \quad (2.31)$$

[see (2.15c) and (1.12)]

$$(\beta\|C_{kq}r\|\beta) = C_{kq} < r^k >_{3d}$$

We have

$$(\beta\ell\|t^k\|\beta\ell) = C_{kq} < r^k >_{3d}(-1)^\ell\sqrt{\frac{2k+1}{4\pi}}\,(2\ell+1)\begin{pmatrix}\ell & k & \ell\\ 0 & 0 & 0\end{pmatrix}, \quad (2.32)$$

For example, for $k = 4$, $\ell = 2$

$$(\beta 2\|t^{(4)}\|\beta 2) = C_{40} < r^4 >_{3d} \frac{3\sqrt{70}}{14\sqrt{\pi}} = 3\sqrt{70}\,Dq \quad . \quad (2.33)$$

where $Dq \equiv \dfrac{C_{40} < r^4 > 3d}{14\sqrt{\pi}}$ is the cubic crystalline field parameter.

We have from (2.15')

$$(d^n\alpha SL\|U_n^{(4)}(2)\|d^n\alpha'S'L')$$

$$= \delta_{SS'}\, n\sqrt{(2L+1)(2L'+1)}\sum_{\alpha_1 S_1 L_1} a(d^n\alpha SL;\alpha_1 S_1 L_1)a(d^n\alpha'S'L',\alpha_1 S_1 L) \times$$

$$(-1)^{L'+L_1}\, W(L2L'2;L_1 4) \quad (2.34)$$

$$U_n^{(4)}(2) = \sum_{i=1}^{n} u_i^{(4)}(2) \qquad (2.34')$$

and $u_i^{(4)}(2) = \dfrac{t^{(4)}(2)}{(\beta 2\|t^{(4)}(2)\|\beta 2)}$. This is called the "one-electron unit tensor operator" by Racah (Racah III), since $(\beta 2\|u_i^{(4)}(2)\|\beta 2) = 1$.

For the actual calculation of the matrix elements crystalline field potential, it is convenient to tabulate Eq. (2.34) for k = 2, 4 and n = 2, 3, 4, 5. We have done this for n = 2, 5, k = 2, 4.* The table for n = 2, 5 and k = 2 is taken from Slater II.

As an actual application of this method in the crystalline field calculations and the usage of the table for $(d^n\alpha SL\|U_n^{(k)}(2)\|d^n\alpha' S'L')$ in Appendix D, let us calculate, for example, the matrix element:

$$I = \langle d^{54}G^4\Gamma_{41}|V_{C.F.}|d^{54}F^4\Gamma_{41}\rangle$$

with

$$V_{C.F.} = \sum_{i=1}^{5} C_{40}r^4\left[Y_{40}(i) + \sqrt{\frac{5}{14}}\,(Y_{44}(i) + Y_{4\bar{4}}(i))\right]$$

$$= T_0^4 + \sqrt{\frac{5}{14}}\,(T_4^4 + T_{\bar{4}}^4) \quad .$$

We have (Griffith, Appendix)

$$|d^{54}G^4\Gamma_{41}\rangle = \frac{1}{\sqrt{2}}\left\{|d^5 S = \frac{3}{2}, M_S, L = 4, M_L = 4\rangle - |d^5, S = \frac{3}{2}, M_S, L = 4, M_L = \bar{4}\rangle\right\}$$

$$= \frac{1}{\sqrt{2}}\,(\phi_{44} - \phi_{4\bar{4}})$$

$$|d^{54}F^4\Gamma_{41}\rangle = |d^5 S = \frac{3}{2}, M_S\ L = 3, M_L = 0\rangle = \phi_{30}$$

Therefore

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*See Appendix D.

$$< d^{54}G^4\Gamma_{41}|V_{C.F.}|d^{54}F^4\Gamma_{41} > \;=\; \frac{1}{\sqrt{2}}(\phi_{44} - \phi_{4\bar{4}}|V_{C.F.}|\phi_{30})$$

$$(\phi_{44}|T^4_0|\phi_{30}) = (\phi_{4\bar{4}}|T^4_0|\phi_{30}) = (\phi_{44}|T^4_{\bar{4}}|\phi_{30}) = (\phi_{4\bar{4}}|T^4_4|\phi_{30}) = 0$$

since $M \neq q + M'$ so the V-C coefficient vanishes in the W-E theorem. Thus

$$I = \frac{1}{\sqrt{2}}\sqrt{\frac{5}{14}}\,[(\phi_{44}|T^4_{\bar{4}}|\phi_{30}) - (\phi_{4\bar{4}}|T^4_4|\phi_{30})]$$

$$= \sqrt{\frac{5}{28}}\left\{\begin{pmatrix}4 & 4 & 3\\ \bar{4} & 4 & 0\end{pmatrix}(d^{54}G\|T^4\|d^{54}F) - \begin{pmatrix}4 & 4 & 3\\ 4 & \bar{4} & 0\end{pmatrix}(d^{54}G\|T^4\|d^{54}F)\right\}$$

But

$$T^4 = (\beta 2\|t^4\|\beta 2)U^{(4)} = 3\sqrt{70}\ Dq\ U^{(4)}(2) \quad \text{by Eq. (2.33)}$$

$$(d^{54}G\|U^{(4)}(2)\|d^{54}F) = -\sqrt{\frac{11}{7}}$$

from Appendix D.

and $-\begin{pmatrix}4 & 4 & 3\\ 4 & \bar{4} & 0\end{pmatrix} = \begin{pmatrix}4 & 4 & 3\\ \bar{4} & 4 & 0\end{pmatrix} = -\dfrac{14}{3\sqrt{7\cdot 10\cdot 11}}$ (from Rotenberg).

Hence,

$$I = \sqrt{\frac{5}{28}}\,3\sqrt{70}\ Dq\left\{2x\left(\sqrt{\frac{11}{7}}\right)\left(\frac{14}{3\sqrt{7\cdot10\cdot11}}\right)\right\} = 2\sqrt{5}\ Dq$$

2.5 MATRIX ELEMENT OF THE SPIN-ORBIT INTERACTION

For the d^n configuration the $H_{s.o.}$ is given by

$$H_{s.o.} = \lambda_{3d}\sum_{i=1}^{n} \underline{s}(i)\cdot\underline{\ell}(i)$$

$$= \lambda_{3d}\sum_{i}\sum_{\mu=-1}^{1}(-1)^{\mu}s_{-\mu}(i)\ell_{\mu}(i)$$

$$= \lambda_{3d}\sum_{\mu=-1}^{1}(-1)^{\mu}\,T^{11}_{n\bar{\mu}\mu} \qquad (2.35)$$

where $T^{11}_{n\bar{\mu}\mu} = \sum s_{-\mu}(i)\ell_{\mu}(i)$ as in Eq. (1.26). Therefore, from Eq. (1.51) we have in the representation $|d^n\alpha SLJM>$,

$$I \equiv \langle d^n\alpha SLJM|H_{S.O.}|d^n\alpha'S'L'J'M'\rangle$$

$$I = \langle d^n\alpha SLJM|\lambda_{3d}\sum_{\mu}(-1)^{\mu}\, T^{11}_{n\mu\mu}|d^n\alpha'S'L'J'M'\rangle$$

$$= \delta_{JJ'}\delta_{MM'}(-1)^{L+S'+J}\begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix}(d^n\alpha SL\|\lambda_{3d}T^{11}_n\|d^n\alpha'S'L'). \quad (2.36)$$

We see that $H_{S.O.}$ is diagonal with respect to J^2 and J_z. The J dependence of the matrix element is given by the factor $(-1)^{L+S'+J}\begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix}$. Especially, for the diagonal element ($L' = L$, $S' = S$, $J' = J$, $M' = M$), we have

$$\begin{Bmatrix} S & L & J \\ L & S & 1 \end{Bmatrix}(-1)^{S+L+J} = \frac{J(J+1) - S(S+1) - L(L+1)}{2\,[S(S+1)(2S+1)L(L+1)(2L+1)]^{1/2}} \quad (2.37)$$

in which the factor $J(J+1) - S(S+1) - L(L+1)$ is just the J dependence which gives rise to the Lande interval rule. The reduced matrix element $(\alpha SL\|\lambda_{3d}T^{11}\|\alpha'S'L')$ is given by Eq. (2.13):

$$(d^n\alpha SL\|\lambda_{3d}T^{11}_n\|d^n\alpha'S'L') = n\sqrt{(2S+1)(2S'+1)(2L+1)(2L'+1)}\,(-1)^{\frac{1}{2}+S'+L'} \times$$

$$\sum_{\alpha_1 S_1 L_1}(-1)^{S_1+L_1} a(d^n\alpha SL;\alpha_1 S_1 L)a(d^n\alpha'S'L';\alpha_1 S_1 L_1) \times \quad (2.13)$$

$$\times\ W(S\tfrac{1}{2}S'\tfrac{1}{2};S_1 1)W(L2L'2;L_1 1)(\beta\tfrac{1}{2}\ell\|\lambda_{3d}t^{11}\|\beta\tfrac{1}{2}\ell)\ .$$

We again notice that the factor besides $(\beta\frac{1}{2}\ell\|\lambda_{3d}t^{11}\|\beta\frac{1}{2}\ell)$ is independent of the nature of the double tensor T^{11}. Therefore, we call it $\sqrt{\frac{2}{3}}\,(d^n\alpha SL\|V^{11}\|d^n\alpha'S'L')$ as in Eq. (2.13a), i.e.,

$$(d^n\alpha SL\|\lambda_{3d}T^{11}\|d^n\alpha'S'L') = (d^n\alpha SL\|V^{11}\|d^n\alpha'S'L')\sqrt{\frac{2}{3}} \times (\beta\tfrac{1}{2}\ell\|\lambda_{3d}t^{11}\|\beta\tfrac{1}{2}\ell) \quad (2.38)$$

The matrix $(d^n\alpha SL\|V^{11}\|d^n\alpha'S'L')$ is tabulated for d^2 and d^5 in Appendix D. We have to evaluate

$$(\beta\tfrac{1}{2}\ell\|t^{11}\lambda_{3d}\|\beta\tfrac{1}{2}\ell), \qquad \text{since } t^{11} = \underline{S}\underline{\ell}$$

$$(\beta\tfrac{1}{2}\ell\|\lambda_{3d}t^{11}\|\beta\tfrac{1}{2}\ell) = (\tfrac{1}{2}\|s\|\tfrac{1}{2})(\ell\|\underline{\ell}\|\ell)(\beta\|\lambda_{3d}\|\beta) \quad .$$

But since

$$(j\|\underline{J}\|j) = \sqrt{j(j+1)(2j+1)} \qquad (2.15b)$$

we have

$$(\beta\tfrac{1}{2}\ell\|\lambda_{3d}t^{11}\|\beta\tfrac{1}{2}\ell) = \bar{\lambda}_{3d}\sqrt{\tfrac{3}{2}}\sqrt{\ell(\ell+1)(2\ell+1)} = \bar{\lambda}_{3d}\sqrt{45}$$

$$(d^n\alpha SL\|\lambda_{3d}T^{11}\|d^n\alpha'S'L') = \bar{\lambda}_{3d}\sqrt{30}\,(d^n\alpha SL\|V''\|d^n\alpha'S'L') \quad . \qquad (2.39)$$

Hence, for d^n configurations

$$< d^n\alpha SLJM|H_{S.O.}|d^n\alpha'S'L'J'M' >$$
$$= \bar{\lambda}_{3d}\sqrt{30}\,\delta_{JJ'}\delta_{MM'}(-1)^{L+S'+J}\begin{Bmatrix} S & L & J \\ L' & S' & 1 \end{Bmatrix}(d^n\alpha SL\|V^{11}\|d^n\alpha'S'L') \quad . \qquad (2.40)$$

In some cases, one is interested in the matrix element in the $|d^n\alpha SM_SLM_L>$ representation. Using Eq. (1.49) we obtain

$$I \equiv < d^n\alpha SM_SLM_L|\lambda_{3d}\sum_{\mu}(-1)^{\mu}T^{11}_{\bar{\mu}\mu}|d^n\alpha'S'M_S'L'M_L' >$$
$$= \bar{\lambda}_{3d}\sum_{\mu}(-1)^{\mu} < d^n\alpha SM_SLM_L|T^{11}_{\bar{\mu}\mu}|d^n\alpha'S'M_S'L'M_L' >$$

$$I = \bar{\lambda}_{3d}\sum_{\mu}(-1)^{\mu}(-1)^{S-M_S+L-M_L}\begin{pmatrix} S & 1 & S' \\ \bar{M}_S & \bar{\mu} & M_S' \end{pmatrix}\begin{pmatrix} L & 1 & L' \\ \bar{M}_L & \mu & M_L' \end{pmatrix}(d^n\alpha SL\|T^{11}\|d^n\alpha'S'L')$$

$$= \bar{\lambda}_{3d}\sqrt{30}\,(d^n\alpha SL\|V^{11}\|d^n\alpha'S'L')(-1)^{S-M_S+L-M_L}\sum_{\mu}(-1)^{\mu}\begin{pmatrix} S & 1 & S' \\ \bar{M}_S & \bar{\mu} & M_S' \end{pmatrix}\begin{pmatrix} L & 1 & L' \\ \bar{M}_L & \mu & M_L' \end{pmatrix}$$

(2.40')

using Eq. (2.39) for $(d^n\alpha SL\|T^{11}\|d^n\alpha'S'L')$.

Both (2.40) and (2.40') show that spin-orbit interaction depends on one parameter $\bar{\lambda}_{3d}$ only.

2.6 MATRIX ELEMENT OF THE SPIN-SPIN INTERACTION

$$H^{ij}_{S.S.} = -a^2 r_{ij}^{-5} \, [3(\underline{s}_i \cdot \underline{r}_{ij})(\underline{s}_j \cdot \underline{r}_{ij}) - (\underline{s}_i \cdot \underline{s}_j)\, r_{ij}^2] \quad (2.41)$$

where $a^2 = e/mc$, can be converted into a standard form using tensor product analogous to example given in Eq. (1.17)

$$H^{ij}_{S.S.} = -3 \sum_{\mu} (-1)^{\mu} \{\underline{S}_i \times \underline{S}_j\}^{(2)}_{\mu} \{\underline{R} \times \underline{R}\}^{(2)}_{\bar{\mu}} \quad (2.42)$$

where

$$\underline{R} = a r_{ij}^{-\frac{5}{2}} \underline{r}_{ij}$$

Thus

$$H_{S.S.} = \sum_{i>j}^{n} U^{(2)}(ij) \cdot T^{(2)}(ij)$$

$$= \sum_{i>j}^{n} (-1)^{\mu} \, t^{22}_{\bar{\mu}\,\mu}\,(ij)$$

which is the scalar product of two second rank tensors each of which contains two indices ij. This is the form we discussed in Section 2.2 in which we derived the recursion formula.

First from Eq. (1.51), we have

$$< d^n \alpha SLJM | H_{S.S.} | d^n \alpha' S'L'J'M' >$$

$$= \delta_{JJ'} \delta_{MM'} (-1)^{L+S'+J} \begin{Bmatrix} S & L & J \\ L' & S' & 2 \end{Bmatrix} (d^n \alpha SL \| T^{22}_n (ij) \| d^n \alpha' S'L') \quad . \quad (1.51)$$

The J dependence is again contained in the 6-j symbol. For the diagonal element, we have for the J dependence

$$(-1)^{L+S+J} \begin{Bmatrix} S & L & J \\ L & S & 2 \end{Bmatrix} = \begin{Bmatrix} \frac{(2S-2)!(2L-2)!}{(2S+3)!(2L+3)!} \end{Bmatrix}^{1/2} 2\,[3K(K+1) - 4L(L+1)S(S+1)]$$

where $K = J(J+1) - L(L+1) - S(S+1)$.

The reduced matrix element in Eq. (1.51) can be evaluated by the recursion formula (2.19):

$$(d^n\alpha SL\|T_n^{22}\|d^n\alpha' S'L') = (-1)^{L+S-\frac{1}{2}} \frac{n}{n-2} [(2S+1)(2S'+1)(2L+1)(2L'+1)]^{1/2} \times$$

$$\sum_{\substack{\alpha_1 S_1 L_1 \\ \alpha_2 S_2 L_2}} (-1)^{L_2+S_2} a(d^n\alpha SL;\alpha_1 S_1 L_1) a(d^n\alpha' S'L';\alpha_2 S_2 L_2)(d^{n-1}\alpha_1 S_1 L_1\|T_{n-1}^{22}\|d^{n-1}\alpha_2 S_2 L_2) \times W(S_1 S S_2 S';\tfrac{1}{2}2) W(L_1 L L_2 L';22) \qquad (2.19)$$

The matrix elements of d^2 configuration was calculated by Marvin. He obtained for the non-vanishing elements in d the following:

$$^3F_3\ ,\ ^3F_3 = -\ 6M_o + 228\ M_2$$

$$^3P_1\ ,\ ^3P_1 = 14\ M_o + 168\ M_2$$

$$^3F_2\ ,\ ^3P_2 = \left(\frac{14}{25}\right)^{1/2} (24\ M_o - 312\ M_2)$$

where

$$M_o = M^o(ab) = \frac{C\hbar^2}{4} \int_0^\infty\int_0^\infty \frac{1}{r_>^3} R_1^2(a) R_2^2(b) dr_1 dr_2$$

$$M_2 = M^2(ab) = \frac{C\hbar^2}{4} \int_0^\infty\int_0^\infty \frac{r_<^2}{r_>^5} R_1^2(a) R_2^2(b) dr_1 dr_2 \quad .$$

Starting from these values, $(d^2\alpha SL\|T_2^{22}(ij)\|d^2\alpha' S'L')$ can be found. Then the recursion formula (2,19) is used to get reduced matrix elements for all d^n configurations. This work was done by Trees (Trees, 1951). He found that non-vanishing matrix elements exist only between states with the same seniority number, and the values of the $(d^n\alpha SL\|T_n^{22}\|d^n\alpha' S'L')$ are fully defined if $\alpha = \nu$, S, L are given, i.e.

$$(d^n\nu SL\|T_n^{22}\|d^n\nu' S'L') = \delta_{\nu\nu'}(d^\nu \nu SL\|T_n^{22}\|d^\nu \nu S'L') \quad .$$

For the calculations of 210 elements for all ten configurations in d^n one needs only to evaluate 48 $(d^\nu \nu SL\|T_n^{22}\|d^\nu \nu S'L')$ due to above relation. These 48 elements are tabulated in Trees' paper (1951).

2.7 MATRIX ELEMENTS OF NUCLEAR-ELECTRON MAGNETIC INTERACTION (Trees, 1953)

The nuclear-electron magnetic interactions contain three terms: $H_{I,\ell}$, $H_{I,S}$, $H'_{I,S}$ i.e.

$$H_{h.f.} = H_{I,\ell} + H_{I.S.} = \sum_{i=1}^{n} a_\ell \underline{I}\cdot\underline{\ell}_i + \sum_{i=1}^{n} -a_\ell \underline{I}\cdot\left\{\underline{S}_i - \frac{3\underline{r}_i(\underline{r}_i\cdot\underline{S}_i)}{r_i^2}\right\} ; \quad \ell \neq 0$$

$$H_{h.f.} = H'_{I,S} = \sum_{i=1}^{n'} a_S \underline{I}\cdot\underline{S}_i, \quad (n' = \text{no. of unpaired S-electrons}); \quad \ell = 0$$

where

$$a_\ell = R\alpha^2 a_0^3 \left(\frac{m_e}{m_p}\right) < \frac{1}{r_\ell^3} \, g_I$$

$$a_S = \frac{8\pi}{3} R\alpha^2 a_0^2 \left(\frac{m_e}{m_p}\right)|\psi(0)|^2 g_I \quad .$$

As we have seen in Section 1.2, B,

$$\left\{\underline{S}_i - \frac{3\underline{r}_i(\underline{r}_i\ \underline{S}_i)}{r_i^2}\right\} = \sqrt{10}\ [\underline{S}_i x C_i^{(2)}]^{(1)} = \underline{X}_i^{(1)}$$

all three terms $H_{I,\ell}$, $H_{I,S}$, $H'_{I,S}$ have the same form

$$\sum_i \underline{I}\cdot\underline{V}_i$$

which is a scalar product of two first rank tensors. The matrix element of it in representation $|d^n\alpha_e J,\alpha_I I, FM_F>$ is given by Eq. (1.48).

$$< d^n\alpha_e J,\alpha_I I,FM_F|\underline{I}\cdot\sum_i \underline{V}_i|d^n\alpha'_e J',\alpha_I I,F'M'_F >$$

$$= \delta_{FF'}\delta_{M_F M'_F}(-1)^{F+I+J'}\begin{Bmatrix} J & I & F\\ I & J' & 1\end{Bmatrix}(\alpha_I I\|\underline{I}\|\alpha_I I)(d^n\alpha_e J\|\sum_i V_i\|d^n\alpha'_e J')$$

$$= \delta_{FF'}\delta_{M_F M'_F}\ (-1)^{F+I+J'}\sqrt{I(I+1)(2I+1)}\begin{Bmatrix} J & I & F\\ I & J' & 1\end{Bmatrix}\ (d^n\alpha_e J\|\sum_i V_i\|d^n\alpha'_e J') \,. \quad (2.43)$$

Consider first the diagonal element ($J = J'$). The F dependence of the first order energy is contained in the factor

$$(-1)^{F+I+J}\begin{Bmatrix} J & I & F \\ I & J & 1 \end{Bmatrix} = \frac{F(F+1) - J(J+1) - I(I+1)}{2[I(I+1)(2I+1)J(J+1)(2J+1)]^{1/2}} \cdot \quad \text{[Appendix C (Eq. C.15)]}$$

For the evaluation of the reduced matrix $(d^n\alpha_e J\| \sum_i \underline{V}_i \|d^n\alpha_e' J')$ we have the following three cases:

A.
$$H_{I,\ell} = \underline{I} \cdot \sum_i a_\ell \underline{\ell}_i = \underline{I} \cdot \sum_i \underline{V}_i$$

$$\sum_i \underline{V}_i = a_\ell \sum_i \ell_i = a_\ell (\ell\|\underline{\ell}\|\ell) U^{(1)}(2)$$

$$= a_\ell \sqrt{\ell(\ell+1)(2\ell+1)}\, U^{(1)}(2)$$

$$= a_\ell \sqrt{30}\, U^{(1)}(2)$$

Therefore by Eq. (1.37)

$$(d^n\alpha_e J\| \sum_i V_i \|d^n\alpha_e' J') = a_\ell\sqrt{30}\, (d^n\alpha SLJ\|U^{(1)}(2)\|d^n\alpha' S' L' J')$$

$$= a_\ell \sqrt{30}\, (-1)^{J+S+L'+1}\sqrt{(2J+1)(2J'+1)}\begin{Bmatrix} J & L & S \\ L' & J' & 1 \end{Bmatrix}(d^n\alpha SL\|U^{(1)}(2)\|d^n\alpha' S' L')$$

The reduced matrix element of the unit operator $U^K(2)$ can be evaluated easily by observing that

$$[\ell(\ell+1)(2\ell+1)]^{-1/2} L_\mu \quad (\mu = -1,0,1)$$

is a unit operator, for which

$$< d^n\alpha S M_S L M_L \,|\, [\ell(\ell+1)(2\ell+1)]^{-1/2} L_0 \,|d^n\alpha' S' M_S L' M_L >$$

$$= \delta_{\alpha\alpha'}\delta_{SS'}\delta_{LL'} M_L [\ell(\ell+1)(2\ell+1)]^{-1/2}$$

$$= (-1)^{L-M_L}\begin{pmatrix} L & 1 & L' \\ \overline{M}_L & 0 & M_L \end{pmatrix}(d^n\alpha SL\|U^{(1)}(2)\|d^n\alpha' S' L') \quad . \qquad (2.44)$$

Since

$$(-1)^{L-M_L}\begin{pmatrix} L & 1 & L \\ \overline{M}_L & 0 & M_L \end{pmatrix} = \frac{M_L}{\sqrt{L(L+1)(2L+1)}} \quad \text{(Appendix C-7)} \qquad (2.45)$$

Substituting Eq. (2.45) into Eq. (2.44), we obtain

$$(d^n\alpha SL\|U^{(1)}(2)\|d^n\alpha'S'L') = \delta_{\alpha\alpha'}\delta_{SS'}\delta_{LL'}\sqrt{\frac{L(L+1)(2L+1)}{\ell(\ell+1)(2\ell+1)}}$$

$$= \delta_{\alpha\alpha'}\delta_{SS'}\delta_{LL'}\sqrt{\frac{L(L+1)(2L+1)}{30}} \qquad (2.46)$$

B. $$H'_{I,S} = \underline{I}\cdot\sum a_S\underline{S}_i = \underline{I}\cdot\sum_i \underline{V}_i$$

$$\sum_i \underline{V}_i = a_S\sum \underline{S}_i = a_S(\tfrac{1}{2}\|\underline{S}\|\tfrac{1}{2})U^{(1)}(1) = a_S\sqrt{\tfrac{3}{2}}\,U^{(1)}(1)$$

Therefore

$$(d^n\alpha_e J\|\sum_i \underline{V}_i\|d^n\alpha_e'J')$$

$$= a_S\sqrt{\tfrac{3}{2}}(d^n\alpha_e J\|U^{(1)}(1)\|d^n\alpha_e'J')$$

$$= a_S\sqrt{\tfrac{3}{2}}(d^n\alpha SLJ\|U^{(1)}(1)\|d^n\alpha'S'L'J') \qquad \text{by Eq. (1.39)}$$

$$= a_S\sqrt{\tfrac{3}{2}}(-1)^{J'+S+L+1}\sqrt{(2J+1)(2J'+1)}\begin{Bmatrix} S & J & L \\ J' & S' & 1 \end{Bmatrix}(d^n\alpha SL\|U^{(1)}(1)\|d^n\alpha'S'L') \qquad (2.47)$$

again, analogous to Eq. (2.46) we have

$$(d^n\alpha SL\|U^{(1)}(1)\|d^n\alpha'S'L') = \delta_{\alpha\alpha'}\delta_{SS'}\delta_{LL'}\sqrt{\frac{S(S+1)(2S+1)}{\frac{1}{2}(\frac{1}{2}+1)(1+1)}} \qquad (2.48)$$

Substituting Eq. (2.48) into Eq. (2.47), we have finally:

$$(d^n\alpha_e J\|\sum_i \underline{V}_i\|d^n\alpha_e'J')$$

$$= \delta_{\alpha\alpha'}\delta_{SS'}\delta_{LL'}a_S(-1)^{J'+S+L+1}[(2J+1)(2J'+1)(2S+1)(S+1)S]\begin{Bmatrix} S & J & L \\ J' & S & 1 \end{Bmatrix} \quad (2.49$$

C. $$H_{I,S} = I \cdot \sum_i -a_\ell \left\{ \underline{S}_i - \frac{3\underline{r}_i(\underline{r}_i \cdot \underline{S}_i)}{r_j^2} \right\} = \underline{I} \cdot \sum_i \underline{V}_i$$

$$\therefore \quad \sum_i \underline{V}_i = -\sqrt{10}\, a_\ell \sum_i [\underline{S}_i \times C_i^{(2)}]^{(1)}$$

$$(d^n\alpha_e J \| \sum_i \underline{V}_i \| d^n\alpha_e' J')$$

$$= -\sqrt{10}\, a_\ell (d^n\alpha SLJ \| \sum_i [\underline{S}_i \times C_i^{(2)}]^{(1)} \| d^n\alpha' S'L'J')$$

$$= -\sqrt{10}\, a_\ell \sqrt{(2+1)(2J+1)(2J'+1)} \begin{Bmatrix} S & L & J \\ S' & L' & J' \\ 1 & 2 & 1 \end{Bmatrix} (d^n\alpha SL \| \sum_i S_i C_i^{(2)} \| d^n\alpha' S'L')$$

by Eq. (1.42)

$$\sum_i S_i C_i^{(2)} = (\ell \| C^{(2)} \| \ell) V^{12}$$

knowing
$$(\ell \| C^{(2)} \| \ell) = (-1)^\ell (2\ell+1) \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}$$

we have
$$(\ell \| C^{(2)} | \ell) = -\sqrt{\frac{\ell(\ell+1)(2\ell+1)}{(2\ell-1)(2\ell+3)}}$$

$$= -\sqrt{\frac{10}{7}} \qquad \text{for } \ell = 2$$

$$(d^n\alpha_e J \| \sum_i \underline{V}_i \| d^n\alpha_e' J')$$

$$= 10\sqrt{\frac{3}{7}} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} S & L & J \\ S' & L' & J' \\ 1 & 2 & 1 \end{Bmatrix} (d^n\alpha SL \| V^{12} \| d^n\alpha' S'L') \qquad (2.50)$$

where the last factor is given by Eq. (2.13), and the numerical values for d^2 and d^5 are given in Appendix D.

2.8 MATRIX ELEMENTS OF NUCLEAR-ELECTRON QUADRUPOLE INTERACTION (Trees, 1953)

The electrostatic interaction between a nucleus with z protons and n equivalent electrons is given by

$$H_{I,e} = \sum_{i=1}^{n} \sum_{p=1}^{z} \frac{e_i e_p}{|\underline{r}_i - \underline{r}_p|}$$

$$= \sum_{i,p,\ell} e_i e_p \frac{r_p^{\ell}}{r_i^{\ell+1}} P_\ell(\cos \theta_{ip}) \quad .$$

In this expansion, $\ell = 0$ term is the electrostatic interaction between point changes, $\ell = 1$ term the dipole interaction and $\ell = 2$ term the quadrupole interaction. Thus

$$H_Q = \sum_{ip} e_i e_p \frac{r^2_p}{r_i^3} P_2(\cos \theta_{ip})$$

$$= \sum_{ip} e_i e_p \frac{r^2_p}{r_i^3} C^{(2)}(\theta_i \phi_i) \circ C^{(2)}(\theta_p \phi_p) \quad \text{by Eq. (1.18)}$$

$$= V^{(2)} \cdot Q^{(2)}$$

where

$$V^{(2)} = \sum_i \frac{e_i}{r_i^3} C^{(2)}(\theta_i \phi_i)$$

$$Q^{(2)} = \sum_p e_p r_p^2 C^{(2)}(\theta_p \phi_p) \quad .$$

We are interested in the matrix element in the representation $|\alpha_e SLJ, \alpha_p I, FM_F>$, i.e.

$$< \alpha_e J, \alpha_p I, FM_F | H_Q | \alpha_e' J', \alpha_p I, F'M_F' >$$

$$= < \alpha_e J, \alpha_p I, FM_F | V^{(2)} \cdot Q^{(2)} | \alpha_e' J', \alpha_p I, F'M_F' >$$

$$= \delta_{FF'} \delta_{M_F M_F'} (-1)^{F+I+J'} \begin{Bmatrix} J & I & F \\ I & J' & 2 \end{Bmatrix} (\alpha_e J \| V^{(2)} \| \alpha_e' J')(\alpha_p I \| Q^{(2)} \| \alpha_p I) \quad , \tag{2.51}$$

using Eq. (1.48) for the matrix element of scalar product of two commuting tensors.

For the diagonal element ($J = J'$), the F dependence of the matrix element is contained in the factor

$$(-1)^{F+I+J}\begin{Bmatrix} J & I & F \\ I & J & 2 \end{Bmatrix} = \frac{3K(K-1) - 4J(J+1)I(I+1)}{2[(2J-1)J(J+1)(2J+1)(2J+3)(2I-1)I(I+1)(2I+1)(2I+3)]^{1/2}}$$

where

$$K = J(J+1) + I(I+1) - F(F+1) \quad .$$

The reduced matrix elements in Eq. (2.51) can be evaluated as follows:

A. $(\alpha_e J \| V^{(2)} \| \alpha_e' J')$

$$= e(d^n \alpha SLJ \| \sum_i r_i^{-3} C_i^{(2)} \| d^n \alpha' S' L' J')$$

$$= e < \frac{1}{r_d^3} > (\alpha SLJ \| \sum_i C_i^{(2)} \| \alpha' S' L' J')$$

$$= e < \frac{1}{r_d^3} > (\ell \| C^{(2)} \| \ell)(d^n \alpha SLJ \| U^{(2)}(2) \| d^n \alpha' S' L' J')$$

$$= -e < \frac{1}{r_d^3} > \sqrt{\frac{\ell(\ell+1)(2\ell+1)}{(2\ell-1)(2\ell+3)}} (-1)^{J+S+L'+2} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & L & S \\ L' & J' & 2 \end{Bmatrix}$$

$$(d^n \alpha SL \| U^{(2)} \| d^n \alpha' S' L') \qquad \text{by Eq. (1.37)}$$

$$= -\sqrt{\frac{10}{7}}\, e < \frac{1}{r_d^3} > (-1)^{J+S+L'} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & L & S \\ L' & J' & 2 \end{Bmatrix} (d^n \alpha SL \| U^{(2)}(2) \| d^n \alpha' S' L') \qquad (2.52)$$

B. $(\alpha_p I \| Q^{(2)} \| \alpha_p I)$

Since

$$Q^{(2)} = e \sum_p r_p^2\, C^{(2)}(\theta_p \phi_p)$$

$$Q_0^{(2)} = e \sum_p r_p^2\, C_0^{(2)}(\theta_p \phi_p)$$

$$= \frac{e}{2} \sum_p (3z_p^2 - r_p^2)$$

consider the matrix element of $Q_0^{(2)}$ between states $|\alpha_p I M_I >$ with $M_I = I$:

$$< \alpha_p II | Q_0^{(2)} | \alpha_p II > \;=\; \frac{e}{2} < \alpha_p II | \sum_p (3z_p^2 - r_p^2) | \alpha_p II >$$

$$= \begin{pmatrix} I & 2 & I \\ \bar{I} & 0 & I \end{pmatrix} (\alpha_p I \| Q^{(2)} \| \alpha_p I) \qquad (2.53)$$

where

$$\begin{pmatrix} I & 2 & I \\ \bar{I} & 0 & I \end{pmatrix} = \begin{pmatrix} I & I & 2 \\ I & \bar{I} & 0 \end{pmatrix} = \sqrt{\frac{I(2I-1)}{(2I+3)(2I+1)(I+1)}} \qquad \text{(Appendix III-7'')}$$

Define

$$Q = < \alpha_p II | \sum_p (3z_p^2 - r_p^2) | \alpha_p II > \;.$$

Then Eq. (2.53) becomes

$$\frac{e}{2} Q = \sqrt{\frac{I(2I-1)}{(2I+3)(2I+1)(I+1)}} (\alpha_p I \| Q^{(2)} \| \alpha_p I) \;.$$

Therefore

$$(\alpha_p I \| Q^{(2)} \| \alpha_p I) = \frac{eQ}{2} \sqrt{\frac{(2I+3)(2I+1)(I+1)}{I(2I-1)}} \;. \qquad (2.54)$$

Equations (2.51), (2.52), and (2.54) combine to give finally

$$< d^n d_e J, \alpha_p I, F M_F | H_Q | d^n \alpha_e' J', \alpha_p I, F' M_F' >$$

$$= \delta_{FF'} \delta_{M_F M_F'} \delta_{SS'} (-1)^{F+I+J+J'+S+L'+1} \frac{e^2 Q}{2} \sqrt{\frac{10}{7}} < \frac{1}{r^3}>_d \sqrt{\frac{(2J+1)(2J'+1)(2I+3)(2I+1)(I+1)}{I(2I-1)}}$$

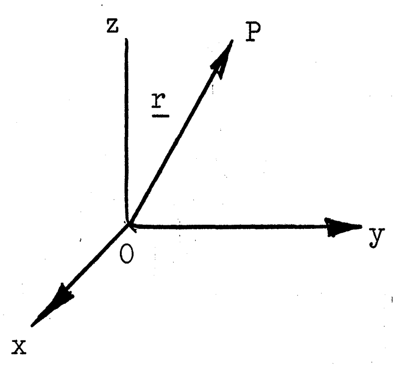
$$\times \begin{Bmatrix} J & I & F \\ I & J' & 2 \end{Bmatrix} \begin{Bmatrix} J & L & S \\ L' & J' & 2 \end{Bmatrix} (d^n\, SL \| U^{(2)}(2) \| d^n \alpha' SL') \qquad (2.55)$$

where the last factor is given in Eq. (2.15) and its numerical values tabulated in Appendix D.

APPENDIX A

ROTATION OF COORDINATE SYSTEM AND ROTATION OF FIELD

Consider a point P in space which is described by a coordinate (x,y,z) or



or a vector $\underline{r}$ in a coordinate system S. If we perform a rotation $R(\alpha\beta\gamma)$ of the coordinate system, where $(\alpha\beta\gamma)$ denote the Euler angles, then in the new coordinate system S" the point P is described by a coordinate (x",y",z",) or a vector $\underline{r}''$ which is connected to the original unprimed one by a rotation matrix $R_{\alpha\beta\gamma}$:

$$\underline{r}'' = R_{\alpha\beta\gamma}\underline{r} \tag{A.1}$$

where $R_{\alpha\beta\gamma}$ is a product of three successive rotation matrices about (a) z-axis by γ, (b) y-axis by β, and (c) z-axis by α

$$\begin{aligned} R_{\alpha\beta\gamma} &= D_{z''}(\alpha)D_{y'}(\beta)D_z(\gamma) \\ &= \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned} \tag{A.2}$$

It can be shown also that the same $R_{\alpha\beta\gamma}$ would be obtained if one rotates, instead of the coordinate system, the point P successively about (a) the z-axis by α, (b) the y-axis by β, and (c) the z-axis by γ (Edmonds, 1.3), i.e.

$$R_{\alpha\beta\gamma} = D_z(\gamma)D_y(\beta)D_z(\alpha) \quad . \tag{A.3}$$

Therefore, we may consider $\underline{r}''$ as either the same vector $\overline{op}$ expressed in the new coordinate system S" or a new rotated vector $\overline{OQ}$ in the old coordinate system S, and in each case (x",y",z") and (x,y,z) are connected by $R_{\alpha\beta\gamma}$ as in Eq. (A.1).

Next, consider a scalar field $\psi(P)$ for which there is a definite value for each space point P. Suppose in coordinate system S the scalar field is expressed by a function $\psi(\underline{r})$, then in the rotated coordinate system the field is in general expressed by a different function $\psi'(\underline{r}')$. Suppose that $\underline{r}$ and $\underline{r}'$ correspond to the same point P in space, that is, they are connected by a rotation matrix $R_{\alpha\beta\gamma}$ as in Eq. (A.1), i.e.

$$\underline{r}' = R_{\alpha\beta\gamma}\underline{r} \quad . \tag{A.1}$$

Then by the definition of a scalar field, one must have

$$\psi'(\underline{r}') = \psi(\underline{r}) \tag{A.4}$$

Equation (A.1) together with Eq. (A.4), then, expresses the transformation law of a scalar field under coordinate rotations.

However, we may consider Eq. (A.1) and (A.4) from a different point of view. The difference in functional form of ψ' and ψ allow us to imagine that associated with the rotation of coordinate system $R(\alpha\beta\gamma)$ one has an operator P_R which, upon acting on the function ψ, converts it into ψ', i.e. $P_R\psi = \psi'$. Then Eq. (A.4) can be written as

$$P_R\psi(\underline{r}') = \psi(\underline{r}) \tag{A.5}$$

or

$$P_R\psi(R_{\alpha\beta\gamma}\underline{r}) = \psi(\underline{r})$$

or

$$P_R\psi(\underline{r}) = \psi(R^{-1}_{\alpha\beta\gamma}\underline{r}) \quad . \tag{A.5}$$

Equation (A.5) effectively defines the operational effect of P_R on $\psi(\underline{r})$, e.g.

replace $\underline{r}$ by $R^{-1}_{\alpha\beta\gamma}\underline{r}$. It is shown in Wigner, p. 106, that operator P_R is unitary and linear, and further, for two successive rotations, R and S, one has

$$P_{SR} = P_S \cdot P_R \qquad . \qquad (A.6)$$

Now, as we have mentioned earlier, Eq. (A.6) can be interpreted equivalently as rotating the field point P about the fixed axes of the coordinate system S in a reverse order. This interpretation, together with Eq. (A.5), allows us to picture the process as "rotation of the field." In this picture, (A.1) states that $R(\alpha\beta\gamma)$ we rotate the point P(x,y,z) to a point Q(x',y',z') in the same coordinate system S and Eq. (A.5) says that then the value of the rotated function $P_R\psi$ evaluated at the new point Q is equal to the value of original function ψ evaluated at old point P.

Next, suppose we have a spinor field $\psi(\underline{r})\chi^{1/2}_{\tau}$ (τ = -1/2, 1/2). Then associated with every rotation $R(\alpha\beta\gamma)$ there is a unitary, linear operator O_R such that the transformation law is given by:

$$O_R\psi(\underline{r})\chi^{1/2}_{\tau} = \sum_{\tau'} D^{(1/2)}_{\tau'\tau}(R)\psi(R^{-1}_{\alpha\beta\gamma}\underline{r})\chi^{1/2}_{\tau'} \qquad . \qquad (A.7)$$

Careful inspection of Eq. (A.7) reveals that O_R can be decomposed into a product of two operators P_R and Q_R such that each of them operate on space part and spin part of the spinor field, respectively, e.g.

$$O_R = P_R Q_R \qquad (A.8)$$

$$P_R\psi(\underline{r})\chi^{1/2}_{\tau} = \psi(R^{-1}_{\alpha\beta\gamma}\underline{r})\chi^{1/2}_{\tau} \qquad (A.9)$$

$$Q_R\psi(\underline{r})\chi^{1/2}_{\tau} = \sum_{\tau'} D^{(1/2)}_{\tau'\tau}(R)\psi(\underline{r})\chi^{1/2}_{\tau'} \qquad . \qquad (A.10)$$

Wigner (p. 223) showed that both P_R and Q_R are linear, unitary and further, they commute, i.e.

$$P_R Q_R = Q_R P_R \quad . \qquad (A.11)$$

This separation of O_R into P_R and Q_R is possible only when the wave function is separable into product of space part and spin part which is the basic assumption of the Pauli spin theory.

In atomic problems, one is interested in a spinor field of the type

$$\psi^n_{\ell m}(\underline{r})\chi^{1/2}_\tau$$

the transformation properties of which is given by

$$O_R\psi^n_{\ell m}(\underline{r})\chi^{1/2}_\tau = P_R\psi^n_{\ell m}(\underline{r})Q_R\chi^{1/2}_\tau$$

$$= \sum_{m'} D^{(\ell)}_{m'm}(R)\psi^n_{\ell m'}(\underline{r}) \sum_{\tau'} D^{(1/2)}_{\tau'\tau}(R)\chi^{1/2}_{\tau'}$$

$$= \sum_{m',\tau'} D^{(\ell)}_{m'm}(R)D^{(1/2)}_{\tau'\tau}(R)\psi^n_{\ell m'}(\underline{r})\chi^{1/2}_{\tau'} \qquad (A.12)$$

that is, the one-electron eigenfunctions transform irreducibly under P_R and Q_R separately, but not irreducibly under O_R. One can take a linear combination of these one-electron functions (with same n and ℓ) to get an eigenfunction of L^2, L_z, S^2, S_z, $|\alpha S M_S L M_L>$ which transforms irreducibly under P_R and Q_R, respectively, i.e.

$$P_R|\alpha S M_S L M_L> = \sum_{M_L'} D^{(L)}_{M_L' M_L}(R)|\alpha S M_S L M_L'> \qquad (A.13)$$

$$P_R|\alpha S M_S L M_L> = \sum_{M_S'} D^{(S)}_{M_S' M_S}(R)|\alpha S M_S' L M_L> \quad . \qquad (A.14)$$

It is easily seen that $|\alpha S M_S L M_L>$ does not transform irreducibly under O_R

but according to the product representation $D^{(L)}(R) \cdot D^{(S)}(R)$. However, one can form linear combinations of $|\alpha S M_S L M_L>$ by the help of the V-C coefficient and obtain eigenfunctions of L^2, S^2, J^2, J_z which rotate irreducibly under O_R, i.e.

$$|\alpha SLJM> = \sum_{M_S M_L} |\alpha S M_S L M_L> < S M_S L M_L | JM >$$

$$O_R |\alpha SLJM> = \sum_{M'} D^{(J)}_{M'M}(R) |\alpha SLJM'> \qquad (A.15)$$

Lastly, for an operator T^k_q which acts on the field $\psi_T(\underline{r})$, by requiring the invariance of the sealar product under the coordinate rotations we have

$$(\psi, T^k_q \phi) = (O_R\psi, O_R T^k_q \phi)$$
$$= (O_R\psi, O_R T^k_q O^{-1}_R O_R\phi).$$

But we know under rotations

$$\psi \to O_R\psi \; ; \; \phi \to O_R\phi \; .$$

Therefore, under the rotation, the operator T^k_q must transform according to

$$T^k_q \to O_R T^k_q O_R^{-1} .$$

APPENDIX B

PROOF OF THE WIGNER-ECKART THEOREM

The validity of this theorem depends essentially only on the rotational properties of the wave function $|\alpha JM>$ and of the operator T^k_q.

Write $\psi^{\alpha J}_M = |\alpha JM>$ in the following. One assumes

$$O_R \psi^{\alpha J}_M \equiv \sum_{M'} \psi^{\alpha J}_{M'} D^{(J)}_{M'M}(R) \tag{B.1}$$

and

$$O_R T^k_q O_R^{-1} = \sum_{q'} T^k_{q'} D^{(k)}_{q'q}(R) \quad . \tag{B.2}$$

Since $< \alpha JM|T^k_q|\alpha'J'M' > \equiv (\Psi^{\alpha J}_M, T^k_q \Psi^{\alpha'J'}_{M'})$ is just a number, it is invariant under rotation, i.e.

$$I \equiv (\Psi^{\alpha J}_M, T^k_q \Psi^{\alpha'J'}_{M'})$$

$$= (O_R\Psi^{\alpha J}_M, O_R T^k_q \Psi^{\alpha'J'}_{M'})$$

$$= (O_R\Psi^{\alpha J}_M, O_R T^k_q O_R^{-1} O_R \Psi^{\alpha'J'}_{M'}$$

$$= \sum_{m,q'm'} D^{*(J)}_{mM}(R) D^{(k)}_{q'q}(R) D^{(J')}_{m'M'} < \alpha Jm|T^k_{q'}|\alpha'J'm' > \quad \text{by (II-1) and (II-2)}$$

The product of two representations can be decomposed into sum of irreducible representations by the V-C coefficient (Edmonds, 4.3.1), i.e.

$$D^{(k)}_{q'q}(R) D^{(J')}_{m'M'}(R) = \sum_{N=|k-J'|}^{k+J'} < kq'J'm'|N,q'+m' >< N,q+M'|kqJ'M' > D_{q'+m',q+M'} \quad . \tag{B.3}$$

Thus

$$I = \sum_N \sum_{mq'm'} < kq'J'm'|N,q'+m' > < N,q+M'|kqJ'M' >$$

$$< \alpha Jm|T^k_{q'}|\alpha'J'm' > D^{*(J)}_{mM} D^{(N)}_{q'+m',q+M'} \quad . \qquad \text{(B.4)}$$

Integrate both sides of Eq. (B.4) with respect to all rotations $R(\alpha\beta\gamma)$, i.e.

$$\int dR \equiv \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta d\beta \int_0^{2\pi} d\gamma \qquad (\alpha,\beta,\gamma \text{ Euler angles}) \quad .$$

We have

$$\int IdR = \sum_N \sum_{mq'm'} < kq'J'm'|N,q'+m' > < N,q+M'|kqJ'M' > < \alpha JM|T^k_{q'}|\alpha'J'M' >$$

$$\times \int D^{*(J)}_{mM} D^{(N)}_{q'+m',q+M'} dR \quad . \qquad \text{(B.5)}$$

But from the orthogonality properties of $D^{(J)}$'s, we have

$$\int D^{*(J)}_{mM} D^{(N)}_{q'+m',q+M'} dR = \delta_{m,q'+m'} \delta_{M,q+M'} \delta_{J,N} \frac{8\pi^2}{2J+1} \qquad \text{(B.6)}$$

and

$$\int IdR = 8\pi^2 I \quad . \qquad \text{(B.7)}$$

From Eq. (B.5), (B.6), and (B.7), we obtain

$$I = \sum_N \sum_{mq'm'} < kq'J'm'|N,q'+m' > < N,q+M'|kqJ'M' > < \alpha Jm|T^k_{q'}|\alpha'J'm' >$$

$$\times \frac{\delta_{JN}\delta_{m,q'+m'}\delta_{M,q+M'}}{2J+1}$$

$$= \sum_{q'm'} < kq'J'm'|Jq'+M' > < JM|kqJ'M' > < \alpha Jq'+m'|T^k_{q'}|\alpha'J'm' > \frac{\delta_{M,q+M'}}{2J+1}$$

$$= \frac{< J'M'kq|JM >}{(2J+1)^{1/2}} \sum_{q'm'} \frac{1}{(2J+1)^{1/2}} < J'm'kq'|Jq'+m' > < \alpha Jq'+m'|T^k_{q'}|\alpha'J'm' >$$

$$= < J'M'kq|JM > \frac{(\alpha J\|T^k\|\alpha'J')}{(2J+1)^{1/2}}$$

where

$$(\alpha J\|T^k\|\alpha' J') = \frac{1}{(2J+1)^{1/2}} \sum_{q'm'} < J'm'k'q'|J,q'+m' > < \alpha J q'+m'|T^k_{q'}|\alpha' J'm' >$$

is independent of M, M' and q.

It may be remarked that this theorem holds whenever T^k_q rotates like Eq. (B.2). Therefore, even if T^k_q is a one-electron operator and $|\alpha JM>$ is a many-electron wave function, the theorem is also true.

APPENDIX C

DEFINITIONS AND PROPERTIES OF 3-j, 6-j, and 9-j SYMBOLS

1. 3-j SYMBOL

a. Definition:

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} = \frac{(-1)^{j_1-j_2-m}}{\sqrt{2j+1}} < j_1m_1j_2m_2|j\bar{m} > \qquad (C.1)$$

b. Properties:

(1)
$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} = 0 \quad \text{unless} \quad \begin{matrix} \Delta(j_1j_2j) & & \\ m_1+m_2+m & = & 0 \\ j_1+j_2+j & = & \text{integer} \end{matrix} \qquad (C.2)$$

(2) Even permutations of columns leave the numerical value unchanged, i.e.

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \qquad (C.3)$$

Odd permutation is equivalent to multiplication by $(-1)^{j_1+j_2+j_3}$

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

(3) Simultaneous change of signs of m's multiplies the numerical value by $(-1)^{j_1+j_2+j_3}$ i.e.

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ \bar{m}_1 & \bar{m}_2 & \bar{m}_3 \end{pmatrix} \qquad (C.4)$$

(4) Orthogonality properties:

$$\sum_{j,m} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ m_1' & m_2' & m \end{pmatrix} = \delta_{m_1m_1'}\delta_{m_2m_2'} \qquad (C.5)$$

$$\sum_{m_1m_2} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m' \end{pmatrix} = \frac{\delta(j_1j_2j)}{2j+1} \delta_{jj'} \delta_{mm'} \qquad (C.6)$$

where $\delta(j_1j_2j) = 1$ if $\Delta(j_1j_2j)$ and zero otherwise.

(5) Specialized formulas:

$$\begin{pmatrix} j_1 & j_2 & 0 \\ m_1 & m_2 & 0 \end{pmatrix} = (-1)^{j_1-m_1}(2j_1+1)^{-1/2}\delta_{j_1j_2}\,\delta_{m_1\bar{m}_2} \qquad (C.7)$$

$$\begin{pmatrix} J & J & 1 \\ M & \bar{M} & 0 \end{pmatrix} = (-1)^{J-M} \frac{M}{\sqrt{J(J+1)(2J+1)}} \qquad (C.7')$$

$$\begin{pmatrix} J & J & 2 \\ M & \bar{M} & 0 \end{pmatrix} = (-1)^{J-M} \frac{3M^2 - J(J+1)}{[(2J+3)(J+1)(2J+1)J(2J-1)]^{1/2}} \qquad (C.7'')$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{-J/2} \left[\frac{(j_1+j_2-j_3)!(j_1+j_3-j_2)!(j_2+j_3-j_1)!}{(j_1+j_2+j_3+1)!}\right]^{1/2} \frac{(\frac{1}{2}J)!}{(\frac{1}{2}J-j_1)!(\frac{1}{2}J-j_2)!(\frac{1}{2}J-j_3)!}$$

if $j_1 + j_2 + j_3 = J$ = even

(C.8)

$= 0$ if $j_1 + j_2 + j_3 = J$ = odd

2. 6-j SYMBOL

a. Definition:

The 6-j symbol is defined in terms of the recoupling coefficient of three angular momenta, j_1, j_2, and j_3 and is in turn expressible as a sum of products of four V-C coefficients, i.e.

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{Bmatrix} = (-1)^{j_1+j_2+j_3+J} [(2j_{12}+1)(2j_{23}+1)]^{-1/2} \langle (j_1j_2)j_{12}, j_3, J | j_1, (j_2j_3)j_{23}, J \rangle$$

$$= (-1)^{j_1+j_2+j_3+J} [(2j_{12}+1)(2j_{23}+1)]^{-1/2} \times$$

$$\sum_{m_1m_2} \langle j_1m_1j_2m_2 | j_{12}m_1+m_2 \rangle \langle j_{12}m_1+m_2j_3M-m_1-m_2 | JM \rangle \times$$

$$\langle j_2m_2j_3M-m_1-m_2 | j_{23}M-m_1 \rangle \langle j_1m_1j_{23} M-m_1 | JM \rangle \qquad (C.9)$$

or in terms of 3-j symbol, a more symmetrical expression:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix} \frac{\delta_{j_3j_3'}\delta_{m_3m_3'}}{2j_3+1} = \sum_{\substack{M_1M_2M_3 \\ m_1m_2}} (-1)^{J_1+J_2+J_3+M_1+M_2+M_3} \begin{pmatrix} J_1 & J_2 & j_3 \\ M_1 & \bar{M}_2 & m_3 \end{pmatrix} \times \qquad (C.10)$$

$$\begin{pmatrix} J_2 & J_3 & j_1 \\ M_2 & \bar{M}_3 & m_1 \end{pmatrix} \begin{pmatrix} J_3 & J_1 & j_2 \\ M_3 & \bar{M}_1 & M_2 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix}$$

Relation to Racah coefficient:

6-j symbol is identical to the Racah coefficient within a phase factor:

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{Bmatrix} = (-1)^{j_1+j_2+J+j_3} W(j_1 j_2 J j_3; j_{12} j_{23}) \qquad (C.11)$$

b. Properties:

(1) Symmetry properties:

(a) 6-j symbol is invariant under any permutation of the columns.

(b) 6-j symbol is invariant against interchange of the upper and lower arguments in each of any two columns. For example:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix} = \begin{Bmatrix} j_1 & j_5 & j_6 \\ j_4 & j_2 & j_3 \end{Bmatrix}$$

(a) and (b) together consist of twenty-four operations which leave 6-j symbol invariant.

(c) $\begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix} = 0$ unless $\Delta(j_1 j_2 j_3)$, $\Delta(j_1 \ell_2 \ell_3)$, $\Delta(\ell_1 j_2 \ell_3)$, $\Delta(\ell_1 \ell_2 j_3)$

(2) Two important relations between 3-j and 6-j symbols.

(a)

$$(-1)^{j_2+J_2-m_1-M_1} \begin{pmatrix} j_1 & J_2 & J_3 \\ m_1 & M_2 & \bar{M}_3 \end{pmatrix} \begin{pmatrix} J_3 & j_2 & J_1 \\ M_3 & m_2 & M_1 \end{pmatrix} = \sum_{j_3} (2j_3+1) \begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix} \times \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & \bar{m}_3 \end{pmatrix} \begin{pmatrix} j_3 & J_2 & J_1 \\ m_3 & M_2 & \bar{M}_1 \end{pmatrix} \qquad (C.12)$$

(b)

$$\sum_{M_1 M_2 M_3} (-1)^{J_1+J_2+J_3+M_1+M_2+M_3} \begin{pmatrix} j_1 & J_2 & J_3 \\ m_1 & M_2 & \bar{M}_3 \end{pmatrix} \begin{pmatrix} J_1 & j_2 & J_3 \\ M_1 & m_2 & M_3 \end{pmatrix} \begin{pmatrix} J_1 & J_2 & j_3 \\ M_1 & \bar{M}_2 & m_3 \end{pmatrix}$$

$$= \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix} \qquad (C.13)$$

(3) Orthogonality property.

$$\sum_{j} (2j+1)(2j''+1) \begin{Bmatrix} j_1 & j_2 & j' \\ j_3 & j_4 & j \end{Bmatrix} \begin{Bmatrix} j_3 & j_2 & j \\ j_1 & j_4 & j'' \end{Bmatrix} = \delta_{j'j''} \qquad (C.14)$$

that is $\sqrt{(2j+1)(2j'+1)} \begin{Bmatrix} j_1 & j_2 & j' \\ j_3 & j_4 & j \end{Bmatrix}$ forms a real orthogonal matrix, with rows and columns rabelled by j and j' respectively.

(4) Two particular values of the 6-j symbol.

$$\begin{Bmatrix} J & S & L \\ 1 & L & S \end{Bmatrix} = (-1)^{J+S+L} \frac{J(J+1) - S(S+1) - L(L+1)}{2\,[S(S+1)(2S+1)L(L+1)(2L+1)]^{1/2}}$$

$$\begin{Bmatrix} J & S & L \\ 2 & L & S \end{Bmatrix} = (-1)^{J+S+L} \frac{3X(X-1) - 4S(S+1)L(L+1)}{2\,[S(S+1)(2S-1)(2S+1)(2S+3)L(L+1)(2L-1)(2L+1)(2L+3)]^{1/2}} \qquad (C.15)$$

$$\text{where} \quad X = S(S+1) + L(L+1) - J(J+1) \qquad (C.16)$$

3. 9-j SYMBOL

a. Definition:

The 9-j symbol is defined in terms of the recoupling coefficient of four angular momenta:

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} = [(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)]^{-1/2} \times$$

$$\langle (j_1j_2)j_{12},(j_3j_4)j_{34},j \,|\, (j_1j_3)j_{13},(j_2j_4)j_{24},j \rangle \qquad (C.17)$$

or in terms of 6-j symbols.

$$\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix} = \sum_{K} (-1)^{2K}(2K+1) \begin{Bmatrix} j_{11} & j_{21} & j_{31} \\ j_{32} & j_{33} & K \end{Bmatrix} \begin{Bmatrix} j_{12} & j_{22} & j_{32} \\ j_{21} & K & j_{23} \end{Bmatrix} \begin{Bmatrix} j_{13} & j_{23} & j_{33} \\ K & j_{11} & j_{12} \end{Bmatrix} \qquad (C.18)$$

or in terms of 3-j symbols,

$$\begin{Bmatrix} j_1 & j_2 & J_{12} \\ j_3 & j_4 & J_{34} \\ J_{13} & J_{24} & J \end{Bmatrix} \begin{pmatrix} J_{13} & J_{24} & J \\ M_{13} & M_{24} & M \end{pmatrix} = \sum_{\substack{m_1 m_2 m_3 m_4 \\ m_{12} M_{34}}} \begin{pmatrix} j_1 & j_2 & J_{12} \\ m_1 & m_2 & M_{12} \end{pmatrix} \begin{pmatrix} j_3 & j_4 & J_{34} \\ m_3 & m_4 & M_{34} \end{pmatrix} \begin{pmatrix} j_1 & j_3 & J_{13} \\ m_1 & m_3 & M_{13} \end{pmatrix} \tag{C.19}$$

$$\times \begin{pmatrix} J_{12} & J_{34} & J \\ M_{12} & M_{34} & M \end{pmatrix}$$

b. Properties:

Look upon $\begin{Bmatrix} j_{11} & j_{12} & j_{13} \\ j_{21} & j_{22} & j_{23} \\ j_{31} & j_{32} & j_{33} \end{Bmatrix}$ as a matrix.

(1) Odd permutation of rows or columns produces sign change of

$(-1)^{j_{11}+j_{12}+j_{13}+j_{21}+j_{22}+j_{23}+j_{31}+j_{32}+j_{33}}$.

(2) Even permutation or a transposition (with respect to both diagonals) leaves the symbol unchanged.

(3) Special value of the 9-j symbol.

$$\begin{Bmatrix} a & b & e \\ c & d & e \\ f & f & 0 \end{Bmatrix} = \frac{(-1)^{b+c+e+f}}{\sqrt{(2\ell+1)(2f+1)}} \begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} \quad . \tag{C.20}$$

APPENDIX D

NUMERICAL TABLES FOR: $(d^n \alpha SL \| U^{(K)} \| d^n \alpha' S' L')$, k = 2,4 n = 2,5
AND $(d^n \alpha SL \| V^{1k} \| d^n \alpha' S' L')$, n = 2,4, k = 1,2

TABLE D-1*

$(d^2 \alpha LS \| U^{(2)}(2) \| d^2 \alpha' L' S')$

$\alpha' S' L'$ / αSL	^3_2F	^3_2P	^1_2D	^1_2G	^1_0S
^3_2F	$\frac{\sqrt{6}}{5}$	$\frac{2}{5}\sqrt{6}$	0	0	0
^3_2P	$\frac{2}{5}\sqrt{6}$	$-\frac{1}{5}\sqrt{21}$	0	0	0
^1_2D	0	0	$-\frac{3}{7}$	$\frac{12}{35}\sqrt{5}$	$\frac{2}{5}\sqrt{5}$
^1_2G	0	0	$\frac{12}{35}\sqrt{5}$	$\frac{3}{7}\sqrt{22}$	0
^1_0S	0	0	$\frac{2}{5}\sqrt{5}$	0	0

*Taken from Slater II, Appendix 26.

TABLE D-2

$(d^2\alpha LS\|U^{(4)}(2)\|d^2\,\alpha'L'S')$

αSL \ $\alpha'S'L'$	${}^3_2F$	${}^3_2P$	${}^1_2D$	${}^1_2G$	${}^1_0S$
${}^3_2F$	$-\sqrt{\frac{11}{5}}$	$-\sqrt{\frac{2}{5}}$	0	0	0
${}^3_2P$	$-\sqrt{\frac{2}{5}}$	0	0	0	0
${}^1_2D$	0	0	$\frac{4}{7}$	$\frac{\sqrt{110}}{7}$	0
${}^1_2G$	0	0	$\frac{\sqrt{110}}{7}$	$\frac{1}{7}\sqrt{\frac{143}{5}}$	$\frac{2}{\sqrt{5}}$
${}^1_0S$	0	0	0	$\frac{2}{\sqrt{5}}$	0

TABLE D-3*

$(d^J\alpha SL\|U^{(2)}(2)\|d^5\alpha'S'L')$

αSL \ $\alpha'S'L'$	${}^6_5S$	${}^4_5G$	${}^4_3P$	${}^4_5D$	${}^4_3F$
${}^6_5S$	0	0	0	0	0
${}^4_5G$	0	0	0	0	$-\frac{3}{7}\sqrt{14}$
${}^4_3P$	0	0	0	$\frac{\sqrt{15}}{5}$	0
${}^4_5D$	0	0	$-\frac{\sqrt{15}}{5}$	0	$\frac{8}{35}\sqrt{35}$
${}^4_3F$	0	0	0	$-\frac{8}{35}\sqrt{35}$	0

*Taken from Slater II, Appendix 26

$(d^5 \alpha SL \| U^{(2)}(2) \| d^5 \alpha' S' L')$

αSL \ $\alpha' S' L'$	${}^{2}_{5}I$	${}^{2}_{3}H$	${}^{2}_{3}G$	${}^{2}_{5}G$	${}^{2}_{3}F$	${}^{2}_{5}F$	${}^{2}_{1}D$	${}^{2}_{3}D$	${}^{2}_{5}D$	${}^{2}_{3}P$	${}^{2}_{5}S$
${}^{2}_{5}I$	0	$-\frac{\sqrt{13}}{5}$	$\frac{4}{35}\sqrt{273}$	0	0	0	0	0	0	0	0
${}^{2}_{3}H$	$\frac{\sqrt{13}}{5}$	0	0	$-\frac{6}{35}\sqrt{70}$	0	$-\frac{2}{35}\sqrt{462}$	0	0	0	0	0
${}^{2}_{3}G$	$\frac{4}{35}\sqrt{273}$	0	0	$\frac{9}{35}\sqrt{30}$	0	$-\frac{4}{35}\sqrt{42}$	$-\frac{2}{7}\sqrt{21}$	0	$\frac{4}{7}\sqrt{6}$	0	0
${}^{2}_{5}G$	0	$\frac{6}{35}\sqrt{70}$	$\frac{9}{35}\sqrt{30}$	0	0	0	0	$-\frac{6}{35}\sqrt{55}$	0	0	0
${}^{2}_{3}F$	0	0	0	0	0	$-\frac{\sqrt{30}}{5}$	$\frac{2}{5}\sqrt{5}$	0	0	0	0
${}^{2}_{5}F$	0	$-\frac{2}{35}\sqrt{462}$	$\frac{4}{35}\sqrt{42}$	0	$-\frac{\sqrt{30}}{5}$	0	0	$-\frac{2}{7}\sqrt{7}$	0	$\frac{4}{35}\sqrt{105}$	0
${}^{2}_{1}D$	0	0	$-\frac{2}{7}\sqrt{21}$	0	$-\frac{2}{5}\sqrt{5}$	0	0	$\frac{3}{7}\sqrt{7}$	0	$\frac{1}{5}\sqrt{30}$	0
${}^{2}_{3}D$	0	0	0	$-\frac{6}{35}\sqrt{55}$	0	$\frac{2}{7}\sqrt{7}$	$\frac{3}{7}\sqrt{7}$	0	$\frac{\sqrt{2}}{7}$	0	$\frac{4}{35}\sqrt{70}$
${}^{2}_{5}D$	0	0	$\frac{4}{7}\sqrt{6}$	0	0	0	0	$\frac{\sqrt{2}}{7}$	0	$-\frac{\sqrt{105}}{7}$	0
${}^{2}_{3}P$	0	0	0	0	0	$\frac{4}{35}\sqrt{105}$	$-\frac{1}{5}\sqrt{30}$	0	$\frac{\sqrt{105}}{7}$	0	0
${}^{2}_{5}S$	0	0	0	0	0	0	0	$\frac{4}{35}\sqrt{70}$	0	0	0

*Taken from Slater II, Appendix 26.

TABLE D-4

$(d^5 \alpha SL \| U^4(2) \| d^5 \alpha' S' L')$

αSL \ $\alpha' S' L'$	${}^6_5S$	${}^4_5G$	${}^4_3P$	${}^4_5D$	${}^4_3F$
${}^6_5S$	0	0	0	0	0
${}^4_5G$	0	0	$-\sqrt{2}$	0	$-\sqrt{\frac{11}{7}}$
${}^4_3P$	0	$\sqrt{2}$	0	0	0
${}^4_5D$	0	0	0	0	$-\sqrt{\frac{10}{7}}$
${}^4_3F$	0	$\sqrt{\frac{11}{7}}$	0	$\sqrt{\frac{10}{7}}$	0

TABLE D-4'

$(d^5\alpha SL\|U^4(2)\|d^5\alpha' S' L')$

αSL \ $\alpha' SL'$	${}^{2}_{5}I$	${}^{2}_{3}H$	${}^{2}_{3}G$	${}^{2}_{5}G$	${}^{2}_{3}F$	${}^{2}_{5}F$	${}^{2}_{1}D$	${}^{2}_{3}D$	${}^{2}_{5}D$	${}^{2}_{3}P$	${}^{2}_{5}S$
${}^{2}_{5}I$	0	$\frac{2}{3}\sqrt{13}$	$-\frac{1}{2}\sqrt{\frac{13}{21}}$	0	$\frac{1}{6}\sqrt{91}$	0	0	$\frac{2}{3}\sqrt{\frac{13}{7}}$	0	0	0
${}^{2}_{3}H$	$-\frac{2}{3}\sqrt{13}$	0	0	$\frac{1}{2}\sqrt{\frac{13}{7}}$	0	$-\frac{1}{6}\sqrt{\frac{143}{7}}$	$-\frac{1}{3}\sqrt{22}$	0	$-\frac{2}{3}\sqrt{\frac{11}{7}}$	0	0
${}^{2}_{3}G$	$-\frac{1}{2}\sqrt{\frac{13}{21}}$	0	0	$-\frac{3}{14}\sqrt{39}$	0	$-\frac{3}{14}\sqrt{\frac{77}{3}}$	$\sqrt{\frac{22}{21}}$	0	$-\frac{1}{14}\sqrt{\frac{11}{3}}$	0	$2\sqrt{\frac{2}{21}}$
${}^{2}_{5}G$	0	$-\frac{1}{2}\sqrt{\frac{13}{7}}$	$-\frac{3}{14}\sqrt{39}$	0	$-\frac{1}{2}\sqrt{7}$	0	0	$\frac{3}{7}\sqrt{\frac{5}{2}}$	0	$-\frac{1}{2}\sqrt{\frac{11}{7}}$	0
${}^{2}_{3}F$	$-\frac{1}{6}\sqrt{91}$	0	0	$\frac{1}{2}\sqrt{7}$	0	$-\frac{\sqrt{11}}{6}$	$\frac{1}{3}\sqrt{10}$	0	$\frac{1}{6}\sqrt{35}$	0	0
${}^{2}_{5}F$	0	$-\frac{1}{6}\sqrt{\frac{143}{7}}$	$\frac{3}{14}\sqrt{\frac{77}{3}}$	0	$-\frac{\sqrt{11}}{6}$	0	0	$\frac{11}{3}\sqrt{\frac{1}{14}}$	0	$\frac{3}{2}\sqrt{\frac{1}{7}}$	0
${}^{2}_{1}D$	0	$\frac{1}{3}\sqrt{22}$	$\sqrt{\frac{22}{21}}$	0	$-\frac{1}{3}\sqrt{10}$	0	0	$-\frac{5}{3}\sqrt{\frac{1}{7}}$	0	0	0
${}^{2}_{3}D$	$\frac{2}{3}\sqrt{\frac{13}{7}}$	0	0	$\frac{3}{7}\sqrt{\frac{5}{2}}$	0	$-\frac{11}{3}\sqrt{\frac{1}{14}}$	$-\frac{5}{3}\sqrt{\frac{1}{7}}$	0	$\frac{10}{21}\sqrt{2}$	0	0
${}^{2}_{5}D$	0	$\frac{2}{3}\sqrt{\frac{11}{7}}$	$-\frac{1}{14}\sqrt{\frac{11}{3}}$	0	$-\frac{1}{6}\sqrt{35}$	0	0	$\frac{10}{21}\sqrt{2}$	0	0	0
${}^{2}_{3}P$	0	0	0	$\frac{1}{2}\sqrt{\frac{11}{7}}$	0	$\frac{3}{2}\sqrt{\frac{1}{7}}$	0	0	0	0	0
${}^{2}_{5}S$	0	0	$2\sqrt{\frac{2}{21}}$	0	0	0	0	0	0	0	0

TABLE D-5*

$(d^2\alpha SL\|V^{1p}\|d^2\alpha'S'L')$ $p = 1,2$

	V"	V^{12}
${}^{3}_{2}F \rightarrow {}^{3}_{2}F$	$\sqrt{105}/5$	$3/5$
${}^{3}_{2}F \rightarrow {}^{3}_{2}P$	0	$6/5$
${}^{3}_{2}F \rightarrow {}^{1}_{2}G$	$-3\sqrt{10}/10$	$-3\sqrt{42}/14$
${}^{3}_{2}F \rightarrow {}^{1}_{2}D$	$\sqrt{30}/5$	$4\sqrt{105}/35$
${}^{3}P \rightarrow {}^{3}P$	$\sqrt{30}/5$	$-3\sqrt{14}/10$
${}^{3}_{2}P \rightarrow {}^{1}_{2}D$	$-\sqrt{105}/10$	$-3\sqrt{5}/10$
${}^{3}_{2}P \rightarrow {}^{1}_{0}S$	$\sqrt{15}/5$	0
${}^{1}_{2}G \rightarrow {}^{1}_{2}G$	0	0
${}^{1}_{2}G \rightarrow {}^{1}_{2}D$	0	0
${}^{1}_{2}D \rightarrow {}^{1}_{2}D$	0	0
${}^{1}_{2}D \rightarrow {}^{1}_{0}S$	0	0

*Owing to the limited space, the following two tables are presented in a different form. Matrix components are zero for transitions omitted from the table. When there are two signs in front of the numerical value, the lower one refers to the component taken in the opposite order.** These two tables are taken from Slater II, Appendix 26.

**The relation $(d^n\alpha SL\|V^{pq}\|d^n\alpha'S'L') = (1)^{L+S-L'-S'}(d^n\alpha'S'L'\|V^{pq}\|d^n\alpha SL)$ holds for all the table.

TABLE D-6

$(d^5\alpha SL \| V^{1p} \| d^5\alpha' S' L')$ $p = 1,2$

	V"	V^{12}
${}^6_5S \rightarrow {}^4_5D$	0	$\pm\sqrt{3}$
${}^6_5S \rightarrow {}^4_3P$	$\sqrt{3}$	0
${}^4_5G \rightarrow {}^4_5G$	0	$-\sqrt{330}/7$
${}^4_5G \rightarrow {}^4_3F$	$\pm\sqrt{2}$	0
${}^4_5G \rightarrow {}^4_5D$	0	$-4\sqrt{3}/7$
${}^4_5G \rightarrow {}^2_5I$	0	$\mp\sqrt{2730}/35$
${}^4_5G \rightarrow {}^2_3H$	$-\sqrt{110}/5$	0
${}^4_5G \rightarrow {}^2_3G$	$\pm\sqrt{15}/5$	0
${}^4_5G \rightarrow {}^2_5G$	0	$\pm\sqrt{3}/7$
${}^4_5G \rightarrow {}^2_3F$	$\sqrt{5}$	0
${}^4_5G \rightarrow {}^2_5F$	0	$\sqrt{105}/5$
${}^4_5G \rightarrow {}^2_5D$	0	$2\sqrt{15}/7$
${}^4_3F \rightarrow {}^4_3F$	0	$-\sqrt{10}/5$
${}^4_3F \rightarrow {}^4_5D$	$\pm 2\sqrt{6}/3$	0

TABLE D-6 (Cont)

	V''	V^{12}
${}^{4}_{3}F \rightarrow {}^{4}_{3}P$	0	$-2\sqrt{10}/5$
${}^{4}_{3}F \rightarrow {}^{2}_{3}H$	0	$\pm 2\sqrt{385}/35$
${}^{4}_{3}F \rightarrow {}^{2}_{3}G$	0	$-9\sqrt{35}/35$
${}^{4}_{3}F \rightarrow {}^{2}_{5}G$	$-\sqrt{55}/5$	0
${}^{4}_{3}F \rightarrow {}^{2}_{3}F$	0	$\pm 7/5$
${}^{4}_{3}F \rightarrow {}^{2}_{5}F$	$\pm\sqrt{21}/3$	0
${}^{4}_{3}F \rightarrow {}^{2}_{1}D$	$-2\sqrt{105}/15$	0
${}^{4}_{3}F \rightarrow {}^{2}_{3}D$	0	$2\sqrt{210}/35$
${}^{4}_{3}F \rightarrow {}^{2}_{5}D$	$-\sqrt{30}/15$	0
${}^{4}_{3}F \rightarrow {}^{2}_{3}P$	0	$\pm 11\sqrt{14}/35$
${}^{4}_{5}D \rightarrow {}^{4}_{5}D$	0	$\sqrt{15}/7$
${}^{4}_{5}D \rightarrow {}^{4}_{3}P$	$\pm\sqrt{21}/3$	0
${}^{4}_{5}D \rightarrow {}^{2}_{5}G$	0	$\pm 4\sqrt{330}/35$
${}^{4}_{5}D \rightarrow {}^{2}_{3}F$	$4\sqrt{15}/15$	0

TABLE D-6 (Cont)

	V''	V^{12}
${}^{4}_{5}D \rightarrow {}^{2}_{3}D$	$\pm 2\sqrt{6}/3$	0
${}^{4}_{5}D \rightarrow {}^{2}_{5}D$	0	$\mp 6\sqrt{3}/7$
${}^{4}_{5}D \rightarrow {}^{2}_{3}P$	$2\sqrt{15}/15$	0
${}^{4}_{5}D \rightarrow {}^{2}_{5}S$	0	$\pm 3\sqrt{105}/35$
${}^{4}_{3}P \rightarrow {}^{4}_{3}P$	0	$\sqrt{35}/5$
${}^{4}_{3}P \rightarrow {}^{2}_{3}F$	0	$\pm 4/5$
${}^{4}_{3}P \rightarrow {}^{2}_{1}D$	$-4\sqrt{30}/15$	0
${}^{4}_{3}P \rightarrow {}^{2}_{3}D$	0	$-2\sqrt{10}/5$
${}^{4}_{3}P \rightarrow {}^{2}_{5}D$	$-2\sqrt{105}/15$	0
${}^{4}_{3}P \rightarrow {}^{2}_{3}P$	0	$\pm 2/5$
${}^{4}_{3}P \rightarrow {}^{2}_{5}S$	$\sqrt{105}/15$	0
${}^{2}_{5}I \rightarrow {}^{2}_{5}I$	0	$-\sqrt{858}/22$
${}^{2}_{5}I \rightarrow {}^{2}_{3}H$	$\pm\sqrt{390}/10$	0
${}^{2}_{5}I \rightarrow {}^{2}_{3}G$	0	0

TABLE D-6 (Cont)

	V"	V^{12}
${}^{2}_{5}I \rightarrow {}^{2}_{5}G$	0	$4\sqrt{30,030}/385$
${}^{2}_{5}I \rightarrow {}^{2}_{3}H$	0	$-\sqrt{2,002}/70$
${}^{2}_{3}H \rightarrow {}^{2}_{2}G$	0	$\mp 6\sqrt{77}/35$
${}^{2}_{3}H \rightarrow {}^{2}_{5}G$	$\pm 2\sqrt{10}/5$	0
${}^{2}_{3}H \rightarrow {}^{2}_{3}F$	0	$-2\sqrt{385}/35$
${}^{2}_{3}H \rightarrow {}^{2}_{5}F$	0	0
${}^{2}_{3}G \rightarrow {}^{2}_{3}G$	0	$3\sqrt{33}/70$
${}^{2}_{3}G \rightarrow {}^{2}_{5}G$	$-\sqrt{165}/10$	0
${}^{2}_{3}G \rightarrow {}^{2}_{3}F$	0	$\mp 3\sqrt{35}/70$
${}^{2}_{3}G \rightarrow {}^{2}_{5}F$	$\mp 3\sqrt{15}/10$	0
${}^{2}_{3}G \rightarrow {}^{2}_{1}D$	0	0
${}^{2}_{3}G \rightarrow {}^{2}_{3}D$	0	$-6\sqrt{2}/7$
${}^{2}_{3}G \rightarrow {}^{2}_{5}D$	0	0
${}^{2}_{5}G \rightarrow {}^{2}_{5}G$	0	$25\sqrt{23}/154$
${}^{2}_{5}G \rightarrow {}^{2}_{3}F$	$\pm\sqrt{55}/10$	0

TABLE D-6 (Cont)

	V"	V^{12}
${}^{2}_{5}G \rightarrow {}^{2}_{5}F$	0	$\mp \sqrt{1,155}/70$
${}^{2}_{5}G \rightarrow {}^{2}_{3}D$	0	0
${}^{2}_{5}G \rightarrow {}^{2}_{5}D$	0	$- 2\sqrt{165}/35$
${}^{2}_{3}F \rightarrow {}^{2}_{3}F$	0	$- 11/10$
${}^{2}_{3}F \rightarrow {}^{2}_{5}F$	$- \sqrt{21}/6$	0
${}^{2}_{3}F \rightarrow {}^{2}_{1}D$	$\mp 2\sqrt{105}/15$	0
${}^{2}_{3}F \rightarrow {}^{2}_{3}D$	0	$\pm 2\sqrt{210}/35$
${}^{2}_{3}F \rightarrow {}^{2}_{5}D$	$\mp 4\sqrt{30}/15$	0
${}^{2}_{3}F \rightarrow {}^{2}_{3}F$	0	$- 4\sqrt{14}/35$
${}^{2}_{5}F \rightarrow {}^{2}_{5}F$	0	$- 3/2$
${}^{2}_{5}F \rightarrow {}^{2}_{3}D$	$\pm 2\sqrt{3}/3$	0
${}^{2}_{5}F \rightarrow {}^{2}_{5}D$	0	$\pm 2\sqrt{21}/7$
${}^{2}_{5}F \rightarrow {}^{2}_{3}P$	0	0
${}^{2}_{1}D \rightarrow {}^{2}_{1}D$	0	$\sqrt{6}/2$
${}^{2}_{1}D \rightarrow {}^{2}_{3}D$	$- \sqrt{42}/16$	0

TABLE D-6 (Concl)

	V''	V^{12}
$^2_1D \rightarrow {}^2_3P$	$\pm\sqrt{105}/15$	0
$^2_3D \rightarrow {}^2_3D$	0	$-\sqrt{6}/14$
$^2_3D \rightarrow {}^2_5D$	$\sqrt{3}/3$	0
$^2_3D \rightarrow {}^2_3P$	0	$\mp 4\sqrt{35}/35$
$^2_3D \rightarrow {}^2_5S$	0	0
$^2_5D \rightarrow {}^2_5D$	0	$3\sqrt{6}/14$
$^2_5D \rightarrow {}^2_3P$	$\mp\sqrt{30}/30$	0
$^2_5D \rightarrow {}^2_5S$	0	$-2\sqrt{210}/35$
$^2_3P \rightarrow {}^2_3P$	0	$-19\sqrt{14}/70$
$^2_3P \rightarrow {}^2_5S$	$\pm 2\sqrt{30}/15$	0

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