Lecture 27 Supplement #3: A User's Guide to Angular Momentum Theory

The wavefunctions for both atoms and molecules in the gas phase may be factored into a *molecule-specific* radial part and a *universal* angular part. An enormously powerful one-size-fits-all theory exists for deriving the universal angular part of molecular basis-states and eigen-states, and calculation of the angular part of all matrix elements. This lecture is an attempt to provide a user's guide to angular momentum theory. It is adapted from pages 152-175 of Rotational Spectroscopy of Diatomic Molecules, John Brown and Alan Carrington, Cambridge University Press, 2003, and Angular Momentum, Richard N. Zare, Wiley, 1988, pages 180-200. The outline is:

- Commutation Rule definition of an angular momentum
- Matrix elements of the magnitude ($\mathbf{j}^2$) and components ($\mathbf{j}_x$, $\mathbf{j}_y$, $\mathbf{j}_z$, $\mathbf{j}_+$, $\mathbf{j}_-$) of a single angular momentum operator
- Uncoupled and Coupled representations for two angular momenta, $\mathbf{j}_1$ and $\mathbf{j}_2$, coupled to make a total angular momentum, $\mathbf{j}=\mathbf{j}_1+\mathbf{j}_2$
- Vector-coupling, Clebsch-Gordan, and 3-*j* coefficients for the transformation between coupled and uncoupled representations
- Commutation rule definition of a spherical tensor operator, T^k_μ (*k* rank, μ component, $-k \le \mu \le k$: scalar *k*=0, vector *k*=1, and *k*=2 2nd rank tensor)
- Combinations of three or more angular momenta to form composite basis states: 6-*j* and 9-*j* coefficients
- Combination of two or more angular momenta to form a composite spherical tensor operator, $\mathbf{T}^k_\mu(\mathbf{A},\mathbf{B})$
- Wigner-Eckart Theorem for matrix elements of spherical tensor operators
- Wigner-Eckart Theorem for matrix elements of composite spherical tensor operators.

I will illustrate each step with a worked example.

Commutation Rule Definition of an Angular Momentum

$$[\mathbf{J}_i, \mathbf{J}_j] = i\hbar \sum_k \varepsilon_{ijk} \mathrm{J}_k$$

is the universal signature of any operator that qualifies for the name "angular momentum."

* This angular momentum commutation rule can be derived from the most important commutation rule in Quantum Mechanics

$$\left[\hat{x}, \hat{p}_x\right] = i\hbar$$

* This angular momentum commutation rule is useful in deriving all of the properties of $\hat{J}^2, \hat{J}_x, \hat{J}_y, \hat{J}_z, \hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$ acting on any simultaneous eigenstate of $\hat{J}^2$ and $\hat{J}_z, |JM_J\rangle$:

$$\hat{J}^2|JM\rangle = \hbar^2 J(J+1)|JM\rangle$$
$$\hat{J}_z|JM\rangle = \hbar M|JM\rangle$$
$$\hat{J}_\pm|JM\rangle = \hbar\left[J(J+1) - M(M\pm1)\right]^{1/2}|JM\pm1\rangle$$

$$\hat{J}_x|JM\rangle = \frac{1}{2}\left(\hat{J}_+ + \hat{J}_-\right)|JM\rangle$$
$$= \frac{\hbar}{2}\left\{\left[J(J+1) - M(M+1)\right]^{1/2}|JM+1\rangle + \left[J(J+1) - M(M-1)\right]^{1/2}|JM-1\rangle\right\}$$

$$\hat{J}_y|JM\rangle = \frac{-i}{2}\left(\hat{J}_+ + \hat{J}_-\right)|JM\rangle$$
$$= \frac{\hbar}{2}(-i)\left\{\left[J(J+1) - M(M+1)\right]^{1/2}|JM+1\rangle - \left[J(J+1) - M(M-1)\right]^{1/2}|JM-1\rangle\right\}$$

* This commutation rule is also surprising because it requires that

$$\hat{J} \times \hat{J} = i\hbar\hat{J} \neq 0$$

because, classically, the cross product of any vector with itself is zero.

* It is more surprising that, while orthogonal linear translations commute, angular translations *do not* commute.

Transformation between Coupled and Uncoupled Representations

We used the $\hat{J}_\pm$ plus orthogonality method to derive the transformation between a coupled representation

$$\text{e.g.} \quad \hat{J} = \hat{L} + \hat{S} \qquad |JLSM_J\rangle$$

and an uncoupled representation: $|LM_LSM_S\rangle$. More generally, one knows that there must exist a unitary transformation between two complete same-dimension basis set representations, as is true for $|JLSM_J\rangle$ and $|LM_LSM_S\rangle$, where the same (L,S) dimension for each basis set is $(2L + 1)(2S + 1)$.

The ladders plus orthogonality method is extremely laborious and inelegant, but it is based on easily remembered matrix elements. There is a much better way, based on complete tables of transformation coefficients between coupled and uncoupled representations. The relationship between the coupled and uncoupled representations is obtained via completeness:

$$\left|JLSM_J\right\rangle = \sum_{M_L,M_S}\left|LM_LSM_S\right\rangle\left\langle LM_LSM_S\middle|JLSM_J\right\rangle.$$

Two simplifications may be made

$$\left|LM_LSM_S\right\rangle \equiv \left|LM_L\right\rangle\left|SM_S\right\rangle$$

and, based on $M_L + M_S = M_J$, the double-sum over M_L,M_S may be replaced by a single sum

$$\left|JLSM_J\right\rangle = \sum_{M_S=-S}^{S}\left|L,M_L = M_J - M_S,SM_J\right\rangle\left\langle L,M_L = M_J - M_S,SM_J\middle|JLSM_J\right\rangle.$$

The factor on the RHS is called a **vector coupling coefficient**. Since the coupled↔uncoupled transformation is unitary [$\mathbf{U}^{-1} = \mathbf{U}^{\dagger}$], the inverse transformation is given by

$$\left|L,M_L = M_J - M_S,SM_S\right\rangle = \sum_{M_S=-S}^{S}\left\langle JLS,M_J = M_L + M_S\middle|L,M_L = M_J - M_S,SM_S\right\rangle^{*}\left|JLS,M_J = M_L + M_S\right\rangle.$$

The transformation coefficient in the above equation is the conjugate transform of the transformation coefficient in the previous equation. These vector coupling coefficients are typically expressed (and tabulated) in a slightly more compact form as **Clebsch-Gordan coefficients**.

$$\left|JLSM_J\right\rangle = \sum_{M_S=-S}^{S}\left|LM_L\right\rangle\left|SM_S\right\rangle\left\langle LM_LSM_S\middle|JM_J\right\rangle$$

and

$$\left|LM_L\right\rangle\left|SM_S\right\rangle = \sum_{\substack{J=|L-S|\\ M_J=M_L+M_S}}^{L+S}\left|JM_J\right\rangle\left\langle JM_J\middle|LM_LSM_S\right\rangle.$$

The factor $\langle LM_L,SM_S|JM_J\rangle$ is the **Clebsch-Gordan coefficient**. It has been simplified by suppression of the redundant L,S quantum numbers in the ket. The M_J quantum number could have been suppressed as well because $M_J = M_L + M_S$.

A more compact and useful expression of the transformation between the coupled and uncoupled representations is given by the **Wigner 3-*j* symbols**. Formally, one can think of the 3-*j* symbol as expressing the coupling of three angular momenta { $|J,M_J\rangle$, $|LM_L\rangle$ and $|SM_S\rangle$} to make a "scalar" quantity, symbolized by $|0,0\rangle$ (see Brown and Carrington, page 154). One obtains a relationship between the 3-*j* symbol and a Clebsch-Gordan coefficient

$$\underbrace{\langle LM_L SM_S | JM_J \rangle}_{\textbf{CLEBSCH-GORDAN}} = (-1)^{L-S+M_J}(2J+1)^{1/2} \underbrace{\begin{pmatrix} L & S & J \\ M_L & M_S & M_J \end{pmatrix}}_{\textbf{3-}j}.$$

Thus

$$|JM_J(LS)\rangle = (-1)^{L-S+M_J}(2J+1)^{1/2} \sum_{\substack{M_L,M_S \\ M_L+M_S=M_J}} \begin{pmatrix} L & S & J \\ M_L & M_S & -M_J \end{pmatrix} |LM_L SM_S\rangle.$$

The $-M_J$ in the 3-*j* coefficient is initially puzzling, but it expresses the requirement that $M_L + M_S = M_J$ or that the three *M* quantum numbers in the 3-*j* symbol must sum to zero:

$$M_L + M_S - M_J = 0.$$

Using a computer to compute and use 3-*j* coefficients requires significantly less time and effort than for you to look up a tabulated 3-*j* coefficient.

What is so great about 3-*j* coefficients? (i) the three angular momenta are treated symmetrically; (ii) the m_i and associated j_i appear together in a single column of the 3-*j* symbol; (iii) an odd interchange of columns (123 → 213 but not an even interchange 123 → 312) is obtained by

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

and a sign reversal of all *m* in the bottom row is given by

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

and the general transformation is

$$|j_3m_3(j_1j_2)\rangle = (-1)^{j_1-j_2+m_3}(2j_3+1)^{1/2} \sum_{m_1,m_2=m_3-m_1} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} |j_1m_1\rangle |j_2m_2\rangle.$$

The inverse transformation (from coupled to uncoupled) is given by

$$\left|j_1 m_1 j_2 m_2\right\rangle = \sum_{\substack{j_3=|j_1-j_2| \\ m_3=m_1+m_2}}^{j_1+j_2} (-1)^{j_2-j_1-m_3}\left(2j_3+1\right)^{1/2}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}\left|j_1 j_2 j_3 m_3\right\rangle.$$

Notice that the same 3-j symbol appears in the coupled→uncoupled and uncoupled→coupled representations, but the sum is carried out over $m_1(m_2 = m_3 - m_1)$ in the uncoupled↔coupled transformation and over j_3 in the coupled→uncoupled transformation.

Example of coupled to uncoupled transformation

Suppose we are interested in the Zeeman effect for the J,M_J components of a ^3F ($S = 1$, $L = 3$) state. We know that, at zero-field, the ^3F state has $J = 4, 3, 2$ spin-orbit components and that

$$\mathbf{H}_{SO} = A\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}A\left[J(J+1) - L(L+1) - S(S+1)\right]$$

$$\text{because } \mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2 \qquad \text{thus } \mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right)$$

$$E_{^3F_2} = E^{(0)}_{^3F} + \frac{1}{2}A[6-12-2] = E^{(0)}_{^3F} - 4A$$

$$E_{^3F_3} = E^{(0)}_{^3F} + \frac{1}{2}A[12-12-2] = E^{(0)}_{^3F} - A$$

$$E_{^3F_4} = E^{(0)}_{^3F} + \frac{1}{2}A[20-12-2] = E^{(0)}_{^3F} + 3A$$

We need the uncoupled representation to compute the Zeeman effect for each of the J,M_J levels. In the uncoupled representation $\mathbf{H}^{\text{Zeeman}} = -\hbar\mu_0 B_z(\mathbf{L}_z + 2\mathbf{S}_z)$ (μ_0 is the Bohr magneton). We want to know what $\mathbf{L}_z$ and $\mathbf{S}_z$ do to each $|LSJM_J\rangle$ coupled basis state. Here are a few examples of coupled→uncoupled $|LSJM_J\rangle \to |LM_LSM_S\rangle$ transformations:

$$\left|3144\right\rangle = a\left|3311\right\rangle$$
$$\left|3143\right\rangle = b\left|3310\right\rangle + c\left|3211\right\rangle$$
$$\left|3133\right\rangle = d\left|3310\right\rangle + e\left|3211\right\rangle$$
$$\left|3132\right\rangle = f\left|331-1\right\rangle + g\left|3210\right\rangle + h\left|3111\right\rangle$$
$$\left|3122\right\rangle = i\left|331-1\right\rangle + j\left|3210\right\rangle + k\left|3111\right\rangle$$
$$\left|3121\right\rangle = l\left|321-1\right\rangle + m\left|3110\right\rangle + n\left|3011\right\rangle$$

where the mixing coefficients a–n are evaluated using tabulated 3-j coefficients.

$$a = \begin{pmatrix} L & S & J \\ M_L & M_S & -M_J \end{pmatrix} = \begin{pmatrix} 3 & 1 & 4 \\ 3 & 1 & -4 \end{pmatrix} = 1.000$$

$\left\langle L_z + 2S_z \right\rangle = 5\hbar$ for ${}^3F_4 M_J = 4$

$$b = \begin{pmatrix} 3 & 1 & 4 \\ 3 & 0 & -3 \end{pmatrix} = 0.500$$

$$c = \begin{pmatrix} 3 & 1 & 4 \\ 2 & 1 & -3 \end{pmatrix} = 0.866$$

$\left\langle L_z + 2S_z \right\rangle = 3.75\hbar$ for ${}^4F_3 M_J = 3$

$$d = \begin{pmatrix} 3 & 1 & 3 \\ 3 & 0 & -3 \end{pmatrix} = 0.866$$

$$e = \begin{pmatrix} 3 & 1 & 3 \\ 2 & 1 & -3 \end{pmatrix} = -0.500$$

$\left\langle L_z + 2S_z \right\rangle = 3.25\hbar$ for ${}^3F_3 M_J = 2$

$$f = \begin{pmatrix} 3 & 1 & 3 \\ 3 & -1 & -2 \end{pmatrix} = 0.500$$

$$g = \begin{pmatrix} 3 & 1 & 3 \\ 2 & 0 & -2 \end{pmatrix} = 0.577$$

$$h = \begin{pmatrix} 3 & 1 & 3 \\ 1 & 1 & -2 \end{pmatrix} = -0.645$$

$\left\langle L_z + 2S_z \right\rangle = 2.16\hbar$ for ${}^3F_3 M_J = 2$

$$i = \begin{pmatrix} 3 & 1 & 2 \\ 3 & -1 & -2 \end{pmatrix} = 0.845$$

$$j = \begin{pmatrix} 3 & 1 & 2 \\ 2 & 0 & -2 \end{pmatrix} = -0.488$$

$$k = \begin{pmatrix} 3 & 1 & 2 \\ 1 & 1 & -2 \end{pmatrix} = 0.218$$

$\left\langle L_z + 2S_z \right\rangle = 1.333\hbar$ for ${}^3F_2 M_J = 2$

$$l = \begin{pmatrix} 3 & 1 & 2 \\ 2 & -1 & -1 \end{pmatrix} = 0.690$$

$$m = \begin{pmatrix} 3 & 1 & 2 \\ 1 & 0 & -1 \end{pmatrix} = -0.617$$

$$n = \begin{pmatrix} 3 & 1 & 2 \\ 0 & 1 & -1 \end{pmatrix} = 0.378$$

$\left\langle L_z + 2S_z \right\rangle = 0.666\hbar$ for ${}^3F_2 M_J = 1$

These results are consistent with a formula given on page 381 of Condon and Shortley.

$$\mathbf{H}^{\text{Zeeman}} = \gamma B_z g_{\text{JLS}} \hbar M_J$$
$$g_{\text{JLS}} = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

Definition of Spherical Tensor Operators

We know how to use 3-*j* coefficients to couple two angular momentum operators to make a third angular momentum. We define an angular momentum operator by a commutation rule

$$\left[\hat{J}_i, \hat{J}_j\right] = i\hbar \sum_k \varepsilon_{ijk} J_k .$$

If we can re-express all angle-dependent operators as a sum of angular momenta-like operators (irreducible tensor operators), then we can use 3-*j*-like coefficients to evaluate the angle dependent factors of all matrix elements. There is also a special feature of the **H** matrix. In field-free space **H** acts like a scalar operator

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

where k is the rank ($k = 0$ is Scalar, $k = 1$ is vector, $k = 2$ is 2nd rank tensor) and q is the component ($-k \le q \le k$). For a Scalar Operator ($q = 0$, $k = 0$) the commutation rule definition tells us that

$$\left[\hat{J}_\pm, \hat{T}_0^0\right] = 0$$
$$\left[\hat{J}_z, \hat{T}_0^0\right] = 0$$

which means that $\hat{T}_0^0$ acts like an M-independent constant

$$\left\langle JM \middle| \hat{T}_0^0 \middle| J'M' \right\rangle = c_J \delta_{JJ'} \delta_{MM'}$$

with exclusively diagonal matrix elements in the J, M_J basis set. For a Vector Operator,

$$\hat{V}_0 = \hat{V}_z$$
$$\hat{V}_\pm = \mp 2^{-1/2}\left(\hat{V}_x \pm i\hat{V}_y\right)$$
$$\left[J_z, V_0\right] = \hbar T_q^1 = \hbar V_q$$
$$\left[J_z, V_\pm\right] = \hbar V_{\pm 1}$$
$$\left[J_\pm, V_0\right] = \pm\hbar\left[\mp(1\pm 1)\right]^{1/2} V_\pm$$
$$\left[J_\pm, V_+\right] = \pm\hbar[(1\mp 1)(q\pm 1+1)]^{1/2} V_0$$
$$\left[J_\pm, V_-\right] = \pm\hbar\left[(1\pm 1)(1\mp 1+1)\right]^{1/2} V_0$$

Example

The spherical tensor classification of operators depends on the choice of the angular momentum operator used in the classification commutation rules. For example, the spin-orbit operator, $\mathbf{AL}\cdot\mathbf{S}$, is a scalar operator with respect to **J** but a vector operator with respect to both **L** and **S**

$$\left[\mathbf{J}^2, \mathbf{AL}\cdot\mathbf{S}\right] = A\left[\mathbf{J}^2, \mathbf{L}\cdot\mathbf{S}\right]$$
$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right)$$
$$\left[\mathbf{J}^2, \mathbf{AL}\cdot\mathbf{S}\right] = \frac{1}{2}A\left[\mathbf{J}^2, \mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right] = 0$$
$$\begin{aligned}\left[\mathbf{J}_z, A\mathbf{L}\cdot\mathbf{S}\right] &= A\left[\mathbf{J}_z, \mathbf{L}_x\mathbf{S}_x + \mathbf{L}_y\mathbf{S}_y + \mathbf{L}_z\mathbf{S}_z\right] \\ &= A\left[\mathbf{L}_z, \mathbf{L}_x\mathbf{S}_x + \mathbf{L}_y\mathbf{S}_y + \mathbf{L}_z\mathbf{S}_z\right] \\ &= A\left[\mathbf{S}_z, \mathbf{L}_x\mathbf{S}_x + \mathbf{L}_y\mathbf{S}_y + \mathbf{L}_z\mathbf{S}_z\right] \\ &= i\hbar A\left[\left(\mathbf{L}_y\mathbf{S}_x - \mathbf{L}_x\mathbf{S}_y\right) + \left(\mathbf{L}_x\mathbf{S}_y - \mathbf{L}_y\mathbf{S}_x\right)\right] \\ &= 0\end{aligned}$$

We knew this had to be true because $\mathbf{J}^2$, $\mathbf{J}_z$, $\mathbf{L}^2$, and $\mathbf{S}^2$ are a complete set of commuting operators. But now consider $[\mathbf{L}_z, A\mathbf{L}\cdot\mathbf{S}]$ and $[\mathbf{S}_z, A\mathbf{L}\cdot\mathbf{S}]$ individually.

$$\left[\mathbf{L}_z, A\mathbf{L}\cdot\mathbf{S}\right] = i\hbar A\left(\mathbf{L}_y\mathbf{S}_x - \mathbf{L}_x\mathbf{S}_y\right) \neq 0$$
$$\left[\mathbf{S}_z, A\mathbf{L}\cdot\mathbf{S}\right] = i\hbar A\left(\mathbf{L}_x\mathbf{S}_y - \mathbf{L}_y\mathbf{S}_x\right) \neq 0$$

It is also true that **L** and **S** are scalar operators with respect to each other, because they do not operate on the same coordinates.

Example: Tensor Operators are "like" Angular Momenta

We can use the tensor operator commutation rule definitions

$$\left[J_z, T_q^k\right] = \hbar q T_q^k$$
$$\left[J_\pm, T_q^k\right] = \pm\hbar\left[(k \mp q)(k \pm q + 1)\right]^{1/2} T_{q\pm1}^k$$

to construct operators that "look like" operators with specified angular momentum characteristics with respect to *any classifying angular momentum*. This means that we can use angular momentum coupling methods to calculate matrix elements in the classifying operator's basis set, e.g. $|j,m_j\rangle$. This is the basis for the Wigner-Eckart theorem

$$\left\langle n,j,m_j\left|\mathbf{T}_q^k(\mathbf{A})\right|n',j',m_j'\right\rangle = (-1)^{j-m_j}\begin{pmatrix} j & k & j' \\ -m_j & q & m_j' \end{pmatrix} = \left\langle n,m\left\|\mathbf{T}^k(\mathbf{A})\right\|n',j'\right\rangle.$$

The 3-j coefficient describes the angular momentum-like coupling of $\langle n,j,m_j|$, $\mathbf{T}_q^k(\mathbf{A})$, and $|n',j',m'_j\rangle$, and $\langle n,j||\mathbf{T}^k(\mathbf{A})||n'j'\rangle$ is called a "reduced matrix element" because in it, none of the projection quantum numbers are specified for the bra, the ket, or the tensor operator. *All* information about the projection quantum numbers is expressed in the 3-j coefficient! $\mathbf{T}_q^k(\mathbf{A})$ means that the components of operator **A** are arranged in spherical tensor form. For example, the relationships between Cartesian tensor and spherical tensor form are as follows:

$\mathbf{j}^2$ is a scalar with respect to **j**

$$T_0^0(\mathbf{j}) = \mathbf{j}^2$$

$\vec{\mathbf{j}} = \hat{i}\mathbf{j}_x + \hat{j}\mathbf{j}_y + \hat{k}\mathbf{j}_k$ is a vector with respect to **j**

$$T_1^1(\mathbf{j}) = -2^{-1/2}\left(\mathbf{j}_x + i\mathbf{j}_y\right) = -2^{-1/2}\mathbf{j}_+$$
$$T_0^1(\mathbf{j}) = \mathbf{j}_z$$
$$T_{-1}^1(\mathbf{j}) = 2^{-1/2}\left(\mathbf{j}_x - i\mathbf{j}_y\right) = 2^{-1/2}\mathbf{j}_-.$$

The 9 products $\mathbf{j}_i,\mathbf{j}_j$ are components of a scalar, vector, and second rank tensor with respect to **j**.

$$T_0^0(jj) = -(3)^{-1/2}\left(j_x^2 + j_y^2 + j_z^2\right) = -(3)^{-1/2} j^2$$

$$T_0^1(jj) = i2^{-1/2}\left(j_x j_y - j_y j_x\right) = -\hbar 2^{-1/2} j_z$$

$$T_{\pm1}^1(jj) = \mp(i/2)\left\{\left(j_y j_z - j_z j_y\right) \pm i\left(j_z j_x - j_x j_z\right)\right\}$$

$$= \mp(i/2)\left(i\hbar j_x \mp i\hbar j_y\right) = \pm\frac{\hbar}{2}\left(j_x \pm i j_y\right)$$

$$T_0^2\left(jj\right) = 6^{-1/2}\left\{2j_z^2 - j_x^2 - j_y^2\right\}$$

$$T_{\pm1}^2\left(jj\right) = \mp\frac{1}{2}\left\{\left(j_x j_z + j_z j_x\right) \pm i\left(j_y j_z + j_z j_y\right)\right\}$$

$$T_{\pm2}^2\left(jj\right) = \frac{1}{2}\left\{\left(j_x^2 + j_y^2\right) \pm i\left(j_x j_y + j_y j_x\right)\right\}$$

It is also possible to construct spherical tensor operators out of two vector or tensor operators

$$T_q^k\left(\mathbf{u},\mathbf{v}\right)$$

$$T_Q^K\left(\mathbf{R}^{k_1},\mathbf{R}^{k_2}\right) = \sum_{q_1,q_2}\left\langle k_1,k_2,q_1,q_2\middle|KQ\right\rangle \mathbf{T}_{q_1}^{k_1}(R)\mathbf{T}_{q_2}^{k_2}(R)$$

3-j, 6-j, and 9-j coefficients

Our goal is to be able to evaluate the angular factor of matrix elements of operators composed of products and sums of angular momentum operators. These operators operate on basis states that are simultaneously eigenstates of many angular momenta ($\mathbf{j}^2$) and angular momentum z-components ($\mathbf{j}_z$). The defining angular momentum commutation rule

$$\left[\mathbf{j}_i,\mathbf{j}_j\right] = i\hbar\sum_k \mathbf{j}_k$$

tells us how to define (or construct) angular momentum operators and a similar commutation rule tells us how to define (or construct) spherical tensor operators, $\mathbf{T}_\mu^k(\mathbf{A})$, of rank k and component μ that act like angular momentum operators. The Wigner-Eckart Theorem tells us how to use angular momentum algebra to couple the bra, ket, and tensor operator to make the numerical value of the matrix element, which is a scalar quantity.

We need to define the weapons of our angular momentum arsenal. 3-j coefficients tell us how to relate the coupled $|j_1,j_2,j,m_j\rangle$ and uncoupled $|j,m_1,j_2,m_2\rangle$ basis states so that we can evaluate matrix elements for either the coupled or uncoupled representation, whichever is more convenient. For example, it is more convenient to deal with the spin-orbit operator, $\mathbf{A}(\mathbf{R})\mathbf{L}\cdot\mathbf{S}$, in the coupled representation, whereas the uncoupled representation is more convenient for the Zeeman Hamiltonian

$$\mathbf{H}^{\text{Zeeman}} = -\gamma B_z(\mathbf{L}_z + 2\mathbf{S}_z).$$

Another property of the 3-j coefficients is that they relate schemes where

$$j_1 + j_2 = j$$
$$j - j_1 = j_2$$

and

$$j - j_2 = j_1.$$

This property is explored by permuting two columns of the 3-j coefficient,

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m_j \end{pmatrix}.$$

We are going to need to deal with more than two angular momenta. For example, there is the nuclear spin I of an atom or the separate nuclear spins of N nuclei in an N-atom molecule. There is also the problem of coupling the ℓ_i and s_i of individual electrons into the L and S of a many-electron atom or molecule. 3-j coefficients guide the coupling of the magnitude and the z-component of three angular momenta. 6-j coefficients, guide the coupling of 3 angular momenta $\mathbf{j}_1$, $\mathbf{j}_2$, and $\mathbf{j}_3$ into a total angular momentum,

$$\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2 + \mathbf{j}_3.$$

There are 3 ways to accomplish this:

$$\left|\left(j_1, j_2\right) j_{12}, j_3, j\right\rangle$$
$$\left|\left(j_1, j_3\right) j_{13}, j_2, j\right\rangle$$
$$\left|\left(j_2, j_3\right) j_{23}, j_1, j\right\rangle.$$

So we need j_{12}, j_{23}, and j_{13}. There are six angular momenta (d_1, d_2, d_3, j_{12}, j_{23}, j_{13}) to couple to form the total angular momentum, j. It is easily proved that the dimension of each of the three coupled basis sets is conserved. It is also possible to show that operation by $\mathbf{j}_\pm$ on the various basis sets does not depend on any of the m quantum numbers. So we have tables of 6-j coefficients that describe the relationships between the three coupled representations

$$\left|j_1, j_2, j_3\left(j_{23}\right); j\right\rangle = \sum_{j_{12}} \left|j_1, j_2\left(j_{12}\right) j_3; j\right\rangle \left\langle j_1, j_2\left(j_{12}\right) j_3; j \middle| j_1, j_2, j_3\left(j_{23}\right); j\right\rangle$$

where

$$\left\langle j_1, j_2\left(j_{12}\right) j_3; j \middle| j_1, j_2, j_3\left(j_{23}\right); j \right\rangle = (-1)^{j_1+j_2+j_3+j}\left[\left(2j_{12}+1\right)\left(2j_{23}+1\right)\right]^{1/2}\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix}.$$

The 6-j coefficients are invariant under any interchange of columns and an interchange of any 2 numbers in the bottom row with the corresponding 2 numbers in the top row

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{Bmatrix} = \begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix}$$

where the second 6-j is how the tables of 6-j coefficients are arranged. The values of the 6-j coefficients are unchanged by permutations of any two columns

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \ell_3 \end{Bmatrix} = \begin{Bmatrix} j_2 & j_1 & j_3 \\ \ell_2 & \ell_1 & \ell_3 \end{Bmatrix} = \text{etc.}$$

or interchange of any two upper and lower pairs

$$= \begin{Bmatrix} \ell_1 & \ell_2 & j_3 \\ j_1 & j_2 & \ell_3 \end{Bmatrix} = \text{etc.}$$

When there are four angular momenta, the basis set transformations are given by 9-j coefficients

$$\left|\left[j_1, j_2\left(j_{12}\right), \left(j_3, j_4\right) j_{34}\right] j\right\rangle = \sum_{j_{13}, j_{24}} \left[\left(2j_{13}+1\right)\left(2j_{24}+1\right)\left(2j_{12}+1\right)\left(2j_{34}+1\right)\right]^{1/2}\begin{Bmatrix} j_1 & j_3 & j_{13} \\ j_2 & j_4 & j_{24} \\ j_{12} & j_{34} & j \end{Bmatrix}$$

where the value of the 9-j symbol is multiplied by

$$(-1)^{j_1+j_2+j_3+j_4+j_{12}+j_{13}+j_{24}+j_{34}+j}$$

for exchange of any two rows or columns, unchanged for even permutations of rows or columns, multiplied by –1 for odd permutations of rows or columns, and unchanged by reflection about either diagonal. When one argument of a 9-j symbol is zero, we get reduction to a 6-j symbol

$$\left\{\begin{matrix} j_1 & j_3 & j_{13} \\ j_2 & j_4 & j_{24} \\ j_{12} & j_{34} & 0 \end{matrix}\right\} = \delta_{j_{13},j_{24}}\delta_{j_{12},j_{34}}\left[\left(2j_{13}+1\right)\left(2j_{12}+1\right)\right]^{-1/2}(-1)^{j_3+j_{13}+j_2+j_{12}}\left\{\begin{matrix} j_1 & j_3 & j_{13} \\ j_4 & j_2 & j_{12} \end{matrix}\right\}.$$

The 6-j and 9-j symbols are both independent of all m quantum numbers.

The Wigner-Eckart Theorem

The Wigner-Eckart Theorem is a powerful tool. It is *reductionistic* in the sense that it reduces an enormous number of angle-dependent matrix elements to a vastly smaller number of *reduced matrix elements* (independent of all projection quantum numbers). The Wigner-Eckart Theorem often guides further reduction of these reduced matrix elements into a much smaller number of structural parameters. It provides a super-highway from *description* to *insight*. It serves as a roadmap to the assembly of a complete and rigorous description of a complex web of interactions between sub-systems: a molecule and an external field, one molecule and another molecule, electrons and nuclei, inter-electronic interactions, intra-electronic interactions (e.g. spin-orbit), inter-nuclear-spin interactions,… The Wigner-Eckart Theorem suggests interpretive shortcuts. It legitimizes the "vector model". Armed with the Wigner-Eckhart Theorem, the scientist is able to recognize and exploit "regular" patterns to "assign" a spectrum and also to recognize and detect local irregularities in a pattern in order to uncover, identify, and quantitate the physical nature of a previously neglected interaction mechanism. The Wigner-Eckart Theorem is a subject worthy of a full semester graduate course as well as one that invites a lifetime of discovery of new uses for it.

Matrix Elements of a Vector Operator

In spherical tensor form a vector operator (a rank-one tensor operator) is expressed as

$$\mathbf{V}_{+1}(\mathbf{J}) = -2^{-1/2}\left(\mathbf{J}_x + i\mathbf{J}_y\right) = -2^{-1/2}\mathbf{J}_+$$
$$\mathbf{V}_0(\mathbf{J}) = \mathbf{J}_z$$
$$\mathbf{V}_{-1}(\mathbf{J}) = 2^{-1/2}\left(\mathbf{J}_x - i\mathbf{J}_y\right) = -2^{-1/2}\mathbf{J}_-$$

and the scalar product of two vector operators **A** and **B** is

$$\mathrm{V(A)\cdot V(B)} = \sum_{q=-1}^{+1}(-1)^q \mathrm{V}_q(\mathrm{A})\mathrm{V}_q(\mathrm{B}) = \mathrm{A\cdot B}$$

The Wigner-Eckart Theorem for a vector operator, **V**, that is defined by its commutation rules with components of **J**, as a vector with respect to **J**, can be reduced to

$$\left\langle \eta jm \middle| \mathbf{V}_\pm \middle| \eta jm' \right\rangle = \alpha\left(\eta, j\right)\left\langle \eta jm \middle| \mathbf{J}_\pm \middle| \eta jm' \right\rangle$$
$$\left\langle \eta jm \middle| \mathbf{V}_0 \middle| \eta jm' \right\rangle = \alpha\left(\eta, j\right)\left\langle \eta jm \middle| \mathbf{J}_z \middle| \eta jm' \right\rangle$$

or

$$\left\langle \eta jm\pm 1\left|\mathbf{V}_{\pm}\right|\eta jm'\right\rangle = \alpha\left(\eta, j\right)\hbar\left[j(j+1)-m(m\pm 1)\right]^{1/2}$$
$$\left\langle \eta jm\left|\mathbf{V}_{0}\right|\eta jm'\right\rangle = \alpha\left(\eta, j\right)\hbar m\delta_{mm'}$$

η symbolizes a collection of other identifiers of the state. The above equations are the $\Delta j = 0$ reduced set of matrix elements of **V**. Non-zero $\Delta j = \pm 1$ matrix elements are often between basis states for which $\left|E_j^{(0)} - E_{j\pm 1}^{(0)}\right| \gg V_{jm,j\pm 1m}$ (e.g. hyperfine components, a single spin-orbit component of an L–S–J state) and the effects of these $\Delta j \neq 0$ interactions are often small enough to be ignored.

One special value of this reduction to a $\Delta j = 0$ state space is the existence of "operator replacements." For example, for the Zeeman effect

$$\mathbf{H}^{\text{Zeeman}} = -\boldsymbol{\mu}_L \cdot \mathbf{B} - \boldsymbol{\mu}_S \cdot \mathbf{B}$$
$$\boldsymbol{\mu}_L = -\beta\mathbf{L},\ \ \boldsymbol{\mu}_S = -2\beta\mathbf{S}$$
$$\boldsymbol{\mu}_L = -\beta\left\langle \ell m_\ell = \ell\left|\mathbf{L}_z\right|\ell m_\ell = \ell\right\rangle = -\beta\hbar\ell$$

Similarly for $\boldsymbol{\mu}_s$ (s = 1/2 for an electron)

$$\boldsymbol{\mu}_S = -2\beta\mathbf{S} = -\beta\hbar \text{ (for s = 1/2).}$$

If the magnetic field is along the laboratory Z direction

$$\mathbf{H}^{\text{Zeeman}} = \beta B_Z(\mathbf{L}_Z + 2\mathbf{S}_Z).$$

Here is where the operator replacement trick comes in

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \equiv \mathbf{V}$$
$$\left\langle \alpha jm \,|\, \mathbf{V} \,|\, \alpha jm'\right\rangle = C\left\langle \alpha jm \,|\, \mathbf{J} \,|\, \alpha jm'\right\rangle$$

The constant C is evaluated by the following series of tricks

$$\left\langle \alpha jm \,|\, \mathbf{V}\cdot\mathbf{J} \,|\, \alpha jm\right\rangle = \sum_{m'} \left\langle \alpha jm \,|\, \mathbf{V} \,|\, \alpha jm'\right\rangle\left\langle \alpha jm' \,|\, \mathbf{J} \,|\, \alpha jm\right\rangle$$

completeness

$$= C\sum_{m'} \left\langle \alpha jm \,|\, \mathbf{J} \,|\, \alpha jm'\right\rangle\left\langle \alpha jm' \,|\, \mathbf{J} \,|\, \alpha jm\right\rangle$$
$$= C\hbar^2 j(j+1)$$
$$C = \frac{\left\langle \alpha jm \,|\, \mathbf{V}\cdot\mathbf{J} \,|\, \alpha jm\right\rangle}{\hbar^2 j(j+1)}$$

thus

$$\left\langle \alpha jm \,|\, \mathbf{V} \,|\, \alpha jm'\right\rangle = \frac{\left\langle \alpha jm \,|\, \mathbf{V}\cdot\mathbf{J} \,|\, \alpha jm\right\rangle}{\hbar^2 j(j+1)}\left\langle \alpha jm \,|\, \mathbf{J} \,|\, \alpha jm'\right\rangle$$

This formula, called the Landé formula, is a special case of the Wigner-Eckart Theorem. Now we use this formula to evaluate matrix elements of $\mathbf{H}^{\text{Zeeman}}$ in the coupled basis

$$\left\langle \ell sjm \middle| \mathbf{L}_Z + 2\mathbf{S}_Z \middle| \ell sjm \right\rangle = \frac{\left\langle \ell sjm \middle| (\mathbf{L}+2\mathbf{S})\bullet\mathbf{J} \middle| \ell sjm \right\rangle}{\hbar^2 j(j+1)} \underbrace{\left\langle \ell sjm' \middle| \mathbf{J}_Z \middle| \ell sjm \right\rangle}_{\hbar m \delta_{mm'}}$$

$$(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{J} = (\mathbf{J} + \mathbf{S}) \cdot \mathbf{J} = \mathbf{J}^2 + \mathbf{S}\cdot\mathbf{J}$$
$$\mathbf{L} = \mathbf{J} - \mathbf{S}$$
$$\mathbf{L}^2 = \mathbf{J}^2 + \mathbf{S}^2 - 2\mathbf{S}\cdot\mathbf{J}$$
$$\mathbf{S}\cdot\mathbf{J} = 1/2(\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2)$$
$$(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{J} = \mathbf{J}^2 + \mathbf{S}\cdot\mathbf{J} = 1/2[3\mathbf{J}^2 + (\mathbf{S}^2 - \mathbf{L}^2)]$$

and, at last,

$$\left\langle \ell sjm \middle| \mathbf{L}_Z + 2\mathbf{S}_S \middle| \ell sjm \right\rangle = \frac{\left\langle \ell sjm \middle| \left(\mathbf{L}+2\mathbf{S}\right)\cdot\mathbf{J} \middle| \ell sjm \right\rangle}{\hbar^2 j(j+1)} \hbar m \delta_{mm'}$$
$$= \frac{\hbar m}{j(j+1)}\left[\frac{3}{2}J(J+1) + \frac{1}{2}S(S+1) - \frac{1}{2}L(L+1)\right].$$

This gives the Landé g-factor formula

$$\mathbf{H}^{\text{Zeeman}} = B_Z \hbar M_J g_{\mathbf{LSJ}}$$
$$g_{\mathbf{LSJ}} = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}.$$

Page 1054 of CTDL derives a similar operator replacement formula called the Projection Theorem. For any vector quantity, **v**, in the body-fixed coordinate system, the projection of **v** on **j**, $\mathbf{v}_{\|}$ is conserved

$$\mathbf{v}_{\|} = \frac{\mathbf{j}\cdot\mathbf{v}}{\mathbf{j}^2}\mathbf{j}$$

or, in operator terminology

$$\mathbf{V} = \frac{\langle \eta j | \mathbf{J}\cdot\mathbf{V} | \eta j \rangle}{\hbar^2 j(j+1)}\mathbf{J}$$

This is the basis for the **vector model**, which tells us how body frame quantities, averaged over body-rotation, are communicated to the laboratory frame. The vector model is an amazingly insightful interpretive tool!

The Wigner-Eckart Theorem reduces matrix elements of a commutation-rule-classified spherical tensor operator to a reduced matrix element times a 3-*j* coefficient

$$\left\langle \eta' j' m' \middle| \mathbf{T}_q^k(\mathbf{A},\mathbf{B}) \middle| \eta j m \right\rangle = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \left\langle \alpha' j' \middle\| \mathbf{T}^k(\mathbf{A},\mathbf{B}) \middle\| \alpha j \right\rangle$$

There are several ways to evaluate the reduced matrix elements. One way, illustrated by the treatment of $\mathbf{H}^{\text{Zeeman}}$, involves tricks with reduced-validity (e.g. $\Delta j = 0$ only) replacement operators. Another more general way is to evaluate the matrix element directly for a specific choice of m, m', and q (usually "stretched state", $m = m' = j$ and $q = 0$) and then exploit the m, m', q-independence of the reduced matrix element to obtain its value from the single explicitly evaluated m, m', q-dependent matrix element.

In order to evaluate one specific matrix element of $\mathbf{T}_q^k(\mathbf{A},\mathbf{B})$ it is necessary to know how to construct "compound irreducible tensor operators." Once this is done, matrix elements of simpler $\mathbf{T}_{q'}^{k'}(\mathbf{A})$ and $\mathbf{T}_{q''}^{k''}(\mathbf{B})$ operators may be evaluated in the most convenient basis sets (obtained using 3-*j*, 6-*j*, and 9-*j* coefficients.

Compound Irreducible Tensor Operators

Let **F** be the total of all angular momenta in a system, for example in an AB diatomic molecule

$$\mathbf{F} = \mathbf{J} + \mathbf{I}_{\text{tot}} = \mathbf{R} + \mathbf{L} + \mathbf{S} + \mathbf{I}_{\text{A}} + \mathbf{I}_{\text{B}}$$

One very important insight is that, although $\mathbf{J}$, $\mathbf{I}_A$, $\mathbf{I}_B$, $\mathbf{R}$, $\mathbf{L}$, and $\mathbf{S}$ are all classified as vector operators (first rank tensor) with respect to **F**, because each operates on a different set of coordinates, $\mathbf{R}$, $\mathbf{L}$, $\mathbf{S}$, $\mathbf{I}_A$, $\mathbf{I}_B$ are all scalar operators with respect to each other. This means that a basis set $|R,L,S,I_A,I_B\rangle$ exists which is a simultaneous eigenstate of $\mathbf{R}^2$, $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{I}_A^2$, and $\mathbf{I}_B^2$. There are many choices of intermediate quantum numbers

$$\mathbf{Q} = \mathbf{S} + \mathbf{I}_{\text{tot}}, \quad \mathbf{F} = \mathbf{Q} + \mathbf{N}, \quad \mathbf{N} = \mathbf{R} + \mathbf{L}$$

and we need 6-*j* coefficients to transform among basis sets based on different sets of intermediate quantum numbers. The key point is that we have all of the tools to evaluate matrix elements for any chosen set of intermediate quantum numbers.

If we have products of two commuting angular momenta **A** and **B**, how do we construct spherical tensor operators of rank $k = 2$, 1, and 0? Rank $k = 0$ is special because the field-free Hamiltonian is a scalar ($k = 0$) operator with respect to **F**.

Suppose we have two non-communicating state spaces, 1 and 2, such as those associated with two commuting angular momenta L↔1 and S↔2.

$$\left|j_1, j_2, j, m\right\rangle = \sum_{m_1,m_2} (-1)^{j_1-j_2+m} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \left|j_1, m_1\right\rangle \left|j_2, m_2\right\rangle$$

We are interested in evaluating matrix elements of a compound spherical tensor operator. Suppose that we have a compound spherical tensor operator, $\mathbf{X}_q^k$, that is composed of a product of spherical tensor operators that operate on independent sets of variables in spaces 1 and 2:

$$\mathbf{X}_q^k\left(\mathbf{T}_{q_1}^{k_1}, \mathbf{U}_{q_2}^{k_2}\right) = \sum_{q_1,q_2} (-1)^{k_1-k_2+q} (2k+1)^{1/2} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \mathbf{T}_{q_1}^{k_1} \mathbf{U}_{q_2}^{k_2}$$

and we want to evaluate the general matrix element

$$\left\langle \eta, j_1, j_2, j, m \left| \mathbf{X}_q^k \right| \eta', j_1', j_2', j', m' \right\rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \left\langle \eta, j_1, j_2, j \left\| \mathbf{X}^k \right\| \eta', j_1', j_2', j' \right\rangle.$$

After some algebra we get, for the reduced matrix element:

$$\left\langle \eta, j_1, j_2, j \left\| \mathrm{X}^k \right\| \eta', j_1', j_2', j' \right\rangle = \left[(2j+1)(2j'+1)(2k+1)\right]^{1/2} \begin{Bmatrix} j_1 & j_1' & k_1 \\ j_2 & j_2' & k_2 \\ j & j' & k \end{Bmatrix}$$

$$\times \sum_{\eta''} \left\langle \eta, j_1 \left\| \mathrm{T}^{k_1} \right\| \eta', j_1' \right\rangle \left\langle \eta'', j_2 \left\| \mathrm{U}^{k_2} \right\| \eta', j_2' \right\rangle.$$

We have many extremely useful special cases of this general matrix element. Since the field–free Hamiltonian is a spherical tensor of rank 0, it is a scalar operator. Massive simplifications ensue for the matrix element of $\mathbf{X}_0^0$

$$\mathbf{X}_0^0 \equiv \left[\mathbf{T}^k \otimes \mathbf{U}^k\right]_0^0$$

$$\left\langle \eta, j_1, j_2, j \left\| \mathbf{X}^0 \right\| \eta', j_1', j_2', j' \right\rangle = \left\langle \eta, j_1, j_2, j \left\| \left[\mathbf{T}^k \otimes \mathbf{U}^k \right]_0^0 \right\| \eta', j_1', j_2', j' \right\rangle$$

$$= (-1)^{k+j_2+j+j_1'}(2k+1)^{-1/2}(2j+1)^{1/2} \times \begin{Bmatrix} j_1 & j_2 & j \\ j_2' & j_1' & k \end{Bmatrix} \sum_{\eta''} \left\langle \eta, j_1 \left\| \mathbf{T}^k \right\| \eta'', j_1' \right\rangle \left\langle \eta'', j_2 \left\| \mathbf{U}^k \right\| \eta', j_2' \right\rangle.$$

Rather than express $\mathbf{X}$ as $\left[\mathbf{T}^k \otimes \mathbf{U}^k\right]_0^0$, it is more transparent to express it as $\mathbf{T}^k \cdot \mathbf{U}^k$

$$\left\langle \eta, j_1, j_2, j, m \left| \mathbf{T}^k \cdot \mathbf{U}^k \right| \eta', j_1', j_2', j', m' \right\rangle = \delta_{j,j'} \delta_{m,m'} (-1)^{j_1'+j_2+j} \begin{Bmatrix} j_1 & j_2 & j \\ j_2' & j_1' & k \end{Bmatrix}$$

$$\times \sum_{\eta''} \left\langle \eta, j_1 \left\| \mathbf{T}^k \right\| \eta'', j_1' \right\rangle \left\langle \eta'', j_2 \left\| \mathbf{U}^k \right\| \eta', j_2' \right\rangle.$$

A major simplification occurs when $\mathbf{X}_q^k$ operates only on the variables in *either* space 1 or space 2. If $\mathbf{X}$ operates only on variables in space 1, $\mathbf{X}$ behaves as $\mathbf{T}_{q_1}^{k_1}$, $\mathbf{X}_q^k = \mathbf{T}_{q_1}^{k_1}$, and $\mathbf{U}_{q_2}^{k_2}$ is a constant with respect to $\mathbf{X}$, thus

$$\mathbf{U}_{q_2}^{k_2} = \mathbf{U}_0^0$$

$$\left\langle \eta, j_1, j_2, j \left\| \mathrm{T}^{k_1} \right\| \eta', j_1', j_2', j' \right\rangle$$

$$= \delta_{j_2,j_2'} (-1)^{j_1+j_2+j'+k_1} \left[(2j'+1)(2j+1) \right]^{1/2} \begin{Bmatrix} j_1 & j & j_2 \\ j' & j_1' & k_1 \end{Bmatrix} \left\langle \eta, j \left\| \mathrm{T}^{k_1} \right\| \eta', j_1' \right\rangle,$$

or, if $\mathbf{X}$ operates only on variables in space 2, $\mathbf{X}_q^k = \mathbf{U}_{q_2}^{k_2}$, then

$$\left\langle \eta, j_1, j_2, j \left\| \mathbf{U}^{k_2} \right\| \eta', j_1', j_2', j' \right\rangle = \delta_{j_1,j_1'} (-1)^{j_1+j_2'+j+k} \left[(2j'+1)(2j+1) \right]^{1/2} \begin{Bmatrix} j_2 & j & j_1 \\ j' & j_2' & k_2 \end{Bmatrix} \left\langle \eta, j_2 \left\| \mathbf{U}^{k_2} \right\| \eta', j_2' \right\rangle.$$

An Example:
Consider an example, the spin-orbit interaction for a two-electron configuration:

$$\mathbf{H}^{\mathrm{SO}} = \xi(r_1)\boldsymbol{\ell}_1 \cdot \mathbf{s}_1 + \xi(r_2)\boldsymbol{\ell}_2 \cdot \mathbf{s}_2$$

Let

$$\zeta_{n\ell;n'\ell'} \equiv \int_0^\infty R_{n\ell}(r)\xi(r)R_{n'\ell'}(r)r^2 dr$$

$$\left\langle {}^{2S+1}L_J M_J \middle| \mathbf{H}^{\mathrm{SO}} \middle| {}^{2S'+1}L'_{J'} M'_J \right\rangle = \zeta_{n_1\ell_1;n'_1\ell'_1}\delta_{JJ'}\delta_{M_J,M'_J}(-1)^{L'+S+J}\begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix}\left\langle L\|\ell_1\|L'\right\rangle\left\langle S\|s_1\|S'\right\rangle$$
$$+\zeta_{n_2\ell_2;n'_2\ell'_2}\delta_{JJ'}\delta_{M_J,M'_J}(-1)^{L'+S+J}\begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix}\left\langle L\|\ell_2\|L'\right\rangle\left\langle S\|s_2\|S'\right\rangle.$$

Now to evaluate the reduced matrix elements:

$$\left\langle \ell_1\ell_2 L\|\ell_1\|\ell'_1\ell'_1 L'\right\rangle = \left\langle L\|\ell_1\|L'\right\rangle \equiv \delta_{\ell_2,\ell'_2}(-1)^{\ell_1+\ell_2+L'+1}\left[(2L'+1)(2L+1)\right]^{1/2}\begin{Bmatrix} \ell_1 & L & \ell_2 \\ L' & \ell'_1 & 1 \end{Bmatrix}\left\langle \ell_1\|\ell_1\|\ell_1{}'\right\rangle$$

and similarly for $\left\langle L\|\ell_2\|L'\right\rangle$.

$$\left\langle s_1 s_2 S\|s_1\|s'_1 s'_2 S'\right\rangle = \left\langle S\|s_1\|S'\right\rangle \equiv \delta_{s_2 s'_2}(-1)^{S_1+S_2+S'+1}\left[(2S'+1)(2S+1)\right]^{1/2}\begin{Bmatrix} s_1 & \delta & s_2 \\ s' & s'_1 & 1 \end{Bmatrix}\left\langle s_1\|S_1\|s'\right\rangle$$

and similarly for $\left\langle S\|s_2\|S'\right\rangle$.

We know how to evaluate the reduced matrix elements

$$\left\langle L'\|L^{(1)}\|L\right\rangle = \left[(2L+1)L(L+1)\right]^{1/2}\delta_{L'L}$$
$$\left\langle S'\|S^{(1)}\|S\right\rangle = \left[(2S+1)S(S+1)\right]^{1/2}\delta_{S'S}$$

This enables us to evaluate the $\mathbf{H}^{\mathrm{SO}}$ matrix element

$$\left\langle {}^{2S+1}L_J, M_J \|\mathbf{H}^{\mathrm{SO}}\| {}^{2S'+1}L'_{J'}, M'_{J'} \right\rangle = \zeta_{n_1,\ell_1,n'_1\ell'_1}\delta_{J,J'}\delta_{M_J,M'_J}\delta_{\ell_1,\ell'_1}\delta_{\ell_2,\ell'_2}(-1)^{S+S'+J+\ell_1+\ell_2+1}$$
$$\times\left[(2L'+1)(2L+1)(2S'+1)(2S+1)(2\ell_1+1)\ell_1(\ell_1+1)(3/2)\right]^{1/2}$$
$$\times\begin{Bmatrix} L & S & J \\ S' & L' & 1 \end{Bmatrix}\begin{Bmatrix} \ell_1 & L & \ell_2 \\ L' & \ell_1 & 1 \end{Bmatrix}\begin{Bmatrix} \frac{1}{2} & S & \frac{1}{2} \\ S' & \frac{1}{2} & 1 \end{Bmatrix}$$

and a similar term for $\eta_2\ell_2 s_2$.

Many important conclusions may be drawn for $\mathbf{H}^{\mathrm{SO}}$ expressed in this rigorous and universal way:

1. Selection rules: $\Delta S = 0, \pm 1$, $\Delta L = 0, \pm 1$

2. Within a ${}^{2S+1}L$ multiplet state

$$E({}^{2S+1}L_J) - E({}^{2S+1}L_{J-1}) = AJ \text{ (A is the spin-orbit constant)},$$

which is the Landé interval rule.

3. When either L = 0 or S = 0, there is no spin-orbit splitting
4. Spin-orbit perturbations between two L–S–J states follow a $\Delta J = 0$ selection rule.
5. A single $\zeta_{n\ell}$ parameter characterizes all of the spin-orbit splittings and off-diagonal matrix elements within a given $(n\ell)^p$ configuration.