5.74 RWF Lecture #4

The Wigner-Eckart Theorem

It is always possible to evaluate the angular (universal) angular part of all matrix elements, leaving behind a (usually) unevaluated radial integral. Unfortunately (as in the separation of the hydrogen atom wavefunction into angular and radial factors), the radial factor depends on the values of angular momentum magnitude quantum numbers, but not angular momentum projection quantum numbers. The Wigner-Eckart Theorem provides an automatic way of evaluating the angular parts of matrix elements of many important types of operators. The radial factor is called a "reduced matrix element." Often, explicit relationships between many reduced matrix elements may be derived by multiple applications of the Wigner-Eckart Theorem or by evaluating the matrix element directly for one extreme set of quantum numbers ("stretched state") where one unique basis state in one basis is by definition identical to one unique basis state in a different basis set.

The Wigner-Eckart theorem applies to systems which have lower than spherical (atoms) or cylindrical (linear molecules) symmetry. Any symmetry at all will suffice.

It is essential to express all operators in spherical tensor form. It will become clear that the same operator may be expressed in several different spherical tensor forms. These are useful for evaluation of reduced matrix elements.

The central idea is that operators are classified according to their transformation properties under rotation. The same transformations (Wigner rotation matrices) describe the transformation properties of angular momenta. The Wigner-Eckart Theorem may be viewed as a generalization of the coupling of separate $|AM_A\rangle$ and $|BM_B\rangle$ angular momentum basis states to form coupled $|ABCM_C\rangle$ basis states.

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

The 3-j coefficient is what you would expect for coupling $\left| j_1 = j', m_{j_1} = m'_j \right\rangle$ to $\left| j_2 = k, m_{j_2} = q \right\rangle$ to form $\left| j_3 = j, m_{j_3} = m_j \right\rangle$. The factor with the two pairs of vertical lines is called a reduced matrix element. *It does not depend on m, m'_j, or q!*

For examples (the matrix elements of the $q = 0$ operator component are always easiest to evaluate, especially when one chooses an $m_j = j$ basis state):

$$\begin{aligned} \mathbf{T}_0^1(\mathbf{j}) &= \mathbf{j}_z \\ \mathbf{T}_0^0(\mathbf{j},\mathbf{j}) &= \mathbf{j}^2 \\ \mathbf{T}_0^2(\mathbf{j},\mathbf{j}) &= 6^{-1/2}\left(3\mathbf{j}_z^2 - \mathbf{j}^2\right). \end{aligned}$$

Using the W-E theorem

$$\left\langle jm_j \, \mathbf{T}_0^1(\mathbf{j}) \, j'm'_j \right\rangle = (-1)^{j-m} \begin{pmatrix} j & 1 & j' \\ -m_j & 0 & m'_j \end{pmatrix} \left\langle j \, \mathbf{T}^1(\mathbf{j}) \, j' \right\rangle,$$

but we also know

$$\left\langle jm_j \left| \mathbf{j}_z \right| j'm'_j \right\rangle = \delta_{jj'}\delta_{m_j m'_j} m_j.$$

Thus, using the analytical expression for the 3-j coefficient

$$\begin{pmatrix} j & 1 & j \\ -m_j & 0 & m_j \end{pmatrix} = (-1)^{j-m_j} m_j \left[j(j+1)(2j+1) \right]^{-1/2},$$

we evaluate the reduced matrix element:

$$\left\langle j \, \mathbf{T}^1(\mathbf{j}) \, j' \right\rangle = \delta_{jj'} \left[j(j+1)(2j+1) \right]^{1/2}.$$

Another example:

$$\left\langle jm_j\left|\mathbf{T}_0^0(\mathbf{j},\mathbf{j})\right|j'm_j'\right\rangle = (-1)^{j-m}\begin{pmatrix} j & 0 & j' \\ -m_j & 0 & m_j' \end{pmatrix}\left\langle j\left\|\mathbf{T}^0(\mathbf{j})\right\|j\right\rangle$$

$$= (-1)^{j-m}\delta_{jj'}\delta_{m_j m_j'}\begin{pmatrix} j & 0 & j \\ -m_j & 0 & m_j \end{pmatrix}\left\langle j\left\|\mathbf{T}^0(\mathbf{j})\right\|j\right\rangle$$

But $\begin{pmatrix} j & 0 & j \\ -m_j & 0 & m_j \end{pmatrix} = (-1)^{j-m}(2j+1)^{1/2}$

thus

$$\left\langle jm_j\left|\mathbf{T}_0^0(\mathbf{j},\mathbf{j})\right|j'm_j'\right\rangle = \delta_{jj'}\delta_{m_j m_j'}(2j+1)^{1/2}\left\langle j\left\|\mathbf{T}^0(\mathbf{j},\mathbf{j})\right\|j\right\rangle.$$

But, when the matrix element is evaluated directly, we have

$$\left\langle jm_j\left|\mathbf{j}^2\right|j'm_j'\right\rangle = \delta_{jj'}\delta_{m_j m_j'}j(j+1),$$

thus

$$\left\langle j\left\|\mathbf{T}_0^0(\mathbf{j},\mathbf{j})\right\|j\right\rangle = (2j+1)^{-1/2}j(j+1).$$

You should show that

$$\left\langle j\left\|\mathbf{T}^2(\mathbf{j},\mathbf{j})\right\|j'\right\rangle = \delta_{jj'}24^{-1/2}\left[(2j-1)2j(2j+1)(2j+2)(2j+3)\right]^{1/2}.$$

Next we have an extremely useful result, the operator replacement theorem, which is used to replace the exact operator, for which the matrix elements are unfamiliar or tedious to evaluate, by a simpler operator. This operator replacement is only valid for restricted conditions.

The operator replacement theorem:

$$\left\langle njm_j\left|\mathbf{T}_p^k(\mathbf{S})\right|n'j'm_j'\right\rangle = \frac{\left\langle nj\left\|\mathbf{T}^k(\mathbf{S})\right\|n'j'\right\rangle}{\left\langle nj\left\|\mathbf{T}^k(\mathbf{R})\right\|n'j'\right\rangle}\left\langle njm_j\left|\mathbf{T}_p^k(\mathbf{R})\right|n'j'm_j'\right\rangle.$$

This implies that the matrix elements of the "difficult" operator, $\mathbf{T}_p^k(\mathbf{S})$, are proportional to those of the "easy" operator, $\mathbf{T}_p^k(\mathbf{R})$. This is especially useful when **R** = **j**, because matrix elements of any $\mathbf{T}_p^k(\mathbf{j})$ in

the $\left|njm_j\right\rangle$ basis are diagonal in *j* and all $\left\langle nj\left\|\mathbf{T}^k(\mathbf{j})\right\|nj\right\rangle$ are known. This operator replacement, however, can only be used for $\Delta j = 0$ matrix elements of $\mathbf{T}^k_p(\mathbf{S})$.

Derivation of standard operator replacement for $\mathbf{H}^{SO}$:

$$\mathbf{H}^{SO} = \sum_i \xi(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i \qquad \text{sum is over spin-orbitals.}$$

This is a very inconvenient form for evaluating matrix elements of many-electron basis states.

$$\left\langle JLSM_J \sum_i \zeta(r_i)\ell_i \cdot s_i \, J'L'S' \quad J' \right\rangle =$$

$$\sum_i \sum_{J''L''S''} \sum_{J''} \left\langle JLSM_J \, \zeta(r_i)\ell_i \cdot s_i \, \underbrace{J''L''S'' \quad J''\rangle\langle J''L''S'' \quad J''}_{\text{completeness}} \mathbf{s}_i \, J'L'S' \quad J' \right\rangle.$$

For every value of *i*, the operator $\xi(r_i)\boldsymbol{\ell}_i$ satisfies the commutation rule definition of a $\mathbf{T}^1_q$ vector operator with respect to **L** and **J** and the operator $\mathbf{s}_i$ satisfies the definition of $\mathbf{T}^1_q$ with respect to **S** and **J**. So we can use the operator replacement theorem twice

$$\left\langle JLSM_J \left|\mathbf{H}^{SO}\right| J'L'S' \quad J' \right\rangle = \sum_i \sum_{J''L''S''} \sum_{J''} \left[\frac{\left\langle JLS\left\|\xi(r_i)\ell_i\right\|J''L''S''\right\rangle}{\left\langle JLS\|\mathbf{L}\|J''L''S''\right\rangle} \frac{\left\langle J''L''S''\left\|\mathbf{s}_i\right\|J'L'S'\right\rangle}{\left\langle J''L''S''\|\mathbf{S}\|J'L'S'\right\rangle} \right]$$

$$\times \quad \left\langle JLSM_J|\mathbf{L}|J''L''S'' \quad J''\right\rangle \cdot \left\langle J''L''S'' \quad J''|\mathbf{S}|J'L'S' \quad J'\right\rangle.$$

The components of the operators **L** and **S** are all diagonal in the *L* and *S* quantum numbers, which means that the operator replacement is only valid for $\Delta L = \Delta S = 0$ matrix elements of $\mathbf{H}^{SO}$. The product of ratios of reduced matrix elements collapses to a single constant because the cofactor of the term in [ ] is independent of *i* and we can carry out the completeness sum to contract the matrix element to its nearly final form:

$$\left\langle JLSM_J \, \mathbf{H}^{SO} \, J'LS \quad J' \right\rangle = \zeta(nLS)\left\langle JLSM_J \, \mathbf{L}\cdot\mathbf{S} \, J'LS \quad J' \right\rangle$$

where

$$\zeta(NLS) \equiv \sum_i \sum_{J''} \frac{\left\langle JLS\left\|\xi(r_i)\ell_i\right\|J''LS\right\rangle}{\left\langle JLS\|\mathbf{L}\|J''LS\right\rangle} \frac{\left\langle J''LS\left\|\mathbf{s}_i\right\|J'LS\right\rangle}{\left\langle J''LS\|\mathbf{S}\|J'LS\right\rangle}.$$

However, since $\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}[\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2]$, which is diagonal in J and M_J,

$$\left\langle JLSM_J \middle| \mathbf{H}^{SO} \middle| JLSM_J \right\rangle = \zeta(nLS)\left\langle JLSM_J \middle| \mathbf{L}\cdot\mathbf{S} \middle| JLSM_J \right\rangle$$
$$= \frac{1}{2}\zeta(nLS)\left[J(J+1) - L(L+1) - S(S+1)\right].$$

This is a reduced, but extremely convenient form of $\mathbf{H}^{SO}$. It does not tell us how to evaluate $\Delta L = \pm 1$, $\Delta S = \pm 1$ matrix elements, but we do not need to know about those matrix elements when the energy separation between different L–S terms is much larger than the spin-orbit splittings of each L–S term into its J components.

Now we want to use the W-E theorem to evaluate the reduced matrix elements of composite systems. The $\mathbf{H}^{SO}$ case was an example of a composite system.

Case (i). An operator is a sum of operators, each one operating on a different angular momentum, electron, or atom. We are interested only in matrix elements of the system 1 operator.

$j = j_1 + j_2$
$j_1 j_2 J M_J \rangle$
$\mathbf{T}_q^k(\mathbf{A}_1)$ $\mathbf{A}_1$ operates only on system 1.

Evaluate in the coupled representation:

$$\left\langle j_1 j_2 J M_J \, \mathbf{T}_q^k(\mathbf{A}_1) \, j_1' j_2' J' M_J' \right\rangle = (-1)^{J - M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M_J' \end{pmatrix} \left\langle j_1 j_2 J \, \mathbf{T}^k(\mathbf{A}_1) \, j_1' j_2' J' \right\rangle.$$

Now evaluate the same matrix element by transforming to the uncoupled representation. This generates a separated subsystem reduced matrix element

$$\left\langle j_1 j_2 J M_J \, \mathbf{T}_q^k(\mathbf{A}_1) \, j_1' j_2' J' M_J' \right\rangle = \sum_{m_1, m_2, m_1'} \delta_{j_2 j_2'} \delta_{m_2 m_2'} (-1)^{j_1 - m_1}$$
$$\times \left\langle j_1 j_2 m_1 m_2 \,|\, J M_J \right\rangle \left\langle j_1' j_2' m_1' m_2' \,|\, J M_J \right\rangle \begin{pmatrix} j_1 & k & j_1' \\ -m_1 & q & m_1' \end{pmatrix} \left\langle j_1 \, \mathbf{T}^k(\mathbf{A}_1) \, j_1' \right\rangle.$$

Thus we obtain a relationship between the coupled and uncoupled basis reduced matrix elements.

$$\left\langle j_1 j_2 J \middle\| \mathbf{T}^k(\mathbf{A}_1) \middle\| j_1' j_2' J' \right\rangle = \delta_{j_2 j_2'} (-1)^{j_1'+j_2+J'+k} \left[(2J+1)(2J'+1)\right]^{1/2}$$
$$\times \begin{Bmatrix} j_1' & J' & J \\ J & j_1 & k \end{Bmatrix} \left\langle j_1 \middle\| \mathbf{T}^k(\mathbf{A}_1) \middle\| j_1' \right\rangle.$$

The uncoupled basis reduced matrix elements are more fundamental, but the coupled basis reduced matrix elements are more convenient to use. This is highly relevant to your ^{137}Ba *sd*→*pd* transition moment homework problem.

Examples: (i) expectation values of $\ell_+(1)\ell_-(1)$ in a t=0 non-eigenstate pluck of a two-electron atom.

(ii) transition moment (rank 1) in a two-electron atom: do this.

$$\left\langle \ell_1 \ell_2 L M_L \middle| \mathbf{T}^1_q(\boldsymbol{\mu}(1)) \middle| \ell'_1 \ell'_2 L' \quad {}'_L \right\rangle =$$
$$(-1)^{L-M_L} \begin{pmatrix} L & 1 & L' \\ -M_L & q & M'_L \end{pmatrix} \left\langle \ell_1 \ell_2 L \middle| \mathbf{T}^k(\boldsymbol{\mu}(1)) \middle| L' \ell'_1 \ell'_2 \right\rangle$$

* We see only $L - L' = \pm 1, 0$, $M_L - M'_L = q$.
* We get a different phenomenological transition moment for each ℓ'_1, ℓ'_2, L'.
* We do not get a $\Delta\ell_2$ selection rule.

Now use reduction to single-orbital reduced matrix element

$$\left\langle \ell_1 \ell_2 L M_L \middle| \mathbf{T}^1_q(\boldsymbol{\mu}(1)) \middle| \ell'_1 \ell'_2 L' \quad {}'_L \right\rangle =$$
$$(-1)^{L-M_L} \begin{pmatrix} L & 1 & L' \\ -M_L & q & M'_L \end{pmatrix} \delta_{\ell_2 \ell'_2} (-1)^{\ell'_1+\ell_2+L'+k} \left[(2L+1)(2L'+1)\right]^{1/2}$$
$$\begin{Bmatrix} \ell'_1 & L' & L \\ L & \ell_1 & k \end{Bmatrix} \underbrace{\left\langle \ell_1 \middle| \mathbf{T}^k(\boldsymbol{\mu}(1)) \middle| \ell'_1 \right\rangle}_{\substack{\text{single spin-orbital} \\ \text{reduced matrix} \\ \text{element}}}$$

* $\Delta\ell_2 = 0$, selection rule
* all L' of $\ell_1 - \ell'_1$ transition related to single spin-orbital reduced matrix element

Hidden Redundancy in Spectroscopy

Silly example of $^{17}O\ p^4(^3P) \rightarrow p^3d$

$I = 5/2$

ground state of O_2 is $^3P_2$

p^3d configuration has $[^4S]\ ^3D,\ ^5D$

$[^2D]\ ^1S, ^3S, ^1P, ^3P, ^1D, ^3D, ^1F, ^3F, ^1G, ^3G$

$[^2P]\ ^1P, ^3P, ^1D, ^3D, ^1F, ^3F$

total degeneracy (excluding $I = 5/2$) 200

total degeneracy (including $I = 5/2$) 1200

38 values of J

18 L–S multiplet states

18 different $\zeta(N,L,S)$ spin orbit constants

only 2 values of ζ_{2p} and ζ_{nd}

1 $\langle p|r|d\rangle$ determines 18 transition moments (6 are non-zero)

4 magnetic hf parameters (two $\ell \cdot I$, two $\mathbf{s} \cdot I$) determine hf in 38 J states

The atomic orbital electronic parameters exhibit explicit n-scaling. The many electron parameters conceal this fundamental simplicity.

Case (ii) An operator is a product of two operators, each one acting on a different sub-system. We are going to want to relate reduced matrix elements of the composite operator, $\mathbf{T}_q^K\left[\mathbf{T}^{k_1}(\mathbf{A}_1),\mathbf{T}^{k_2}(\mathbf{A}_2)\right]$, and the sub-system operators, $\mathbf{T}_{q_1}^{k_1}(\mathbf{A}_1)$ and $\mathbf{T}_{q_2}^{k_2}(\mathbf{A}_2)$,

$$\left\langle j_1 j_2 J\middle|\mathbf{T}^K\left[\mathbf{T}^{k_1}(\mathbf{A}_1),\ \mathbf{T}^{k_2}(\mathbf{A}_2)\right]\middle|j_1' j_2' J'\right\rangle = \left[(2J+1)(2k+1)(2J'+1)\right]^{1/2}\begin{Bmatrix} j_1' & j_2' & J' \\ k_1 & k_2 & K \\ j_1 & j_2 & J \end{Bmatrix}$$
$$\times\ \left\langle j_1\middle\|\mathbf{T}^{k_1}(\mathbf{A}_1)\middle\|j_1'\right\rangle\left\langle j_2\middle\|\mathbf{T}^{k_2}(\mathbf{A}_2)\middle\|j_2'\right\rangle.$$

The 9-j coefficient results from the transformation between the $\left((j_1',j_2')J',(k_1,k_2)K\right)J$ coupling scheme to the $\left((j_1',k_1)j_1,(j_2',k_2)j_2\right)J$ coupling scheme.

Example: off-diagonal matrix elements of a$I\cdot S$

$$\mathbf{I}+\mathbf{S}=\mathbf{G}$$
$$I\cdot G = T^0\left[T^1(I),T^1(S)\right]$$
$$\left\langle ISG\middle|T^K\left[T^1(I),T^1(S)\right]\middle|IS'G'\right\rangle$$
$$= \left[(2G+1)(3)(2G'+1)\right]^{1/2}\begin{Bmatrix} I & S' & G' \\ 1 & 1 & 0 \\ I & S & G \end{Bmatrix}$$
$$\left\langle I\middle\|T^1(I)\middle\|I\right\rangle\left\langle S\middle\|T^1(S)\middle\|S'\right\rangle.$$

This is a silly example because I cannot change for an atom and $\left\langle\mathbf{S}\middle\|\mathbf{T}^1(\mathbf{S})\middle\|\mathbf{S}'\right\rangle = \left\langle\mathbf{S}\middle\|\mathbf{T}^1(\mathbf{S})\middle\|\mathbf{S}\right\rangle\delta_{ss'}$.

A much better example would be an interaction between 2 rank 2 (quadrupolar) quantities.

Case (iii) An operator is a composite of two operators, both of which operate on part 1 of a 1,2 coupled scheme. We need the relationship between the $\mathbf{T}^{\mathrm{k}}(\mathbf{A}_1,\mathbf{B}_1)$ and $\mathbf{T}^{k_1}(\mathbf{A}_1)$, $\mathbf{T}^{k_2}(\mathbf{B}_1)$ reduced matrix elements,

$$\mathbf{T}_Q^K(A_1,B_1) \equiv (-1)^{k_1-k_2+Q}(2K+1)^{1/2}\sum_{q_1 q_2}\begin{pmatrix} k_1 & k_2 & K \\ q_1 & q_2 & -Q \end{pmatrix}\times\mathbf{T}_{q_1}^{k_1}(\mathbf{A}_1)\mathbf{T}_{q_2}^{k_2}(\mathbf{B}_1).$$

The relationship between reduced matrix elements, obtained by applying the Wigner-Eckart Theorem to both sides of the above operator-uncoupling equation and inserting completeness between $\mathbf{T}^{k_1}_{q_1}(\mathbf{A}_1)$ and $\mathbf{T}^{k_2}_{q_2}(\mathbf{B}_1)$, is

$$\left\langle nJ\left\|\mathbf{T}^K(\mathbf{A}_1,\mathbf{B}_1)\right\|n'J'\right\rangle = (2K+1)^{1/2}(-1)^{K+J+J'} \times \sum_{n''J''} \begin{Bmatrix} k_1 & k_2 & K \\ J' & J & J'' \end{Bmatrix} \left\langle nJ\left\|\mathbf{T}^{k_1}(\mathbf{A}_1)\right\|n''J''\right\rangle \left\langle n''J''\left\|\mathbf{T}^{k_2}(\mathbf{B}_1)\right\|n'J'\right\rangle$$

$\mathbf{H}^{\mathrm{SO}} = \sum_i \xi(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i$ has the form of $\sum_i \mathbf{T}^K(\boldsymbol{\ell}_i,\mathbf{s}_i)$ where $K = 0$ ($\boldsymbol{\ell}\cdot\mathbf{s}$ is a scalar operator with respect to *j*).

Anomalous Commutation Rules and Consequences

The normal commutation rule, which we use to define an angular momentum, is

$$[J_I, J_J] = i\hbar \sum_K \varepsilon_{IJK} J_K .$$

This applies only to laboratory fixed components. It is necessary to derive the commutation rules for the molecule fixed coordinate system. Some surprises result!

The spherical tensors associated with lab fixed angular momentum components are

$$\mathbf{T}^1_{P=0}[\mathbf{J}] = \mathbf{J}_Z$$
$$\mathbf{T}^1_{P=\pm1}[\mathbf{J}] = \mp 2^{-1/2}(\mathbf{J}_X \pm i\mathbf{J}_Y).$$

You know all of the matrix elements of $\mathbf{T}^1_P[\mathbf{J}]$ on $|JM\rangle$.

However, when the commutation rules for molecule fixed angular mometum components are derived, we find

$$[J_i, J_j] = -i\hbar \sum_k \varepsilon_{ijk} J_k .$$

This turns out to imply that

$$\mathbf{J}_{\pm}|J\Omega M\rangle = \hbar\left[J(J+1) - M(M\mp 1)\right]^{1/2}|J\Omega \mp 1 M\rangle$$

$\mathbf{J}_{\pm}$ acts as a lowering operator.

This anomalous behavior applies for **J, N = J – S, R = J – L – S** but not for **L, S**.

We must be careful about how we construct molecule-fixed spherical tensor operators out of **J**. They do not have the expected form. To find out what form they do have, it is necessary to transform between molecule and lab-fixed systems. We get a useful redefinition of molecule fixed components of **J**.

$$\mathbf{J}_q \equiv \sum_P (-1)^P \mathbf{T}^1_P(\mathbf{J}) \mathscr{D}^{(1)}_{-Pq}(\omega)^*$$

$$\left\langle J\Omega M\middle|\mathbf{J}_q\middle|J'\Omega' M'\right\rangle = (-1)^{J-\Omega}\begin{pmatrix} J & 1 & J \\ -\Omega & q & \Omega' \end{pmatrix}\left[J(J+1)(2J+1)\right]^{1/2}\delta_{JJ'}\delta_{mm'}$$

$q = 0$	$\Omega = \Omega'$	
$q = 1$	$+2^{1/2}\,[J(J+1) - \Omega(\Omega+1)]^{1/2}$	$\Omega - \Omega' = 1$
$q = -1$	$-2^{-1/2}[J(J+1) - \Omega(\Omega-1)]^{1/2}$	$\Omega - \Omega' = -1$

which is the naively expected form for matrix elements of raising and lowering operators.

When we form a scalar product with this form of **J** and other normal operators, we must remember to write

$$\mathbf{J}\cdot\mathbf{P} = \sum_k \mathbf{J}_q \mathbf{T}^1_q[\mathbf{P}]$$

rather than the usual expression for a scalar product of two $\mathbf{T}^1$ operators,

$$\mathbf{T}^k(\mathbf{A})\mathbf{T}^k(\mathbf{B}) = \sum_{p=-k}^{k} (-1)^P \mathbf{T}^k_p(\mathbf{A})\mathbf{T}^k_{-p}(\mathbf{B}).$$