Review of Wigner Eckart theorem:

Formal Statement: given eigenstates of angular momentum J^2 : $|\beta J m\rangle, |\beta' J' m'\rangle$ and a spherical tensor operator T_q^k

$$\boxed{\langle \beta J m | T_q^k | \beta' J' m' \rangle = \frac{\langle \beta J \| T^k \| \beta' J' \rangle}{\sqrt{2J+1}} \langle J' m' ; k q | J m \rangle}$$

This is a statement about rotational symmetry of real space & Hilbert space:

must be related.

$$\left\{ \begin{array}{l} T_q^k \xrightarrow{\text{rotation in real space}} R(T_q^k) \rightarrow \text{new set of operators} \\ |\beta J m\rangle \xrightarrow{\text{rotation of Hilbert space}} R(|\beta J m\rangle) \rightarrow \text{new set of states.} \end{array} \right.$$

examples: look at the matrix formed by:

$$\frac{\langle J' m' ; k q | J m \rangle}{\sqrt{2J+1}}$$

Note: One should be careful, because different authors factor out $\frac{1}{\sqrt{2J'+1}}$, $\frac{1}{\sqrt{2J+1}}$ or nothing in the W-E theorem.

This leads to different values of $\langle \beta J \| T^k \| \beta' J' \rangle$ that are definition dependent.

two rules that help keep things straight:

Always True

$$\left| \langle \beta J M | T_q^k | \beta' J' M' \rangle \right| = \left| \langle \beta' J' M' | T_q^k | \beta J M \rangle \right| \Big\} \; T^k \text{ is Hermitian}$$

and

$$\left| \frac{\langle J M ; k q | J' M' \rangle}{\sqrt{2J'+1}} \right| = \left| \frac{\langle J' M' ; k (-q) | J M \rangle}{\sqrt{2J+1}} \right| \Big\} \; \text{property of Clebsch Gordan coefficients.}$$

In the different definitions, then, the reduced matrix elements have different ratios, depending on definition.

$$\frac{\langle \beta J \| T^k \| \beta' J' \rangle}{\langle \beta' J' \| T^k \| \beta J \rangle} = 1, \left(\frac{2J'+1}{2J+1} \right), \text{ or } \frac{\sqrt{2J'+1}}{\sqrt{2J+1}}$$

$2J+1$ is just the degeneracy of a J state

Example: a vector operator is a collection of 3 operators, (3)
acting on a Hilbert space of size $2J+1$: $\hat{T}_q^{k=1} \equiv \hat{V}_q$

Take $J=1$, 3 states $|J,m\rangle$

$$\begin{pmatrix} |1,-1\rangle \\ |1,0\rangle \\ |1,1\rangle \end{pmatrix}$$

Look at just the matrix of C-G coefficients. $\dfrac{\langle Jm'; 1q | Jm\rangle}{\sqrt{2J+1}}$

$$\hat{V}_{-1} \propto \underbrace{\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix}}_{\text{lowering}} \qquad \hat{V}_{+1} \propto \underbrace{\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}}_{\text{raising} \uparrow} \qquad \hat{V}_0 \propto \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{V}_x = -\frac{V_{+1} + V_{-1}}{\sqrt{2}} \qquad \hat{V}_y = \frac{(V_{+1} + V_{-1})}{\sqrt{2}} i \qquad \hat{V}_z = \hat{V}_0$$

$$\hat{\vec{V}} \propto \left[\underbrace{\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}}_{J_x} \hat{x} + \underbrace{\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}}_{J_y} \hat{y} + \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{J_z} \hat{z} \right]$$

<u>ANY</u> vector operator acting on $J=1$ states must have this form.

This is a specific case of a specific case of the W-E theorem.

The projection theorem: for $J = J'$, $T_q^{k=1} \Rightarrow \hat{\vec{V}}$ vector operator

$$\langle Jm' | \hat{\vec{V}} | Jm\rangle = \frac{\langle J m{=}0 | \hat{\vec{V}} \cdot \hat{\vec{J}} | J m{=}0\rangle}{\hbar^2 J(J+1)} \langle Jm' | \hat{\vec{J}} | Jm\rangle$$

can use any m state, choose $m=0$.

Example 2: a vector operator $\hat{\vec{V}}$ which connects different J states $J=0$, $J'=1$ with Hilbert spaces of $1+3=4$ states total:

$$\begin{pmatrix} |0,0\rangle \\ |1,-1\rangle \\ |1,0\rangle \\ |1,1\rangle \end{pmatrix} \begin{matrix} J=0 \\ \left.\begin{matrix} \\ \\ \\ \end{matrix}\right\} J=1 \end{matrix}$$

For simplicity in the example, assume $\langle J|\hat{\vec{V}}|J\rangle = 0 \quad \langle J'|\hat{\vec{V}}|J'\rangle = 0$

W-E gives
$$\frac{\langle 00;1q|1m\rangle}{\sqrt{2J'+1}} = \frac{1}{\sqrt{3}}\delta_{qm}$$

$$\frac{\langle 1m;1(-q)|00\rangle}{\sqrt{2J+1}} = \frac{1}{\sqrt{3}}(-1)^m\delta_{qm}$$

$$V_{-1} \propto \left(\begin{array}{c|ccc} 0 & 0 & 0 & 1 \\ \hline -1 & & & \\ 0 & & 0 & \\ 0 & & & \end{array}\right) \quad V_{+1} \propto \left(\begin{array}{c|ccc} 0 & 1 & 0 & 0 \\ \hline 0 & & & \\ 0 & & 0 & \\ 1 & & & \end{array}\right) \quad V_0 = \left(\begin{array}{c|ccc} 0 & 0 & 1 & 0 \\ \hline 0 & & & \\ 1 & & 0 & \\ 0 & & & \end{array}\right)$$

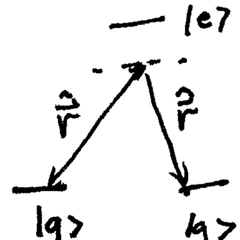
$$\hat{\vec{V}} \propto \frac{1}{\sqrt{2}}\left(\begin{array}{c|ccc} 0 & -1 & 0 & 1 \\ \hline -1 & & & \\ 0 & & 0 & \\ 1 & & & \end{array}\right)\hat{x} + \frac{1}{\sqrt{2}}\left(\begin{array}{c|ccc} 0 & i & 0 & -i \\ \hline -i & & & \\ 0 & & 0 & \\ i & & & \end{array}\right)\hat{y} + \left(\begin{array}{c|ccc} 0 & 0 & 1 & 0 \\ \hline 0 & & & \\ 1 & & 0 & \\ 0 & & & \end{array}\right)\hat{z}$$

$\rightarrow$ no matter what the physical cause of the vector operator $\vec{V}$ is!

Example 3: Second order dipole matrix coupling:

imagine a ground state $|J\rangle$ coupled to itself in second order by a dipole matrix element:

$$\sum_i \frac{\vec{E}^* \cdot \hat{\vec{r}}\, |i\rangle\langle i|\, \hat{\vec{r}} \cdot \vec{E}}{E_0 - E_i}$$



This can be written in terms of a dyadic (a second rank tensor)

$$\hat{M} = \vec{E}^* \cdot \hat{\vec{D}}\hat{\vec{D}} \cdot \vec{E}, \quad \text{where } \hat{\vec{D}} = \sum_{ij} \langle i|\hat{\vec{r}}|j\rangle\, |i\rangle\langle j|$$

($\langle i|\hat{\vec{r}}|j\rangle = 0$ unless opposite parity)

$\hat{\vec{D}}\hat{\vec{D}}$ is a reducible tensor, it can be written as a sum of three parts that rotate like a scalar, a vector, and an irreducible tensor

$\alpha, \beta = x, y$ or z

$$\vec{E}^* \cdot \hat{\vec{D}}\hat{\vec{D}} \cdot \vec{E} = \underbrace{\frac{|E|^2 |\hat{\vec{D}}|^2}{3}}_{E^0 T^0} + \underbrace{\frac{1}{2}(\vec{E}^* \times \vec{E}) \cdot (\hat{\vec{D}} \times \hat{\vec{D}})}_{\sum_q (-1)^q E^1_{-q} T^1_q} + \underbrace{\sum_{\alpha\beta} \left(E^*_\alpha E_\beta \frac{\hat{D}_\alpha \hat{D}_\beta + \hat{D}_\beta \hat{D}_\alpha}{2} - \frac{|E|^2 |D|^2 \delta_{\alpha\beta}}{3} \right)}_{\sum_q (-1)^q E^2_{-q} T^2_q}$$

Take $J=1$ example, linearly polarized light along $\hat{z}$

$E_z \neq 0 \quad E_x, E_y = 0$ pick out the one component of T^2_q, $q=0$

For arbitrary J

$$T^2_0 = \hat{D}_z \hat{D}_z - \frac{|\hat{D}|^2}{3} = \frac{2}{3} D_z D_z$$

$$D_{zz} \propto \frac{3m^2 - J(J+1)}{J(2J-1)}$$

using $\langle Jm; 20 | Jm \rangle$

$$T_0^2 \propto \begin{pmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

depends on m^2 compare to vector shifts

Back to multi-electrons & spin orbit:

take the common case $H_{re} >> H_{so}$

$|L M_L S M_s\rangle$ are good zeroth order states.

$$H_{so} = \sum_i \beta_i \vec{s}_i \cdot \vec{l}_i \xrightarrow{} \text{individual electrons.}$$

is a perturbation.

from the projection theorem,

$$\hat{\vec{s}}_i = \frac{\langle \| \vec{s}_i \cdot \vec{S} \| \rangle}{\hbar^2 S(S+1)} \hat{\vec{S}}$$

$$\hat{\vec{l}}_i = \frac{\langle \| \vec{l}_i \cdot \vec{L} \| \rangle}{\hbar^2 L(L+1)} \hat{\vec{L}}$$

true if $\vec{L}$ & $\vec{S}$ are eigenstates of angular momentum

$$H_{so} = \beta_{so} \hat{\vec{S}} \cdot \hat{\vec{L}} \quad , \quad \beta_{so} = \sum_i \beta_i \frac{\langle \| \vec{s}_i \cdot \vec{S} \| \rangle \langle \| \vec{l}_i \cdot \vec{L} \| \rangle}{\hbar^2 S(S+1)\, \hbar^2 L(L+1)}$$

Now we can treat it just like the Hydrogen case, except that $\vec{S}$ & $\vec{L}$ are total angular momentum

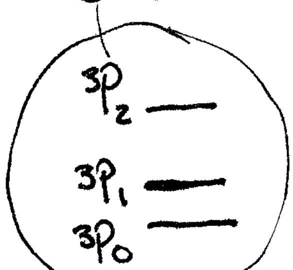
$$[H_{so}, L] \neq 0$$
$$[H_{so}, S] \neq 0$$

$$\langle H_{so} \rangle = \frac{\beta_{so}\hbar^2}{2}\Big(J(J+1) - S(S+1) - L(L+1) \Big) \qquad [H_{so}, J] = 0$$

$J \rightarrow$ eigenstates.

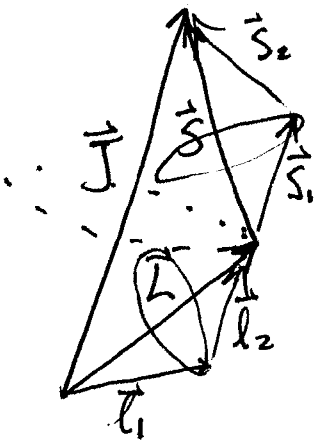
example

He $1s2p$ $^3P_{0,1,2}$ $\quad S=1 \;\; L=1 \quad J = 0, 1, 2$



relative spacing 2 to 1

Classical Vector picture.



$\vec{l}_1, \vec{l}_2$ are strongly coupled, so they precess rapidly around $\vec{L}$, so the average value of $\langle \vec{l}_i \rangle = \frac{\langle \vec{l} \cdot \vec{L} \rangle \vec{L}}{L^2}$

same argument for $\vec{S}_i$

the spin orbit then couples $\vec{L}$ to $\vec{S}$, so they precess but more slowly due to the weaker interaction

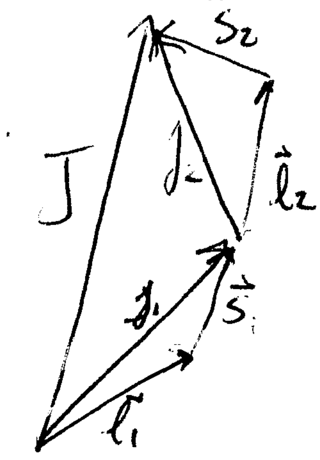
therefore the average $\langle \vec{l}_i \cdot \vec{s}_i \rangle = \frac{\langle \vec{l}_i \cdot \vec{L} \rangle \langle \vec{s}_i \cdot \vec{S} \rangle \, \vec{S} \cdot \vec{L}}{\vec{L}^2 \, \vec{S}^2}$

If $H_{rc} \ll H_{so}$ → then jj coupling is more appropriate.

l_i + s_i are strongly coupled, $\vec{j}_i$ is almost conserved.

so the zeroth order states are

$|JM; j_1 j_2\rangle$ (instead of $|JM; LS\rangle$)



Hyperfine Structure

the nucleus has a magnetic moment

$$\vec{\mu}_I = g_I \mu_N \vec{I} \quad , \vec{I} \text{ nuclear angular momentum.}$$

$$\mu_N = \mu_B \frac{m_e}{m_p} \simeq \frac{\mu_B}{1836} \rightarrow \text{much smaller}$$

An electron makes a magnetic field at the position of the nucleus $\vec{B}_e$

($\vec{B}_e$ arrises for $l=0$ states due to the spin magnetization on the nucleus : $\vec{B}_e = \frac{2}{3}\mu_0 \vec{M}$

$$\vec{M} = -g_s \mu_B \vec{S} |\psi(0)|^2$$

$\vec{B}_e$ arrises for $l \neq 0$ states from the spin + Orbital field generated at the nucleus:

$$B_e = \frac{\mu_0}{4\pi}\left\{ \frac{-e\vec{v} \times (-\hat{r})}{r^3} - \frac{\vec{\mu}_e - 3(\mu_e \cdot \hat{r})\hat{r}}{r^3} \right\}$$
)

in any event, $\vec{B}_e$ is a vector, so application of the projection theorem gives (for J & I good zeroth order quantum #s which is always the case)

$$H_{HFS} = \vec{\mu}_I \cdot \vec{B}_e = A_J \vec{I} \cdot \vec{J}$$

Just like for spin orbit,

$$E_{HFS} = \langle H_{HFS} \rangle = \frac{\hbar^2}{2} A_J \left(F(F+1) - J(J+1) - I(I+1) \right)$$

For nuclear structure, there is another effect: the nucleus is extended in space. We had taken $\vec{R}_N = 0$, but the protons in the nucleus are spread out over a small volume,

$$H_e = \sum_{e,p} \frac{-e^2}{4\pi\epsilon_0 |\vec{r}_e - \vec{R}_p|}$$

$\vec{r}_e$, $\vec{r}_p$ are positions of the electrons & protons, $|\vec{r}_p| << |\vec{r}_e|$

expand in a 3-D Taylor series in spherical coordinates

$$\frac{1}{|\vec{r}_e - \vec{r}_n|} = \sum_k \frac{R_p^k}{r_e^{k+1}} P_k(\cos\theta_{ep})$$

$P_k \rightarrow$ Legendre poly

$\theta_{en} \rightarrow$ angle between $\vec{R}_p$ & $\vec{r}_e$

$$\simeq \sum_e \frac{\cancel{Z}}{r_e} + \underbrace{\sum_{ep} \frac{R_p}{r_e^2} \cos(\theta_{en})}_{\substack{=0 \text{ due to time reversal} \\ \text{symmetry} \rightarrow \text{no permanent electric dipole}}} + \underbrace{\sum_{ep} \frac{R_p^2}{r_e^3} \left(\frac{3\cos\theta_{ep} - 1}{2} \right)}_{H_Q} + \cdots$$

Separate out the e and p dependence using addition of angular momenta:

$$P_k(\cos\theta_{en}) = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} (-1)^q Y^{k,-q}(\theta_p, \phi_p) Y^{kq}(\theta_e, \phi_e)$$

$$H_Q = \frac{1}{4\pi\epsilon_0} \sum_{q=-2}^{2} (-1)^q \left[\sqrt{\frac{4\pi}{5}} \sum e R_p^2 \, Y^{2-q}(\theta_p, \phi_p) \right] \times \left[\sqrt{\frac{4\pi}{5}} \sum_e \frac{e}{r_e^3} Y^{2q}(\theta_e, \phi_e) \right]$$

$$= \frac{1}{4\pi\epsilon_0} \sum_{q=2}^{2} (-1)^q Q_q^2 \, F_q^2$$

Formally, these are operators of $\vec{R}_p$ & $\vec{r}_e$

$$H_Q = \frac{1}{4\pi\epsilon_0} \sum_{q=-2}^{2} (-1)^q \, Q^2_{-q}(\vec{R}_p) \, F^2_q(\vec{r}_e)$$

$Q^2 \rightarrow$ is an electric quadrupole operator

$F^2 \rightarrow$ is a tensor formed from 2^{nd} derivatives of $\frac{1}{r}$: first derivatives of field $\rightarrow$ electric field gradients

Use W-E theorem to define a proportionality constant (choose $q=0$, $M_I = I$, $M_J = J$)

$$Q \equiv \langle I I | \sum_p e R_p^2 \left(\frac{3\cos\theta_p - 1}{2} \right) | I I \rangle$$

$$\frac{\partial^2 V}{\partial z^2} \equiv \langle J J | \sum_e \frac{e}{4\pi\epsilon_0} \frac{(3\cos\theta_e - 1)}{2 r_e^3} | J J \rangle$$

$B_J = Q \langle \frac{\partial^2 V}{\partial z^2} \rangle$, then one can show that:

$$H_Q = \frac{B_J}{2(I(2I-1)J(2J-1)} \left[3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - I(I+1)J(J+1) \right]$$

B_J is the electric quadrupole Hyperfine constant.

We note that as with all Quadrupole operators, we need $I > 1/2$ to have non-zero Q.

If $\vec{J}$ & $\vec{I}$ are pretty good quantum states

$$\boxed{E_{HFS} = \frac{1}{2} A_J K + \frac{B_J}{8I(2I-1)J(2J-1)}\left(3K(K+1) - 4I(I+1)J(J+1)\right)}$$

where $K = F(F+1) - I(I+1) - J(J+1)$

Here we used

$$\langle 3(\vec{I}\cdot\vec{J})^2 \rangle = 3\left(\frac{K}{2}\right)^2 = \frac{3}{4}K^2$$

$$\langle \tfrac{3}{2}(\vec{I}\cdot\vec{J}) \rangle = \frac{3}{4}K$$

if $B_J \simeq 0$, the levels obey the Landé interval rule:

$$\Delta\left(E_{HFS}(J) - E_{HFS}(J-1)\right) = \hbar^2 J A_J$$

$\hbar^2 A_J$ is the unit of Hyperfine energy.