Review of Wigner Eckart theorem:

Formal Statement: given eigenstates of angular momentum $J^2: |\beta J m>, |\beta' J' m'>$ and a spherical tensor operator $T^k_9$

$<\beta J m | T^k_9 | \beta' J m'> = \frac{<\beta J | T^k | \beta' J'>}{\sqrt{2J+1}} \frac{<j\ m'; k q | J m>}{\sqrt{2J+1}}$

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

must be related.

\begin{align*}
T^k_9 & \xrightarrow{\text{rotation in real space}} R(T^k_9) \rightarrow \text{new set of operators} \\
|\beta J m> & \xrightarrow{\text{rotation of Hilbert space}} R(|\beta J m>) \rightarrow \text{new set of states},
\end{align*}

examples: look at the matrix formed by:

$\frac{<j\ m'; k q | J m>}{\sqrt{2J+1}}$
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
\[
\left| \langle \beta JM \| T^k \| \beta' J'M' \rangle \right| = \left| \langle \beta' J'M' \| T^k \| \beta JM \rangle \right| \quad T^k \text{ is Hermitian}
\]

and

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

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, acting on a Hilbert space of size $2J+1$: $\hat{V}_q = \sum_{k=1}^{3} \hat{V}_k$

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, $\frac{\langle Jm'; lq | Jm \rangle}{\sqrt{2J+1}}$

$\hat{V}_- \propto \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix} \quad \hat{V}_+ \propto \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad \hat{V}_0 \propto \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

Raising $\uparrow$

$\hat{V}_x = -\frac{\hat{V}_+ + \hat{V}_-}{\sqrt{2}} \quad \hat{V}_y = (\hat{V}_+ + \hat{V}_-), \quad \hat{V}_z = \hat{V}_0$ 

$\hat{V} \propto \begin{bmatrix}
\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} & \frac{1}{\sqrt{2}} \begin{pmatrix} i & 0 & 0 \\ 0 & i & 0 \\ 0 & 0 & i \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\end{bmatrix}$

Any 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 $J=J'$, $T_k' \equiv \hat{V}$

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

Can use any mass, choose $m=0$. 
Example 2: a vector operator $\hat{V}$ which
connects different $J$ states $J=0$, $J'=1$ with Hilbert
spaces of $I+3=4$ states total:

\[
\begin{pmatrix}
10,0
11,-1
11,0
11,1
\end{pmatrix} J=1
\]

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

W-E gives

\[
\frac{\langle 0m;1q | 1m \rangle}{\sqrt{2J'+1}} = \frac{1}{\sqrt{3}} \delta_{qm}
\]

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

\[
V_{-1} \propto \begin{pmatrix} 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} V_{+1} \propto \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} V_0 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}
\]

\[
\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -10 & 1 \end{pmatrix} \hat{x} + \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \hat{y} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \hat{z}
\]

\[
\rightarrow \text{no matter what the physical cause of}
\text{the vector operator } \hat{V} \text{ is!}
\]
Example 3: Second order dipole matrix coupling:

Imagine a ground state $1S$ coupled to itself in second order by a dipole matrix element:

$$\sum_i \frac{E^* \hat{P}_i |i>|i \hat{P} \cdot E}{E_0 - E_i}$$

This can be written in terms of a dyadic (a second rank tensor):\[\hat{M} = E^* \hat{D} \cdot \hat{D} \cdot E,\] where $\hat{D} = \sum_{ij} \langle i|\hat{P}_i j>|i><j>|$ ($\langle i|\hat{P}_i j> = 0$ unless opposite parity)

$\hat{D} \cdot \hat{D}$ 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 $\alpha, \beta = x, y, z$:

$$E^* \hat{D} \cdot \hat{D} \cdot E = \frac{1}{3} E_0 T^0 + \frac{1}{2} (E^* \times E) \cdot (\hat{D} \times \hat{D}) + \sum_{\alpha \beta} \left( \frac{E^* E_{\alpha} \hat{D}_{\alpha} \hat{D}_{\beta} + E_{\beta} \hat{D}_{\alpha} \hat{D}_{\alpha}}{2} - \frac{1}{3} E^2 D_{\alpha} D_{\beta} \right)$$

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

$E_z \neq 0, E_x, E_y = 0$ pick out the one component of $T_q^z, q=0$

For arbitrary $J$:

$$T_0^2 = \hat{D}_z \hat{D}_z - \frac{1}{3} \hat{D}_z^2 = \frac{2}{3} D_z D_z$$

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

Using

$$\langle Jm_2|20|Jm\rangle \quad T_0^2 \propto \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

depends on $m^2$ depending on $m^2$ compare to vector shifts
Back to multi-electrons + spin orbit:

take the common case $H_{re} \gg H_{so}$

$|LM, S, M_S\rangle$ are good zeroth order states.

$H_{so} = \sum_i \beta_i \vec{S}_i \cdot \vec{l}_i$ is a perturbation.

From the projection theorem,

\[
\hat{S}_i = \frac{\langle \hat{S}_i \hat{S}_i \rangle}{\hat{s}_i \hat{s}_i (S+1)} \hat{S}_i
\]

\[
\hat{l}_i = \frac{\langle \hat{l}_i \hat{l}_i \rangle}{\hat{l}_i \hat{l}_i (L+1)} \hat{l}_i
\]

$H_{so} = \beta_{so} \hat{S} \cdot \hat{L}$,

$\beta_{so} = \sum_i \beta_i \frac{\langle \hat{S}_i \hat{S}_i \rangle \langle \hat{l}_i \hat{l}_i \rangle}{\hat{s}_i \hat{s}_i (S+1) \hat{l}_i \hat{l}_i (L+1)}$

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

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

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

$\langle H_{so} \rangle = \frac{\Delta E}{2} \left( J(J+1) - S(S+1) - L(L+1) \right)$

$[H_{so}, J] = 0$

$J \Rightarrow$ eigenstates.

Example

He 1s 2p $^3P_{0,1,2}$

$S=1$ $L=1$ $J=0, 1, 2$

relative spacing: 2 to 1
Classical Vector picture.

\[ l_1, l_2 \text{ are strongly coupled, so they precess rapidly around } \tilde{L}, \]  
so the average value of \( \langle \hat{l}_1 \rangle = \frac{\langle \hat{l}_1 \cdot \tilde{L} \rangle}{L^2} \)

same argument for \( \hat{s}_i \).

the spin orbit then couples \( \tilde{L} \) to \( \tilde{s}_i \), so they precess but more slowly due to the weaker interaction.

therefore the average \( \langle \hat{l}_1 \cdot \hat{s}_i \rangle = \frac{\langle \hat{l}_1 \cdot \hat{s}_i \cdot \tilde{s}_i \rangle}{L^2 \tilde{s}_i^2} \)

\[ \tilde{s}_i \]

If \( H_{ss} \ll H_{jj} \rightarrow \) then \( jj \) coupling is more appropriate.

\( l_i + s_i \) are strongly coupled, \( \tilde{j}_i \) is almost conserved.

so the zeroth order states are

\[ |jMjj, j_i > \quad (\text{instead of} \quad |jMjj, LS >) \]
Hyperfine Structure
the nucleus has a magnetic moment
\[ \vec{\mu}_n = g_n \mu_n \vec{I} \text{, \(\vec{I}\) nuclear angular momentum} \]
\[ \mu_n = \mu_B \frac{m_e}{m_p} \approx \frac{\mu_B}{1836} \text{, much smaller} \]

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

(\(\vec{B}_e\) arises for \(l=0\) states due to the spin magnetization on the nucleus: \(\vec{B}_e = \frac{2}{3} \mu_0 \vec{M} \)
\[ \vec{M} = g_s \mu_0 \hat{S} |Y(0)| \]

\(\vec{B}_e\) arises for \(l \neq 0\) states from the spin + orbital field generated at the nucleus:
\[ \vec{B}_e = \frac{\mu_0}{4\pi} \left\{ \frac{-e\vec{v} \times \vec{r}}{r^3} - \frac{\vec{M} - 3(\vec{M} \cdot \hat{r})\hat{r}}{r^3} \right\} \]

In any event, \(\vec{B}_e\) is a vector, so application of the projection theorem gives (for \(J > I\) good zeroth order quanta \(H_F\) which is always the case)

\[ H_{\text{HFS}} = \vec{\mu}_n \cdot \vec{B}_e = A_J \vec{I} \cdot \vec{J} \]

Just like for spin orbit,
\[ E_{\text{HFS}} = \langle H_{\text{HFS}} \rangle = \frac{\hbar^2 A_J}{2} \left( F(F+1) - J(J+1) - I(I+1) \right) \]
For nuclear structure, there is another effect: the nucleus is extended in space. We had taken $R_N = 0$, but the protons in the nucleus are spread out over a small volume,

$$H_e = \sum_{e,p} \frac{-e^2}{4\pi\varepsilon_0 |\vec{r}_e - \vec{r}_p|} \quad \vec{r}_e, \vec{r}_p \text{ are positions of the electrons & protons, } |\vec{r}_p| \ll |\vec{r}_e|$$

Expand in a 3-D Taylor series in spherical coordinates

$$\frac{1}{|\vec{r}_e - \vec{r}_n|} = \sum_k \frac{R_p^k}{r_e^{k+1}} P_k(\cos \theta_{en}) \quad P_k \rightarrow \text{Legendre poly}$$

$$\approx \sum_{e,p} \frac{R_p}{r_e} \cos(\theta_{en}) + \sum_{e,p} \frac{R_p^2}{r_e^2} \left( \frac{3 \cos \theta_{en} - 1}{2} \right) + \ldots$$

$= 0$ due to time reversal symmetry $\rightarrow$ no electric dipole permanent

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

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

$$H_\Theta = \frac{1}{4\pi \varepsilon_0} \sum_{q=-2}^{2} (1)^q \left[ \sqrt{\frac{4\pi}{5}} \sum_e \frac{R_p^2}{r_e^2} Y^{2q}_{\theta_e,\phi_e} \right] x$$

$$= \frac{1}{4\pi \varepsilon_0} \sum_{q=-2}^{2} (1)^q Q_q^{2} \frac{e^2}{r_e^3} Y^{2q}_{\theta_e,\phi_e}$$
Formally, these are operators $\hat{R}_p$ and $\hat{E}_e$

$$H_Q = \frac{1}{4\pi\varepsilon_0} \sum_{q=2}^{\infty} (-1)^q Q^2_q (\hat{R}_p) P^2_q (\hat{E}_e)$$

$Q^2$ is an electric quadrupole operator

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

Use W-E theorem to define a proportionality constant

(choose $q=0$, $M_z=I$, $M_s=J$)

$$Q = \langle II | \sum_p eR_p^2 (3\cos\Theta_p - 1) | II \rangle$$

$$\frac{\partial^2 V}{\partial z^2} = \langle JJ | \frac{2}{e} \frac{e (3\cos\Theta e - 1)}{4\pi\varepsilon_0 \frac{2}{r^3}} | JJ \rangle$$

$$B_J = Q \left< \frac{\partial^2 V}{\partial z^2} \right>, \text{ then one can show that:}$$

$$H_Q = \frac{B_J}{2(2I-1)(2J-1)} \left[ 3(I \cdot J)^2 - \sum_{\ell=0}^{\infty} \frac{3}{2} (\ell+\frac{1}{2}) - I(I+1)J(J+1) \right]$$

$B_J$ is the electric quadrupole hyperfine constant.

Note that as with all quadrupole operators, we need $I > \frac{1}{2}$ to have non-zero $Q$. 
If \( \frac{3}{2} \) and \( \frac{1}{2} \) are pretty good quantum states

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

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

Here we used

\[
\langle \frac{3}{2}|\mathbf{\hat{J}}^2|\frac{3}{2} \rangle = \frac{3}{4} K^2 = \frac{3}{4} K^2
\]

\[
\langle \frac{3}{2}|\mathbf{\hat{J}}^2|\frac{1}{2} \rangle = \frac{3}{4} K
\]

If \( B_J = 0 \), the levels obey the Landé interval rule:

\[
\Delta(E_{\text{HFS}}(J) - E_{\text{HFS}}(J-1)) = \hbar^2 \frac{3}{2} A_J
\]

\( \hbar A_J \) is the unit of hyperfine energy.