Now that we've discussed atomic structure, look at transitions between atomic states.

For vector operators (\( \hat{\sigma} \) or \( \hat{\mu} \)) it is useful to use the spherical basis for the vector. e.g., for electric field polarization \( \vec{E} \)

\[
\vec{E}_q = \sigma^+, \pi, \sigma^-
\]

\( q = 1 \quad q = 0 \quad q = -1 \)

\[
\sigma^+ = \frac{x + i y}{\sqrt{2}} \quad \sigma^+ \cdot \sigma^- = 0 \quad \sigma^+ \cdot \sigma^+ = 1
\]

\[
\pi = \frac{z}{\sqrt{2}} \quad \text{etc.}
\]

\[
\sigma^- = \frac{x - i y}{\sqrt{2}}
\]

Note: \( \sigma^+ \) is not just right circularly polarized light! It depends on the axis, quantization!

\[
\text{e.g.}
\]

\[
\begin{align*}
\vec{E}_{\text{linear}} \\
\end{align*}
\]

\[
\begin{align*}
\vec{E}_{\text{right}} & \rightarrow \frac{\pi}{\sqrt{2}} + \frac{\sigma^+ + \sigma^-}{\sqrt{2}} \\
\end{align*}
\]
3-j symbols

Clebsch-Gordan's are sometimes written in terms of the more symmetric 3-j symbols

\[
\langle J' M'_j; K q | J M_j \rangle = (-1)^{J'-K+M_j} \left( \begin{array}{ccc} J' & K & J \\ M'_j & q & -M_j \end{array} \right) \sqrt{2J+1}
\]

\[
\downarrow
\text{a number depending on 6 parameters}
\]

not a matrix! it is a number depending on 6 parameters.

properties of Clebsch-Gordan's or equiv. 3-j's lead to selection rules:

\text{e.g.}

\[
\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} = 0 \text{ unless } M_1 + M_2 + M_3 = 0
\]

\[
\begin{pmatrix} J_1 & J_2 & J_3 \\ 0 & 0 & 0 \end{pmatrix} = 0 \text{ unless } J_1 + J_2 + J_3 \text{ is even}
\]

etc.
# Selection Rules

<table>
<thead>
<tr>
<th>Transition type</th>
<th>E1</th>
<th>M1</th>
<th>E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigorous rules</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. $\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1, \pm 2$</td>
<td></td>
</tr>
<tr>
<td>($O \leftrightarrow O$)</td>
<td>($O \leftrightarrow O$)</td>
<td>($O \leftrightarrow O, \frac{1}{2} \leftrightarrow \frac{1}{2}$)</td>
<td></td>
</tr>
<tr>
<td>2. $\Delta m = 0, \pm 1$</td>
<td>$\Delta m = 0, \pm 1$</td>
<td>$\Delta m = 0, \pm 1, \pm 2$</td>
<td></td>
</tr>
<tr>
<td>($J=0 \leftrightarrow J=0$)</td>
<td>($J=0 \leftrightarrow J=0$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Parity change</td>
<td>No parity change</td>
<td>No parity change</td>
<td></td>
</tr>
<tr>
<td>Rules for negligible configuration</td>
<td>one electron jumping config.</td>
<td>no change in electron config.</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>$\Delta l = \pm 1$</td>
<td>$\Delta l = 0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta n$ arbitrary</td>
<td>$\Delta n = 0$</td>
<td></td>
</tr>
<tr>
<td>LS coupling is good</td>
<td>5. $\Delta S = 0$</td>
<td>$\Delta S = 0$</td>
<td>$\Delta S = 0$</td>
</tr>
<tr>
<td>6. $\Delta L = 0, \pm 1$</td>
<td>$\Delta L = 0$</td>
<td>$\Delta L = 0, \pm 1, \pm 2$</td>
<td></td>
</tr>
<tr>
<td>($L=0 \leftrightarrow L=0$)</td>
<td>(change angle between)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Example: (assume $I=0$)

- $1s^2 2p^1P \rightarrow 1s^2 1S$, $\tau = 1.6\text{ns}$
  - dipole allowed.
  - $1s^2 2S \rightarrow 1s^2 1S$, $\tau = 20\text{ms}$
  - $E1$, $M1$, $E2$ forbidden, goes as a second order transition
  - $1s^2 3S \rightarrow 1s^2 1S$, $\tau = 8000\text{ns}$
  - turns out to be $M1$, but highly suppressed by $\Delta S = 1$ requirement.
What about including nuclear moment \( \mathbf{I} \)?

This leads to coupling of yet more angular momenta, and Wigner 6-j symbols

\[
\begin{align*}
F &= J + I \\
F' &= J' + I
\end{align*}
\]

Example: if \( \hat{T}_k \) acts only on the electronic space:

\[
\hat{T}_k = \frac{1}{\sqrt{3}} (\hat{J} \otimes \mathbb{I}(I))
\]

then

\[
\langle FM_F | \hat{T}_q | F'M_F' \rangle = \sum_{IJ} \left[ \langle FM_F | J M_J I M_I \rangle \langle J M_J I M_I | \hat{T}_q | J' M'_J I' M'_I \rangle \times \langle J' M'_J I' M'_I | F'M_F' \rangle \right]
\]

Use Wieg. Eckart on the \( JJ' \) matrix element:

\[
= \langle J \| \hat{T}_k \| J' \rangle \sum_{MM} \left[ \langle FM_F | J M_J I M_I \rangle \langle J M_J I M_I | K q | J M_J \rangle \langle J M_J I M_I | F' M_F' \rangle \right]
\]

We can also apply Wieg. Eckart to \( FF' \):

\[
\langle FM_F | \hat{T}_q | F'M_F' \rangle = \langle FM_F' | K q | FM_F \rangle \langle FF' | \hat{T}_k | F' \rangle \frac{\sqrt{2J+1}}{\sqrt{2F+1}}
\]

equating these, we can solve for

\[
\frac{\langle FM_F' | K q | FM_F \rangle}{\langle FM_F' | K q | FM_F \rangle} = \frac{\sqrt{2F+1}}{\sqrt{2J+1}} \frac{1}{\langle FF' | \hat{T}_k | F' \rangle} \sum_{MM} \left[ \langle FM_F | J M_J I M_I \rangle \langle J M_J I M_I | K q | J M_J \rangle \langle J M_J I M_I | F' M_F' \rangle \times \langle J M_J I M_I | F'M_F \rangle \right]
\]

the above is independent of \( M_F' \), \( q \), \( M_F = M_F + q \), so it can be evaluated at any convenient value, e.g. \( M_F' = q = M_F = 0 \) (it allowed by selection rules)
Define the $6-j$ symbol as follows:

$$\frac{<F\uparrow \uparrow T^k \downarrow F'>}{<J\uparrow \uparrow T^k \downarrow J'>} = (-1)^{F'+J+K+I} \frac{\sqrt{(2F+1)(2F'+1)}}{\sqrt{(2J+1)(2J'+1)}} \begin{pmatrix} J & J' & K \\ F' & F & I \end{pmatrix}$$

where $\begin{pmatrix} J & J' & K \\ F' & F & I \end{pmatrix}$ is the $6-j$ symbol, that gives a number for any six inputs.

$6-j$'s have a lot of properties, such as they are invariant under permutation of columns or rows.

Given this definition, clearly $<F\uparrow \uparrow T^k \downarrow F'> = <F'\uparrow \uparrow T^k \downarrow F'>$, up to a sign.

Note: there is only one definition of the $6-j$'s. Different definitions are in regard to the reduced matrix elements.

Another $<F\uparrow \uparrow T^k \downarrow F'>$ definition is

$$\frac{<F\uparrow \uparrow T^k \downarrow F'>}{<J\uparrow \uparrow T^k \downarrow J'>} = (-1)^{F'+J+K+I} \frac{\sqrt{(2F+1)(2J+1)}}{\sqrt{(2F'+1)(2J'+1)}} \begin{pmatrix} J & J' & K \\ F' & F & I \end{pmatrix}$$

And $<F\uparrow \uparrow T^k \downarrow F'> = \frac{\sqrt{2F+1}}{\sqrt{2F'+1}} \frac{\sqrt{2J+1}}{\sqrt{2J'+1}} <F\uparrow \uparrow T^k \downarrow F'>$, up to a sign.

I don't know why there isn't a consistent definition.
Example: any second order process in a vector operator.

Scattering

Light shift

Raman Transition

STark induce transition:

etc.

These all will have a form

\[ A^0(E) \hat{T}^0(d) + A^1(E) \hat{T}^1(d) + A^2(E) \hat{T}^2(d) \]

\[ \text{e.g. } |E|^2 |d|^2 + (\mathbf{E} \cdot \mathbf{E}^*) \cdot (d \cdot d) + \frac{2}{3} \mathbf{E} \cdot \mathbf{E} \cdot \frac{d^2}{2} \]

So in principle they can make \( \Delta F = 0, 1 \) or 2 transitions.

this will be limited though by how the F states are coupled from \( J \leftrightarrow \bar{J} \)
Take the case for scattering light, and
Assume typical hyperfine splittings.

SEE MATHEMATICA NOTEBOOK ONLINE

Main result from the example:

\[ \begin{align*}
J &= \frac{3}{2} \\
I &= \frac{1}{2} \\
F &= 2, 1
\end{align*} \]

\[ \begin{align*}
\Delta m = 2 \text{ possible when detuned near hyperfine}
\end{align*} \]

\[ \begin{align*}
J &= \frac{1}{2} \\
I &= \frac{1}{2} \\
F &= 0, 1
\end{align*} \]

\[ \begin{align*}
\Delta m = 2 \text{ not possible because hyperfine splitting is small compared to detuning} \Rightarrow \text{so the nucleus is ignored.}
\end{align*} \]

\[ \begin{align*}
\Delta m = 1 \text{ only possible.}
\end{align*} \]

In the Mathematica Notebook, the couplings are calculated as block off diagonal matrices, e.g.

\[ \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix} \quad \text{Hcouple} \]

\[ \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix} \quad \text{Hcouple}
\]

8x8 total space, but only 4x4 off diagonal parts need to be calculated.
Transition strengths are often given in terms of the classical oscillator strength.

Remember an electron in a spring decays at

$$\Gamma = \frac{e^2 \omega_0^2}{3mc^3} \frac{1}{4\pi E_0} = \frac{\pi e^2}{3mc^2 E_0}$$

An oscillator strength is a unitless measure of a transition strength defined as

$$\Gamma_{ki} = \frac{2\pi e^2}{mc \lambda^2 E_0} \frac{g_i}{g_k} f_{ki}$$

where $g_i$ and $g_k$ are the degeneracy factors for the states. (I don't know where/why the factor of $\frac{2\pi}{3}$ is probably from an average over all directions?)