

Selection Rules (Electric Dipole Transitions)

Matrix Elements

$$\langle \psi_f | \vec{r} | \psi_i \rangle = \langle n'l'm' | \vec{r} | nlm \rangle = \langle n'l'm' | x\hat{i} + y\hat{j} + z\hat{k} | nlm \rangle$$

Using angular momentum commutation relations, we see that:

$$[L_z, x] = i\hbar y \quad [L_z, y] = -i\hbar x \quad [L_z, z] = 0$$

\downarrow
 $xP_y - yPx$

$$0 = \langle n'l'm' | [L_z, z] | nlm \rangle = \langle n'l'm' | L_z z | nlm \rangle - \langle n'l'm' | z L_z | nlm \rangle$$

\rightarrow

$$= \langle z L_z n'l'm' | nlm \rangle - \langle n'l'm' | z L_z | nlm \rangle$$

See Problem 3.5(c) $(\hat{Q}\hat{P})^+ = \hat{P}\hat{Q}$

$$= m'\hbar \langle n'l'm' | z | nlm \rangle - m\hbar \langle n'l'm' | z | nlm \rangle$$

if \hat{P} and \hat{Q} are hermitian

$$\text{Either } \langle n'l'm' | z | nlm \rangle = 0 \quad \text{or } (m' - m) = 0$$

If $\Delta m = 0$ then $\langle n'l'm' | z | nlm \rangle \neq 0$

$$[L_z, x] = i\hbar y$$

$$\begin{aligned} \langle n'l'm' | [L_z, x] | nlm \rangle &= \langle x L_z n'l'm' | nlm \rangle - \langle n'l'm' | x L_z | nlm \rangle \\ &= m'\hbar \langle n'l'm' | x | nlm \rangle - m\hbar \langle n'l'm' | x | nlm \rangle \\ &= (m' - m)\hbar \langle n'l'm' | x | nlm \rangle = i\hbar \langle n'l'm' | y | nlm \rangle \end{aligned}$$

① $\Rightarrow (m' - m)\hbar \langle n'l'm' | x | nlm \rangle = i\hbar \langle n'l'm' | y | nlm \rangle$

$$[L_z, y] = -i\hbar x$$

$$\langle n'l'm' | [L_z, y] | nlm \rangle = \langle y L_z n'l'm' | nlm \rangle - \langle n'l'm' | y L_z | nlm \rangle$$

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$$\begin{aligned} \langle n'l'm' | [L_z, y] | nlm \rangle &= m't\hbar \langle n'l'm' | y | nlm \rangle - m\hbar \langle n'l'm' | ly | nlm \rangle \\ (2) \quad &= (m'-m)t\hbar \langle n'l'm' | ly | nlm \rangle = -it\hbar \langle n'l'm' | x | nlm \rangle \\ \Rightarrow (m'-m)t\hbar \langle n'l'm' | ly | nlm \rangle &= -it\hbar \langle n'l'm' | x | nlm \rangle \end{aligned}$$

Combining ① and ② we find:

$$① \rightarrow \langle n'l'm' | y | nlm \rangle = -i(m'-m) \langle n'l'm' | x | nlm \rangle$$

$$② -i(m'-m)^2 \langle n'l'm' | x | nlm \rangle = -i \langle n'l'm' | x | nlm \rangle$$

$$(m'-m)^2 = 1 \quad \Rightarrow \quad m'-m = \pm 1$$

$$m' = m \pm 1$$

In conclusion:

No electric dipole transitions

occur unless: $\Delta m = 0$ or ± 1

Selection Rules Involving l and l'

E.C.
Problem 9.12 $[L^2, [L^2, \vec{r}]] = 2\hbar^2 (\vec{r} L^2 + L^2 \vec{r})$

$$\begin{aligned} \langle n'l'm' | [L^2, [L^2, \vec{r}]] | nlm \rangle &= \langle n'l'm' | 2\hbar^2 (\vec{r} L^2 + L^2 \vec{r}) | nlm \rangle \\ &= 2\hbar^2 [\langle \vec{r} L^2 | n'l'm' | nlm \rangle + \langle n'l'm' | L^2 \vec{r} | nlm \rangle] \\ &= 2\hbar^2 [l'(l'+1)\hbar^2 \langle n'l'm' | \vec{r} | nlm \rangle + l(l+1)\hbar^2 \langle n'l'm' | \vec{r} | nlm \rangle] \end{aligned}$$

$$\boxed{\langle n'l'm' | [L^2, [L^2, \vec{r}]] | nlm \rangle = 2\hbar^4 (l'(l'+1) + l(l+1)) \langle n'l'm' | \vec{r} | nlm \rangle}$$

Using the Problem 9.12 substitution

Selection Rules (Electric Dipole Transition)

Calculate Again w/o the Problem 9.12 substitution.

$$\begin{aligned}
 \langle n'l'm' | [L^2, [L^2, r]] | nl'm \rangle &= \langle n'l'm' | L^2 [L^2, \vec{r}] - [L^2, \vec{r}] L^2 | nl'm \rangle \\
 &= \langle n'l'm' | L^2 L^2 \vec{r} - L^2 \vec{r} L^2 - L^2 \vec{r} L^2 + \vec{r} L^2 L^2 | nl'm \rangle \\
 &= \langle n'l'm' | L^4 \vec{r} - 2 L^2 \vec{r} L^2 + \vec{r} L^4 | nl'm \rangle \\
 &= [\ell'(\ell'+1)]^2 \hbar^4 \langle n'l'm' | \vec{r} | nl'm \rangle - 2\ell'(\ell'+1)\ell(\ell+1) \langle n'l'm' | \vec{r} | nl'm \rangle \\
 &\quad + [\ell(\ell+1)]^2 \hbar^4 \langle n'l'm' | \vec{r} | nl'm \rangle \\
 &= [\ell'(\ell'+1) - \ell(\ell+1)]^2 \hbar^4 \langle n'l'm' | \vec{r} | nl'm \rangle
 \end{aligned}$$

w/o the Prob. 9.12 substitution

Setting the 2 answers equal to each other we obtain:

$$\begin{aligned}
 2\hbar^4 (\ell'(\ell'+1) + \ell(\ell+1)) &= [\ell'(\ell'+1) - \ell(\ell+1)]^2 \hbar^4 \\
 \Rightarrow [\ell'(\ell'+1) - \ell(\ell+1)]^2 - 2(\ell'(\ell'+1) + \ell(\ell+1)) &= 0
 \end{aligned}$$

However: $\ell'(\ell'+1) - \ell(\ell+1) = (\ell'+\ell+1)(\ell'-\ell)$

$$\begin{aligned}
 \text{so: } &[(\ell'+\ell+1)(\ell'-\ell)]^2 - 2(\ell'(\ell'+1) + \ell(\ell+1)) = 0 \\
 \Rightarrow &[(\ell'+\ell+1)^2 - 1][(\ell'-\ell)^2 - 1] = 0 \quad \begin{matrix} \leftarrow \text{This factorization is not} \\ \text{obvious ... but it's true!!} \\ \text{work it out.} \end{matrix}
 \end{aligned}$$

① not equal to zero unless $\ell' = \ell = 0$ See problem 9.13

② $\ell' - \ell = \pm 1$ or $\ell' = \ell \pm 1$

Thus, the selection rule for ℓ is: $\Delta\ell = \pm 1$ for electric dipole transitions.

N.B. Photon carries of $1\hbar$ of spin angular momentum.