Physics 531: Lecture 9

Selection Rules for atomic absorption/emission

The ability for electromagnetic fields to induce transitions between atomic energy levels is constrained by the conservation laws of physics. Conserved quantities are codified by the quantum numbers of the energy levels. The constraints imposed by conservation laws on changes in the quantum numbers are known as selection rules.

Consider thus atoms described by quantum numbers

\[ |n, l, s, j, m_j \rangle \]

Where

- \( L \) = magnitude of orbital angular momentum of all electrons
- \( S \) = "spin"
- \( J \) = "total angular momentum"
- \( M_j \) = \( z \)-projection of total angular momentum.

Note: Up to this point we have only considered one-electron atoms, but we will define these many-electron atom states in upcoming lectures.

**If we also include hyperfine structure, the relevant quantum numbers are**

\[ |n, l, s, i, j, f, m_f \rangle \]
The atom is driven by "long wave length" radiation i.e. \( k a_o \ll 1 \), \( \hbar = \frac{2\pi}{\lambda} \), \( a_o \) = Bohr radius.

Starting with the Hamiltonian in the (Furry-Zienau-Mosley) gauge:

\[
\hat{H} = \hat{H}_{\text{atom}} + \int d^3x \bar{D} \cdot \vec{E}(\vec{x}, t) + \int d^3x \bar{M} \cdot \vec{B}(\vec{x}, t)
\]

\[\hat{H}_{\text{int}}\]

We can expand the distributions in multipole moments:

\[
\hat{H}_{\text{int}} = -\vec{d} \cdot \vec{E}(0, t) - \vec{\mu} \cdot \vec{B}(0, t) + \frac{1}{2} \sum_{i<j} Q_{ij} (\overrightarrow{r}_{ij} E_{ij}^0)
\]

Center of mass of atom

\( \vec{d} = \int d^3x \bar{\rho}(\vec{x}) = \) electric dipole moment

\( \vec{\mu} = \int d^3x \bar{\mu}(\vec{x}) = \) magnetic dipole moment

\( Q_{ij} = \frac{2}{3} \int d^3x \left( \vec{x}_i \bar{\rho}(\vec{x}) - \frac{1}{3} \vec{x}_i \cdot \bar{\rho}(\vec{x}) \right) = \) electric quadrupole, etc.

\textit{Illustrative Note:} In the small parameter \( k a_o \),

the electric dipole is \( 0^\text{th} \) order, the magnetic dipole and electric quadrupole are \( 1^\text{st} \) order.
Dorellic effect: Electric dipole (E1)

Transition rate \(
\sim \left| \langle \Psi_{\text{final}} | \vec{d} \cdot \vec{E}(0,t) | \Psi_{\text{initial}} \rangle \right|^2
\)

\[1\Psi_{\text{initial}} > = \text{lm, } l, s, j, m_j >
\[1\Psi_{\text{final}} > = \text{lm', } l', s, j', m'_j >
\]

\[\text{Transition rate } \sim \sum_{f} \left| \langle \Psi_{\text{final}} | \vec{d} \cdot \vec{E}(l, s, j, m_j) > \right|^2 / \hbar
\]

Wigner-Eckart theorem

\[\langle n' l' s' j' m'_j | \vec{d} \cdot \vec{E}(l, s, j, m_j) > = \langle \langle \langle j' l' l, s, j, m_j | \vec{d} \rangle \rangle \rangle
\]

(rank-1 tensor)

Selection rule follows from conservation of angular momentum

\[|J' - J| = 0 \text{ or } 1 \text{ (Dirac rule)}
\]

\[|M_j' - M_j| = 0 \text{ or } 1 \quad \text{i.e.} \quad M_j' = M_j + q
\]

\[q = 0, \pm 1
\]

Note: \(J = 0 \rightarrow J' = 0\) not allowed since

\[\langle 0, 0 | 1q, 00 > = 0
\]

(no way to add \(J = 0 + \text{spin} \geq 1 \Rightarrow J' = 0\))
Physically: The intrinsic 3-dim vector nature of the electric field $\Rightarrow$ photon carries intrinsic angular momentum with three components $\Rightarrow$ spin 1.

(There is a subtlety because the photon is massless $\Rightarrow$ transverse field $\Rightarrow$ only two components of angular momentum along propagating direction $+$ and $-$)

Example: $\frac{1}{2}S_{\frac{1}{2}} \rightarrow 2P_{3/2}$ transition

We denote the projection of photon angular momentum along a space-fixed quantization axis $q = 0 \Rightarrow \Pi$ $q = \pm 1 \Rightarrow \sigma^+_\pm$

This should not be confused with the angular momentum along body-fixed $\mathbf{k}$-vector.

Different basis choices $\Rightarrow$ different description but same physics:

Ex: Linear polarization $\uparrow \mathbf{E} \rightarrow \mathbf{k}$

If $\mathbf{E}$ along $\mathbf{k}$ $\Rightarrow \sigma^+_\uparrow$ and $\sigma^-_\downarrow$

If $\mathbf{E}$ along $\mathbf{E}$ $\Rightarrow \Pi$ only
Consider linearly polarized light driving an atom, prepared in $|1s_{1/2}\rangle$, $m_j = \frac{1}{2}$ state.

- Choosing quantization axis along $\vec{e}$

$$\begin{vmatrix}
-\frac{3}{2} & -\frac{1}{2} & \frac{1}{2} & \frac{3}{2} \\
\frac{\sqrt{3}}{3} & \frac{\sqrt{3}}{3} & \frac{\sqrt{3}}{3} & \frac{\sqrt{3}}{3}
\end{vmatrix}$$

$$\text{Rate} = |\langle \frac{3}{2} | \vec{d}_{11} | \frac{1}{2} \rangle |^2$$

$$= \frac{2}{3} |\langle \frac{3}{2} | d_{11} | \frac{1}{2} \rangle |^2$$

- Choosing quantization axis along $\vec{k} = \vec{k_{12}}$

$$\begin{vmatrix}
-\frac{3}{2} & -\frac{1}{2} & \frac{1}{2} & \frac{3}{2} \\
\frac{\sqrt{3}}{3} & \frac{\sqrt{3}}{3} & \frac{\sqrt{3}}{3} & \frac{\sqrt{3}}{3}
\end{vmatrix}$$

$$\text{Rate} = \frac{1}{2} |\langle \frac{3}{2} | d_{11} | \frac{1}{2} \rangle |^2 + \frac{1}{2} |\langle \frac{3}{2} | d_{11} | \frac{1}{2} \rangle |^2$$

half intensity in $\sigma_+$

$$= \frac{2}{3} |\langle \frac{3}{2} | d_{11} | \frac{1}{2} \rangle |^2$$

as before
Actually, with this quantization axis atom is driven into a linear superposition of sublevels. This is just a change of basis:

\[ |g = \frac{3}{2}, m_g = \frac{1}{2} \rangle = \sum_{m_x = -\frac{3}{2}}^{\frac{3}{2}} | j = \frac{3}{2}, m_x = m_g = \frac{1}{2} \rangle \]

**Superposition**

- Further rules for (E1) transition

The coupled electron spin-orbit can be expressed in uncoupled superposition:

\[ \langle n,l,S,j,j^2,M_J | \text{LSJM} \rangle = \sum_{M_L, M_S} \langle jM_J | \text{LM} \rangle \langle \text{LSM} \rangle \langle \text{LSJM} \rangle \]

The electric dipole only acts on motion of atom:

\[ \langle n',l',S',j',j'^2,M'_J | \text{LSJM} \rangle \]

\[ = \sum_{M_L', M_S'} \langle jM_J | \text{LM} \rangle \langle \text{LSM} \rangle \langle \text{LSJM} \rangle \]

\[ \langle n',l',M'_L | \delta_{S,S'} \delta_{M,M'} \rangle \langle \text{LSJM} \rangle \]

\[ \downarrow \]

\[ \langle n',l',d | \text{LSJM} \rangle \langle \text{LSJM} \rangle \]
Thus we have additional constraints

\[ |L - L'| = 0, 1 \quad \text{(no } L = 0 \text{ to } L' = 0) \]

\[ S = S' \]

In addition we have the constraint due to parity

\[ |L - L'| \text{ odd } \Rightarrow \quad |L - L'| \neq 0 \]

\[ |L - L'| = 1 \]

**Summary: Selection rules for E1 transition**

\[ \langle L'S' J' H_f' \rangle \rightarrow \langle L'S' J H_f \rangle \]

- \[ |J' - J| = 0, 1 \quad \text{no } J = 0 \rightarrow J' = 0 \]
- \[ M_J' - M_J = 0, +1, -1 \]
  \(0 = \pi^-\text{-light}\)
  \(\pm 1 = \sigma^-\text{-light}\)
- \[ |L' - L| = 1 \]
- \[ |S' - S| = 0 \]

Finally, if we include hyperfine structure

\[ \langle L'S' J H_f' \rangle \rightarrow \langle L'S' J' F' H_f' \rangle \]

**Additional rule** \[ |F' - F| = 0, 1 \quad \text{no } F = 0 \rightarrow F' = 0 \]

Now \[ M_{f'} - M_{f} = 0, +1, -1 \]

\(M_J\) no longer good \(\tau\)-number
Magnetic dipole transitions (M1)

As with E1 transition, the absorption rate is proportional to the square of the matrix element

\[ W_{\text{M1}} \propto |\langle \Psi_f | \hat{\mu} \cdot \vec{B}(\vec{r}) | \Psi_i \rangle|^2 \]

\[ = |\langle \Psi_f | \hat{\mu}_q^{(0)} | \Psi_i \rangle|^2 \left| \vec{a}_q \cdot \vec{B}(\vec{r}) \right|^2 \]

\[ \Rightarrow \text{Rank 1 tensor operator} \]

For fine structure states \( |nL\ell S J M_J \rangle \):

\[ \langle n' L' \ell' S' J' M'_J | \hat{\mu}_q^{(0)} | nLSJ M_J \rangle = \langle n' L' \ell' S' J' \hat{\mu}^{(0)} | nLSJ \rangle \]

\[ \langle J' M'_J | 1 q J M_J \rangle \]

\[ \Rightarrow \text{As in E1: } \Delta J = 0, \pm 1 \text{ (no } J = 0 \rightarrow J = 0) \]

\[ \Delta M_J = 0, \pm 1 \]

What about \( S \) and \( L \)?

If \( \hat{\mu} \) due to spin \( \Rightarrow \Delta S = 0, \pm 1 \) (multipole electrons)

\[ \Delta L = 0, \pm 1 \text{ by rotation. What about parity} \]

Recall \( \vec{\mu} = \vec{\gamma} \vec{J} \) and \( \vec{J} \) is even under parity (e.g., \( J^0 = \vec{x} \cdot \vec{p} \) even)

\[ \Rightarrow \vec{\mu} \text{ is even under parity} \]

\[ \Rightarrow \Delta L = 0 \]

Summary: (M1)

- \( \Delta J = 0, \pm 1 \)
- \( \Delta M_J = 0, \pm 1 \) depends on polarimeter of \( B \)
- \( \Delta S = 0, \pm 1 \)
- \( \Delta L = 0 \)
Example in Hydrogen, $2P_{3/2} \rightarrow 2P_{1/2}$ transition (10 GHz):

$\Delta j = 1, \quad \Delta L = 0, \quad \Delta S = 0, \quad \Delta M_J = 0, \pm 1$

How does transition rate for M1 compare to E1?

Atomic units:

$\mu_\alpha = e \alpha_o$

$\mu_\alpha = \frac{e^2}{mc} \Rightarrow \alpha = \frac{e}{2c}$

$\Rightarrow \frac{|\mu_\alpha|^2}{10^{16}} = \alpha^2 = \left(\frac{1}{37}\right)^2 \approx 5 \times 10^{-5}$

Recall $\alpha = \frac{\alpha_o}{c}$ in hydrogen $\Rightarrow \alpha = \frac{R}{\lambda} = \frac{\lambda}{\lambda}$ small parameter

Electric Quadrupole\ (E2)

Must consider matrix elements $\langle n_f | \hat{Q}_{ij} | n_i \rangle$ $\hat{Q}_{ij}$

$\hat{Q}_{ij}$ is a symmetric traceless cartesian tensor: involves 5 independent components related to the 5 independent spherical components $\hat{Q}^{(2)}_q$ (see Jackson)

Thus $\langle n' L' S' J' M'_J | \hat{Q}^{(2)}_q | n L S J M_J \rangle = \langle n' L' S' J' | \hat{Q}^{(2)}_q | n L S J \rangle \langle J M_J | 2 q | J M_J \rangle$

$\Rightarrow \Delta J = 0, \pm 1, \pm 2$

$\Delta M_J = 0, \pm 1, \pm 2$

$\Delta S = 0$

$\Delta L = 0, \pm 1, \pm 2$

forbidden by parity (Q is even)
Note: For $\Delta l = 0 \quad M_f = 0 \pm 1$ both $M_1$ and $E_2$ are allowed. They can interfere.

Size of $E_2$ compared to $E_1$ and $M_1$

Transition rate $\sim \frac{Q^2}{D^2}$ where $D$ is the scale over which $E$ has a gradient.

For plane wave: $D = \frac{1}{\lambda} \Rightarrow \frac{1}{D} = k$

$\Rightarrow \frac{Q}{D} \sim \frac{e \alpha^2}{\lambda} = \frac{e \alpha^2}{\lambda} k = \frac{e \alpha^2 \omega}{c}$

$\omega$ = frequency of resonance $\Rightarrow \omega c = \frac{e^2}{\alpha}$

$\Rightarrow \frac{Q}{D} \sim \frac{e \alpha^2 \omega}{\lambda \alpha \lambda} = \alpha e \alpha = M_1$

So for a plane wave with $|E| = |B|$, the strength of $M_1$ and $E_2$ are equal. Of course, in other situations this may not be true. For example, in a microwave cavity or RF coil $B$ can be large, but the gradient of $|E|$ small $\Rightarrow M_1$ transition.

Question: How can $E_2$ transitions generate $\Delta J = 2$ transition? Doesn't the photon only carry one unit of angular momentum? No, this is the spin of the photon. It can also have orbital angular mom.

Partial wave expansion: $e^{i \mathbf{k} \cdot \mathbf{x}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l Y_l^m(\theta, \phi) \mathbf{Y}_l^m$, $\theta$, $\phi$.