Physic 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 <u>selection rules</u>.

Consider, thus atoms described by ~~quantum~~ numbers

$$|n, L, S, J, M_J\rangle$$

Where L = ~~m~~ magnitude of orbital ang. momentum of <u>all</u> electrons

S = " " spin " " "

J = " " total ang moment " "

M_J = Z-projection of total ang. moment.

Note:
- Up to this point we have only considered one-electron atoms, but we will define these many-electron atom states in upcoming lectures
- ~~We~~ 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. $ka_0 \ll 1$ $\quad k = \frac{2\pi}{\lambda}$ $\quad a_0 =$ Bohr radius

Starting with the Hamiltonian in the (Power-Zienau-Woolley) Gauge

$$\hat{H} = \hat{H}_{atom} + \underbrace{\int d^3x\, \vec{P}\cdot\vec{E}(\vec{x},t) + \int d^3x\, \vec{M}\cdot\vec{B}(\vec{x},t)}_{\hat{H}_{int}}$$

We can expand the distribution in multipole moment

$$\Rightarrow \hat{H}_{int} = -\vec{d}\cdot\vec{E}(0,t) - \vec{\mu}\cdot\vec{B}(0,t) + \frac{1}{2}\sum_{ij} \hat{Q}_{ij} \left(\partial_j E_i\right)\Big|_{0,t}$$

center of mass of atom

$\vec{d} = \int d^3x\, \vec{P}(x,t) =$ electric dipole moment

$\vec{\mu} = \int d^3x\, \vec{M}(x,t) =$ magnetic dipole moment

$Q_{ij} = \int d^3x \left(x_i P_j(\vec{x}) - \frac{1}{3}\vec{x}\cdot\vec{P}(\vec{x}) \right) =$ electric quadrupole, etc.

Note: In the small parameter ka_0, the electric dipole is zeroth order, the Magnetic dipole and Electric quadrupole are first order.

Dominate effect : Electric dipole (E1)

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

$|\psi_{initial}\rangle = |n, L, S, J, M_J\rangle$

$|\psi_{final}\rangle = |n', L', S', J', M_J'\rangle$

$\Rightarrow$ Transition rate $\sim \sum_q |\langle n', L', S', J', M_J' | \hat{d}_q | n L S J M_J\rangle|^2 \, |E_{-q}|^2$

Wigner-Eckart Theorem

$$\langle n' L' S' J' M_J' | \underset{\substack{\uparrow \\ \left(\text{rank-1 tensor}\right)}}{d_q} | n L S J M_J \rangle = \langle \alpha' J' \| d \| J \alpha \rangle \langle J' M_J' | 1\, q\, J\, M_J \rangle$$

Selection rules follows from conservation of angular momentum

$\Rightarrow |J' - J| = 0$ or 1 (triangle rule)

$|M_J' - M_J| = 0$ or 1 i.e. $M_J' = M_J + q$

$q = 0, +1, -1$

Note: $J=0 \rightarrow J'=0$ not allowed since

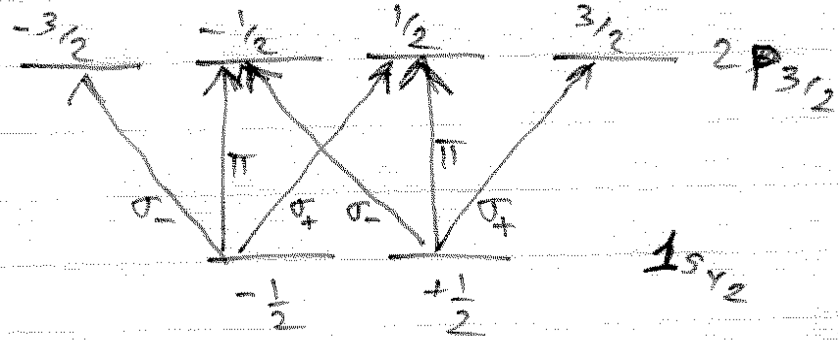
$$\langle 0\, 0 | 1 q\; 0 0 \rangle = 0$$

(no way to add $J=0$ + $J_{photon}=1 \Rightarrow J'=0$)

Physically: The intrinsic 3-dim vector nature of electric field ⇒ photon carries instrinsic angular momentum with three components ⇒ <u>spin 1</u>

(There is a subtlety because the photon is massless ⇒ transverse field ⇒ only two components of angular momentum <u>along propagating direction</u>)
$+\hbar$ and $-\hbar$

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

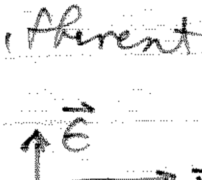


We denote the projection of photon (spin) angular momentum along a <u>space-fixed</u> quantization axis $q=0 \Rightarrow \pi$ $q=\pm 1 \Rightarrow \sigma_\pm$

This <u>should not</u> be confused with the angular momentum along <u>body-fixed $\vec{k}$-vector</u>.

Different basis choices ⇒ different description but same physics:

Ex: Linear polarization

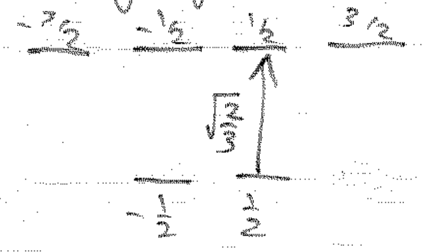


If z along $\vec{k}$ ⇒ σ_+ and σ_-

If z along $\vec{E}$ ⇒ π only

Consider linearly polarized light driving atom, prepared in $1s_{1/2}$, $m_j = 1/2$ state

- Choosing quantization axis along $\vec{\mathcal{E}}$



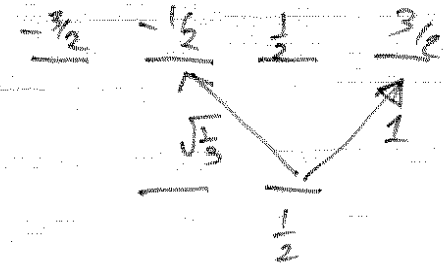
$$\text{Rate} \sim |\langle 2p_{3/2} \| d \| 2s_{1/2}\rangle|^2 \, |\underbrace{\langle \tfrac{3}{2}\,\tfrac{1}{2} | 1\,0\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle}_{\sqrt{2/3}}|^2$$

$$= \frac{2}{3} |\langle 2p_{3/2} \| d \| 2s_{1/2}\rangle|^2$$

- Choosing quantization axis along $\vec{k} = k\vec{e}_z$

$$\vec{\mathcal{E}} = \vec{e}_x = \frac{-\vec{e}_+ + \vec{e}_-}{\sqrt{2}}$$

~~Rate~~



$$\text{Rate} = \underset{\substack{\uparrow \\ \text{half intensity in } \sigma_+}}{\frac{1}{2}} |\langle \tfrac{3}{2}\,\tfrac{3}{2} | \hat{d}_{+1} | \tfrac{1}{2}\,\tfrac{1}{2}\rangle|^2 + \underset{\substack{\uparrow \\ \text{half in } \sigma_-}}{\frac{1}{2}} |\langle \tfrac{3}{2}\,-\tfrac{1}{2} | \hat{d}_{-1} | \tfrac{1}{2}\,\tfrac{1}{2}\rangle|^2$$

$$= \frac{1}{2} |\langle 2p_{3/2} \| d \| 2s_{1/2}\rangle|^2 \left(\underbrace{|\langle \tfrac{3}{2}\,\tfrac{3}{2} | 1\,1\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle|^2}_{=1} + \underbrace{|\langle \tfrac{3}{2}\,-\tfrac{1}{2} | 1\,-1\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle|^2}_{=\frac{1}{3}} \right)$$

$$= \frac{2}{3} |\langle 2p_{3/2} \| d \| 2s_{1/2}\rangle|^2 \quad \text{as before}$$

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

$$|j=3/2, m_{jz}=1/2\rangle = \sum_{m_{jx}=-3/2}^{3/2} \langle j=3/2, m_{jx} | j=3/2, m_{jz}=1/2\rangle \, |j=3/2, m_{jx}\rangle$$

Superposition

- Further rules for (E1) transition

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

$$|nLSJM_J\rangle = \sum_{\substack{M_L \\ M_S = M_J - M_L}} \langle JM_J | LM_L SM_S\rangle \, |nLM_L\rangle \otimes |SM_S\rangle$$

The electric dipole only acts on motion of atom

$$\Rightarrow \langle n'L'S'J'M_J'| \hat{d}_q |nLSJM_J\rangle$$

$$= \sum_{M_L, M_L'} \langle JM_J | LM_L SM_S\rangle \langle L'M_L' S'M_S' | J'M_J'\rangle$$

$$\underbrace{\langle n'L'M_L' | \hat{d}_q | nLM_L\rangle}_{} \quad \underbrace{\langle S'M_S' | SM_S\rangle}_{\delta_{S'S} \; \delta_{M_S M_S'}}$$

$$\Downarrow$$

$$\langle n'L' \| d \| nL\rangle \langle L'M_L' | 1q \, LM_L\rangle$$

Thus we have ~~no~~ addition constraints

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

$$S = S'$$

In addition we have the constraint due to $\underline{\text{parity}} \Rightarrow |L - L'|$ odd $\Rightarrow |L - L'| \neq 0$

$$|L - L'| = \underline{1}$$

$\underline{\text{Summary}}$: Selection rules for $\underline{E1}$ ~~transition~~

$$|n L S J M_J\rangle \rightarrow |n' L' S' J' M_J'\rangle$$

- $|J' - J| = 0,\ \underline{1}$ no $J=0 \rightarrow J'=0$
- $M_J' - M_J = 0, +1, -1$ $0 = \pi$-light, $\pm 1 = \sigma_\pm$-light
- $|L' - L| = \underline{1}$
- $|S' - S| = 0$

Finally, if we include $\underline{\text{hyperfine structure}}$

$$|n L S J I F M_F\rangle \rightarrow |n' L' S' I' F' M_F'\rangle$$

Additional rule $|F' - F| = 0, \underline{1}$ no $F=0 \rightarrow F'=0$

Now $M_F' - M_F = 0, +1, -1$

(M_J no longer good q-number)

Magnetic dipole transitions (M1)

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

$$W_{f\leftarrow i} \sim |\langle \psi_f | \hat{\vec{\mu}} \cdot \vec{B}(\vec{x}_0) | \psi_i \rangle|^2$$

$$= |\langle \psi_f | \underbrace{\hat{\mu}^{(1)}_q}_{\text{Rank 1 tensor operator}} | \psi_i \rangle|^2 \; |\vec{e}_q^{\,*} \cdot \vec{B}(\vec{x}_0)|^2$$

For Fine structure states $|n\,L\,S\,J\,M_J\rangle$:

$$\langle n'L'S'J'M_J' | \hat{\mu}^{(1)}_q | n\,L\,S\,J\,M_J \rangle = \langle n'L'S'J' \| \hat{\mu}^{(1)} \| n\,L\,S\,J \rangle \langle J'M_J' | 1\,q\,J\,M_J \rangle$$

$\Rightarrow$ As in E1: $\Delta J = 0, \pm 1$ (no $J=0 \rightarrow J'=0$)

$\Delta M_J = 0, \pm 1$

What about S and L ?

If $\vec{\mu}$ due to spin $\Rightarrow$ $\Delta S = 0, \pm 1$ (multiple electrons)

$\Delta L = 0, \pm 1$ by rotation. What about parity

Recall $\vec{\mu} = \gamma \vec{J}$ and $\vec{J}$ is even under parity

(e.g. $\vec{J} = \vec{x} \times \vec{p}$ even)

$\Rightarrow$ $\vec{\mu}$ is even under parity

$\Rightarrow$ $\Delta L = 0$.

Summary: (M1)

$\Delta J = 0, \pm 1$ $\quad \Delta M_J = 0, \pm 1$ $\rightarrow$ Depends on polarization of $\vec{B}$

$\Delta S = 0, \pm 1$

$\Delta L = 0$

Example in Hydrogen $2P_{3/2} \to 2P_{1/2}$ transition (10 GHz):

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

How does transition rate for M1 compare to E1?

Atomic units: $d_A = e a_0$

$$\mu_A = \frac{e\hbar}{mc} = e \underset{\substack{\uparrow \\ \text{Compton}}}{\lambda_c} = e(\alpha a_0) \qquad \alpha = \frac{e^2}{\hbar c}$$

$$\Rightarrow \frac{|\mu_A|^2}{|d_A|^2} = \alpha^2 = \left(\frac{1}{137}\right)^2 \cong 5 \times 10^{-5}$$

Recall $\alpha = \frac{v}{c}$ in Hydrogen $\Rightarrow \alpha = \frac{R}{Tc} = \underbrace{\frac{R}{\lambda}}_{\text{small parameter}}$

<u>Electric Quadrupole</u> (E2)

Must consider matrix elements $\langle \psi_f | \hat{Q}_{ij} | \psi_i \rangle \, \partial_j E_i$

$\hat{Q}_{ij}$ is a symmetric traceless cartesian tensor: irreducible

Five independent components related to the five spherical components $\hat{Q}^{(2)}_q$ (see Jackson)

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

$$\Rightarrow \boxed{\begin{array}{l} \Delta J = 0, \pm 1, \pm 2 \\ \Delta M_J = 0, \pm 1, \pm 2 \\ \Delta S = 0 \\ \Delta L = 0, \underset{\substack{\downarrow \\ \text{forbidden by parity}}}{\cancel{\pm 1}}, \pm 2 \qquad (Q \text{ is } \underline{\text{even}}) \end{array}}$$

<u>Note</u>: For $\Delta L = 0$ $\Delta M_J = 0, \pm 1$ <u>both</u> M1 and E2 are allowed. They can interfere.

Size of E2 compared to E1 and M1

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

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

$$\Rightarrow \frac{Q}{D} \sim \frac{e a_0^2}{\lambda} = e a_0^2 k = e a_0^2 \frac{\omega}{c}$$

$\omega \hat{=}$ frequency of resonance $\Rightarrow \hbar\omega = \frac{e^2}{a_0}$

$$\Rightarrow \frac{Q}{D} \sim e a_0^2 \frac{e^2}{\hbar c\, a_0} = \alpha e a_0 = \mu_A$$

So for a <u>plane wave</u> with $|E| = |\vec{B}|$, the strength of M1 and E2 are <u>equal</u>. Of course, in other situations this may not be true. For example, in a microwave cavity, or Rf coil $\vec{B}$ can be large, but the <u>gradient</u> of $|\vec{E}|$ small $\Rightarrow$ M1 transition

<u>Question</u>: How can E2 transitions generate $\Delta J = 2$ transitions. Doesn't the photon only carry one unit of angular momentum? No, this is the <u>spin</u> of the photon. It can also have <u>orbital</u> ang. mom.

Partial wave expansion: $e^{i\vec{k}\cdot\vec{x}} = 4\pi \sum_{l=0}^{\infty} i^l j_l(kr) \sum_{m=-l}^{l} Y^{l*}_m(\hat{e}_k)\, Y^l_m(\hat{e}_r)$

Spherical Bessel funct.