E. Seeing (stimulated) Absorption and Emission from Eq. (12)

- All results follow from analyzing Eq. (13)

$$\hat{H}'(t') = -\vec{\mu}\cdot\vec{\mathcal{E}}_0\cos\omega t = e\vec{r}\cdot\vec{\mathcal{E}}_0\cos\omega t$$

($\vec{\mu}$: atom; $\vec{\mathcal{E}}_0$: light; $\vec{\mu}$: space; $\cos\omega t$: time; $e\vec{r}$: space; $\cos\omega t$: time)

$$a_f(t) = -\left(\int \psi_f^*(\vec{r})\,\vec{\mu}\,\psi_i(\vec{r})\,d^3r\right)\cdot\left(\frac{1}{i\hbar}\vec{\mathcal{E}}_0\int_0^t e^{\frac{i}{\hbar}(E_f-E_i)t'}\cos\omega t'\,dt'\right) \quad (14)$$

(ψ_f^*: atomic state; $(-e\vec{r})$; ψ_i: atomic state)

spatial integrals $\vec{\mu}_{fi}$

"electric dipole matrix element"

$\propto \int \psi_f^*(\vec{r})\,\vec{r}\,\psi_i(\vec{r})\,d^3r$

gives selection rules

- integration over time up to t
- function of t
- set condition on $\hbar\omega$
- 2 terms because $\cos\omega t' = \frac{e^{-i\omega t}+e^{i\omega t}}{2}$

stimulated absorption & emission

$\hat{z}$-polarized $\quad \vec{\mathcal{E}} = \hat{z}\,\mathcal{E}_0 \cos\omega t \;\Rightarrow\; \hat{H}' = ez\,\mathcal{E}_0 \cos\omega t$

then $\vec{\mu}_{fi}$ picks up $\quad \int \psi_f^*(\vec{r})(-ez)\psi_i(\vec{r})\,d^3r$

$$\equiv -e\,z_{fi} = (\mu_z)_{fi}$$

(z-component of $\vec{\mu}_{fi}$) (in general complex)

$$a_f(t) = e\mathcal{E}_0 z_{fi} \frac{1}{i\hbar}\left[\frac{1}{2}\int_0^t e^{\frac{i}{\hbar}(E_f - E_i + \hbar\omega)t'}\,dt' + \frac{1}{2}\int_0^t e^{\frac{i}{\hbar}(E_f - E_i - \hbar\omega)t'}\,dt'\right] \quad (15)$$

if $z_{fi} \neq 0$ possible transition

if $E_i - E_f \cong \hbar\omega$, integral $\neq 0$
otherwise, integrand is oscillating $\Rightarrow \approx 0$
(this is stimulated emission)
$E_i > E_f$ (by $\hbar\omega$)

if $E_f - E_i \cong \hbar\omega$ integral $\neq 0$
otherwise, integrand is oscillating $\Rightarrow \approx 0$
(this is absorption)
$E_f > E_i$ (by $\hbar\omega$)

$$a_f(t) = (-ez_{fi})\frac{\mathcal{E}_0}{2}\left[\underbrace{\frac{e^{\frac{i}{\hbar}(E_f - E_i + \hbar\omega)t} - 1}{E_f - E_i + \hbar\omega}}_{\text{term ①}} + \underbrace{\frac{e^{\frac{i}{\hbar}(E_f - E_i - \hbar\omega)t} - 1}{E_f - E_i - \hbar\omega}}_{\text{term ②}}\right] \quad (16)^{+}$$

↯

initial condition is $a_f(0) = 0$ and $\underbrace{a_i(0) = 1}_{\text{was in } \psi_i \text{ at time } 0}$

term ①: stimulated emission

term ②: (stimulated) absorption

- When term ② is big, term ① is small (consider term ② only for absorption)
- When term ① is big, term ② is small (consider term ① only for stimulated emission)
- $(-ez_{fi})\mathcal{E}_0$ in front is $(\mu_z)_{fi}\mathcal{E}_0$ [generally $(\vec{\mu})_{fi} \cdot \vec{\mathcal{E}}_0$]

+ Formally, we want $|a_f(t)|^2$. Since when one term is important, the other term is negligible. Thus, the "interference" (cross) terms are not important. So, we throw away one term before taking $|a_f(t)|^2$.

(a) Absorption [term (2) only]

Consider two atomic states $(E_2)\ 2$ —— (f) [e.g. 2p] $a_2(0)=0$, $a_2(t)=?$

$(E_1)\ 1$ —— (i) [e.g. 1s] $a_1(0)=1$

From Eq. (16),

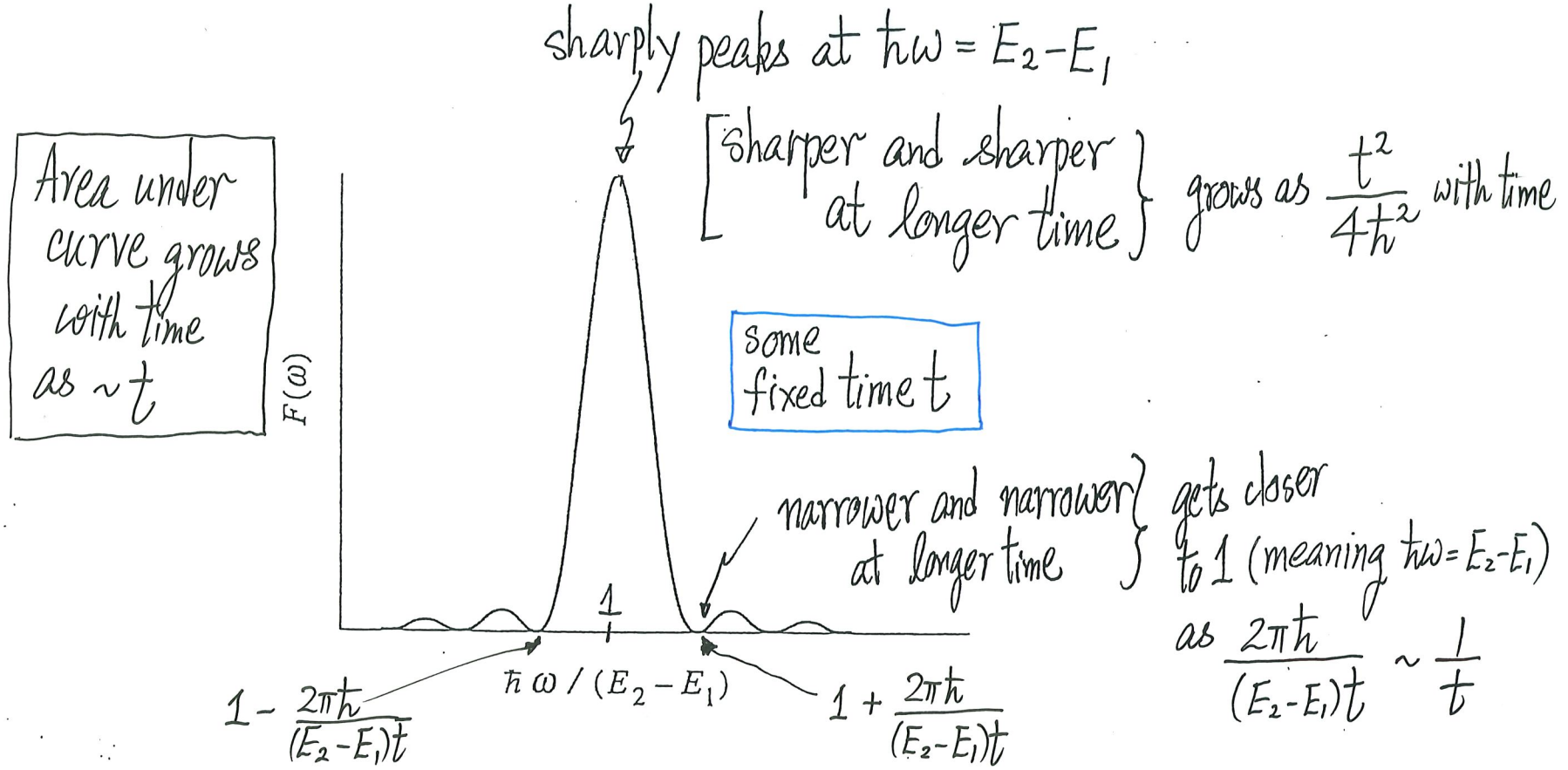
$$a_2(t) = \mathcal{E}_0(-ez_{21})\ \frac{\sin\left[\frac{(E_2-E_1-\hbar\omega)t}{2\hbar}\right]}{E_2-E_1-\hbar\omega}\cdot e^{\frac{i}{2\hbar}(E_2-E_1-\hbar\omega)t}$$

$$|a_2(t)|^2 = \mathcal{E}_0^2 e^2 |z_{21}|^2\ \frac{\sin^2\left[\frac{(E_2-E_1-\hbar\omega)t}{2\hbar}\right]}{(E_2-E_1-\hbar\omega)^2} \qquad (17)$$

(Absorption)

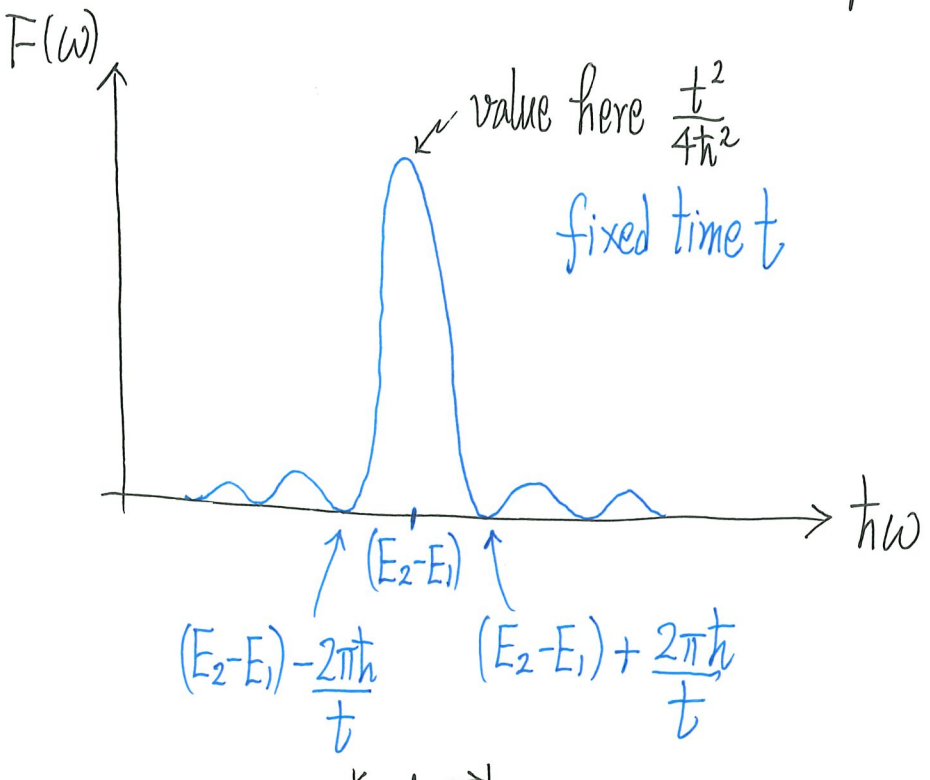
- $|a_2(t)|^2$: Prob. of finding atom in ψ_2 of energy E_2 at time t
- $|z_{21}|^2$: $\neq 0$ (?) [allowed] / $=0$ [forbidden] (selection rule)
- $\frac{\sin^2\left[\frac{(E_2-E_1-\hbar\omega)t}{2\hbar}\right]}{(E_2-E_1-\hbar\omega)^2}$: requires $E_2-E_1=\hbar\omega$ practically (E_2: final, E_1: initial)

Behavior of $F(\omega) = \dfrac{\sin^2\left[\dfrac{(E_2 - E_1 - \hbar\omega)t}{2\hbar}\right]}{(E_2 - E_1 - \hbar\omega)^2}$



The function $F(\omega) = \sin^2[(E_2 - E_1 - \hbar\omega)t/2\hbar]/(E_2 - E_1 - \hbar\omega)^2$, which represents the probability of making a $1 \rightarrow 2$ transition in the time interval 0 to t, plotted against frequency ω. Note that this function peaks when $E_2 - E_1 = \hbar\omega = h\nu$.

For those who want to see the plot with $\hbar\omega$ as x-axis



Q: Also education to F function as a function of t, and as a function of (E_2-E_1) for fixed ω.

- $F(\omega)$ is sharply peaked at $\hbar\omega \approx E_2 - E_1$ (to within $\frac{2\pi\hbar}{t}$ about it)

  $\therefore$ transition probability is appreciable when $\hbar\omega = E_2 - E_1$ (to within $\frac{2\pi\hbar}{t}$)

  $\Rightarrow$ the picture of system (atom) absorbing $\hbar\omega$ to go from ψ_1 to ψ_2 (higher energy)

- Peak grows as $\sim t^2$ and width shrinks as $\sim \frac{1}{t}$ (when seen as function of time)

  area under peak grows as $\sim t$

  $F(\omega)$ has unit of $1/(\text{energy})^2$

  Behavior of $F(\omega)$ is $F(\omega) \to \frac{\pi}{2\hbar} t\, \delta(E_2 - E_1 - \hbar\omega) = \frac{\pi}{2\hbar^2} t\, \delta\left(\frac{E_2 - E_1}{\hbar} - \omega\right)$

  (useful when we have a group of final states around energy E_2)
  (useful when the incident light is non-monochromatic, but with many ω's)

- if at resonance ($\hbar\omega = E_2 - E_1$), peak value $\sim t^2$, thus $|a_2(t)|^2 = \left(\frac{eE_0|Z_{21}|}{2\hbar}\right)^2 \cdot t^2$

(b) Stimulated Emission [term ① only]

(E_1) 1 —— (i) [e.g. 2p] $a_1(0) = 1$

(E_2) 2 —— (f) [e.g. 1s] $a_2(0) = 0$, $a_2(t) = ?$

From Eq. (16),

$$a_2(t) = \mathcal{E}_0 (-e z_{21}) \cdot \frac{\sin\left[\frac{(E_2 - E_1 + \hbar\omega)t}{2\hbar}\right]}{E_2 - E_1 + \hbar\omega} \cdot e^{\frac{i}{2\hbar}(E_2 - E_1 + \hbar\omega)t}$$

a_2: lower energy

$$|a_2(t)|^2 = \mathcal{E}_0^2 e^2 |z_{21}|^2 \underbrace{\frac{\sin^2\left[\frac{\hbar\omega - (E_1 - E_2)}{2\hbar} \cdot t\right]}{(\hbar\omega - (E_1 - E_2))^2}}_{\text{sharply peaks at } \hbar\omega = E_1 - E_2} \qquad (18)$$

$|a_2(t)|^2$: Prob. of finding atom in ψ_2 (lower energy) of energy E_2 at time t

E_1: higher (initial); E_2: lower (final)

Discussions followed (17) also apply here!

If we simply label two states by 1 & 2 via $\hbar\omega$ and consider stimulated absorption and emission between the two states, we have

E_2 —— (higher)

E_1 —— (lower)

(Stimulated) Absorption (Eq. (17))

$$|a_{1\to 2}(t)|^2 = |a_{12}(t)|^2 = \mathcal{E}_0^2 e^2 |z_{21}|^2 \frac{\sin^2\left[\frac{\hbar\omega - (E_2 - E_1)}{2\hbar}\cdot t\right]}{\left(\hbar\omega - (E_2 - E_1)\right)^2}$$

- a QM result
- Einstein (1917) (before QM)

Stimulated Emission (from Eq. (18))

$$|a_{2\to 1}(t)|^2 = |a_{21}(t)|^2 = \mathcal{E}_0^2 e^2 |z_{12}|^2 \frac{\sin^2\left[\frac{\hbar\omega - (E_2 - E_1)}{2\hbar}\cdot t\right]}{\left(\hbar\omega - (E_2 - E_1)\right)^2}$$

higher, lower

But $z_{21} = z_{12}^* \Rightarrow |z_{21}|^2 = |z_{12}|^2$

Stimulated absorption and simulated emission between two states occur with the same probability (and same Prob. per unit time (rate)) under the same conditions (same $\mathcal{E}_0^2$, same time t)!

(C) Selection Rules [Electric Dipole Mechanism]

$|a_{1\to 2}(t)|^2 \propto |Z_{21}|^2$; $|a_{2\to 1}(t)|^2 \propto |Z_{12}|^2 = |Z_{21}|^2$ ($\vec{\mathcal{E}} \parallel \hat{z}$) — linearly polarized

Generally, $(\vec{\mu})_{21}$ or $(\vec{r})_{21}$ determines whether $|a_{1\to 2}|^2 = 0$ or $\neq 0$ — and how big

$\left[\int \psi_2^*(\vec{r})\,(-e\vec{r})\,\psi_1(\vec{r})\,d^3r\right]\cdot\vec{\mathcal{E}}$ matters

OR $\int \psi_2^*(\vec{r}) \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} \psi_1(\vec{r})\,d^3r \begin{Bmatrix} \mathcal{E}_x \\ \mathcal{E}_y \\ \mathcal{E}_z \end{Bmatrix}$ matters

OR x_{21} , y_{21} , z_{21} matters (these are spatial integrals)

x_{21}: x-polarized; y_{21}: y-polarized; together: circularly polarized

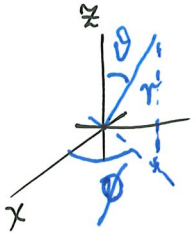
z_{21}: $\vec{\mathcal{E}} \parallel \hat{z}$ (z-polarized)

Consider Z_{21} : Depends on states ψ_2, ψ_1 and "z" in between (of the electron (matter))

- State 1: $\psi_{n\ell m_\ell}(r,\theta,\phi)$ State 2: $\psi_{n'\ell'm_{\ell'}}(r,\theta,\phi)$

$$Z_{21} = \int R^*_{n'\ell'}(r)\, Y^*_{\ell' m_{\ell'}}(\theta,\phi)\, \underbrace{(r\cos\theta)}_{z}\, R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi)\, \underbrace{r^2 \sin\theta\, dr\, d\theta\, d\phi}_{d^3r}$$

$$= \int_0^\infty R^*_{n'\ell'}(r)\, R_{n\ell}(r)\, r^3\, dr \cdot \int_0^{2\pi}\int_0^{\pi} \underbrace{Y^*_{\ell' m_{\ell'}}(\theta,\phi)}_{\sim e^{-im_{\ell'}\phi}}\, \underbrace{Y_{\ell m_\ell}(\theta,\phi)}_{e^{im_\ell\phi}} \cos\theta\, \underbrace{\sin\theta\, d\theta\, d\phi}_{d\Omega}$$



$$\text{"}\phi\text{-integral"} \sim \int_0^{2\pi} e^{-im_{\ell'}\phi} e^{im_\ell\phi}\, d\phi \begin{cases} = 0 & \text{for } m_\ell \neq m_{\ell'} \\ \neq 0 & \text{for } m_\ell = m_{\ell'} \end{cases}$$

$\therefore$ $Z_{21} \neq 0$ only for $m_\ell = m_{\ell'}$ or $\underbrace{\Delta m_\ell = 0}$

selection rule on Δm_ℓ for z-polarized $\vec{\mathcal{E}}$

- Even for ϕ-integral $\neq 0$, we still need to consider the θ-integral

  θ-integral $\neq 0$ only when $\Delta\ell = \pm 1$

- How about x_{21} & y_{21}?

$$x_{21} = \int_0^\infty R^*_{n'\ell'}(r)\, R_{n\ell}(r)\, r^3\, dr \cdot \int Y^*_{\ell' m_{\ell'}}(\theta,\phi)\, Y_{\ell m_\ell}(\theta,\phi)\, \underbrace{[\sin\theta \cos\phi}_{\text{from "x"}}]\, d\Omega$$

$$\therefore \phi\text{-integral} \sim \int_0^{2\pi} e^{-i m_{\ell'}\phi}\, e^{i m_\ell \phi} \left[\frac{e^{i\phi} + e^{-i\phi}}{2}\right] d\phi$$

$$\neq 0 \quad \text{when } \Delta m_\ell = \pm 1$$

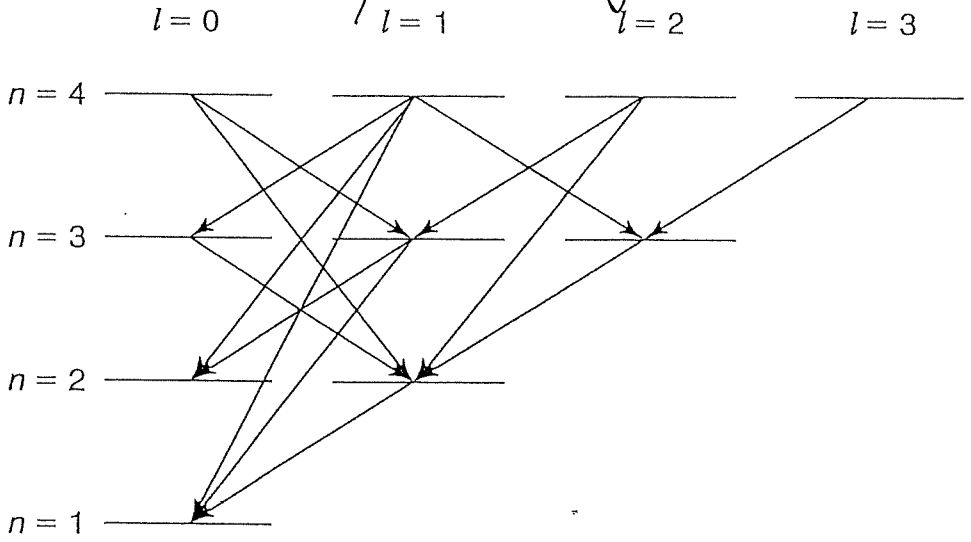
Similarly for y_{21}

$\therefore$ Different polarizations [linearly, circularly, unpolarized] take on different Δm_ℓ selection rules ($\therefore$ can control transition to selected excited states)

Selection rules for unpolarized light

- $\Delta l = \pm 1$; $\Delta m_\ell = 0, \pm 1$ (for electric dipole mechanism) (19)
- Example

Allowed decays in Hydrogen's first four levels ($\Delta l = \pm 1$)



Note: 2s (ψ_{200}) state has no where to decay to!
[via electric dipole mechanism]
It is called a meta-stable state.

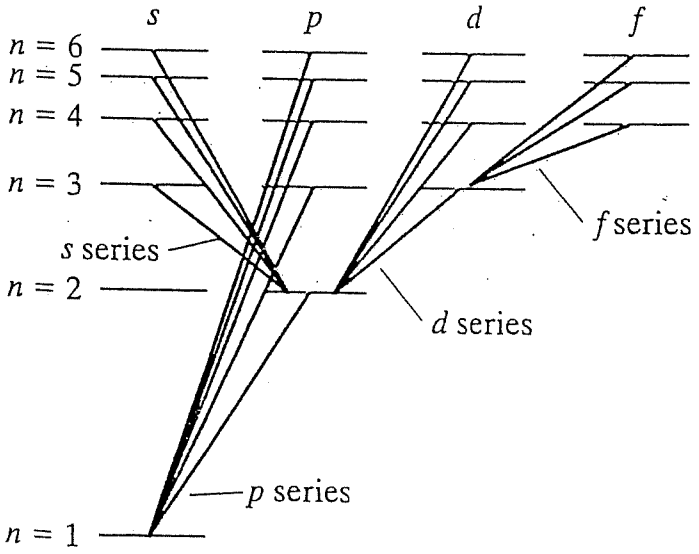
($l=0$) ($l=0$)
$2s \not\to 1s$

- 2s is a metastable state
once there, stay there much longer
- Metastable states are crucial for designing laser

Even for allowed transitions, $|Z_{21}|^2$, $|Y_{21}|^2$, $|X_{21}|^2$ can be big or small, brightness of spectral lines

Once upon a time, spectral lines are labelled as sharp (s), principal (p), diffuse (d), and fundamental (f). These labels were used for transitions giving the spectral lines, before they became labels for states.

Some allowed transitions in H-atom



Some of the allowed transitions observed in the hydrogen atom. Note that each involves a change of l by one unit, as is found to be the case for *all* allowed transitions. Note also that the traditional labels *s* (sharp), *p* (principal), *d* (diffuse), and *f* (fundamental) were originally applied to transitions, not levels.

Remarks (Optional)

- Properties of Spherical Harmonics are key to selection rules

  e.g. θ, ϕ integrals in Z_{21}

  $\cos\theta$ (from z) ← x, y, z behaves like $Y_{1,\text{something}}$

  $$\int Y^*_{\ell' m_\ell'}(\theta,\phi)\, Y_{\ell m_\ell}(\theta,\phi)\, \underbrace{Y_{10}(\theta,\phi)}\, d\Omega \neq 0 \quad \text{when } \Delta\ell = \pm 1 \text{ and } \Delta m_\ell = 0$$

  [related to integration of three $Y_{\ell m}$]

- When a transition is "forbidden", it is forbidden by <u>electric dipole</u> transition

  It may occur via <u>other</u> (<u>weaker</u>/hard to happen) <u>processes</u>

  - quadrupole?
  - $1 \not\to 3$, but $\underbrace{1 \to 2 \text{ and } 2 \to 3}$ may be OK ($\underbrace{\text{involve } \hat{H}' \text{ twice}}_{\text{higher-order process}}$)

    transition rate is much smaller

- Earlier (hydrogen atom part), mentioned that precision spectroscopy was used to study how big the proton is. Some studies used

  $2s \to 1s$, $3s \to 1s$ transitions ("2-photon processes")

  Not electric dipole mechanism

  ↖ ↗ 2s, 3s wavefunctions have bumps in $P(r) = r^2 |R_{n0}|^2$ closer to nucleus

  more sensitive to size of proton