(c) Seeing (Stimulated) Absorption and Emission from Eq. (18)

$$\hat{H}' = -\vec{\mu}\cdot\vec{\mathcal{E}}_0 \cos\omega t \qquad \text{(see Eq. (11), electric dipole mechanism)}$$

$$[\vec{\mu} = -e\vec{r}]$$

$$\hat{H}'(\vec{r},t) = -\tfrac{1}{2}\vec{\mu}\cdot\vec{\mathcal{E}}_0\left(e^{i\omega t} + e^{-i\omega t}\right) \qquad (19)$$

$\therefore$ Eq. (18) becomes

$$i\hbar\frac{da_2(t)}{dt} = -\frac{1}{2}\vec{\mathcal{E}}_0\cdot\underbrace{\left(\int\psi_2^*(\vec{r})\,\vec{\mu}\,\psi_1(\vec{r})\,d^3r\right)}\underbrace{\left[e^{\frac{i}{\hbar}(E_2-E_1+\hbar\omega)t} + e^{\frac{i}{\hbar}(E_2-E_1-\hbar\omega)t}\right]} \qquad (20)$$

- spatial integrals $(\vec{\mu})_{21}$
- "electric dipole matrix element"
- determines selection rules

- time factor
- set conditions relating E_2, E_1, and $\hbar\omega$
- important to note there are 2 terms

[everything follows from Eq. (20)]

- For $\vec{\mathcal{E}}_0 = \mathcal{E}_0 \hat{z}$ (e.g.), $\hat{H}' = e\vec{\mathcal{E}}_0 \cdot \vec{r} \cos\omega t = e\mathcal{E}_0 z \cos\omega t$ (13)

$\hat{H} = \hat{H}_{atom} + \hat{H}'(\vec{r}, t)$; $\psi_1(\vec{r})$ & $\psi_2(\vec{r})$ are <u>atomic states</u>

Eq. (20) reads

$$i\hbar \frac{da_2}{dt} = \frac{e\mathcal{E}_0}{2} \underbrace{z_{21}} \left[e^{\frac{i}{\hbar}(E_2 - E_1 + \hbar\omega)t} + e^{\frac{i}{\hbar}(E_2 - E_1 - \hbar\omega)t} \right] \quad (21)$$

$\int \psi_2^*(\vec{r})\, z\, \psi_1(\vec{r})\, d^3r$

↑ special case of (20) for $\hat{z}$-polarized wave

$-e z_{21} = (\mu_z)_{21}$

↑ z-component of $(\vec{\mu e})_{21}$ ← see Eq. (20)

Find $a_2(t)$ by integrating Eq.(21) over time $\int_0^t (\cdots) dt'$

$$a_2(t) = \frac{e\mathcal{E}_0}{2} z_{21} \frac{1}{i\hbar} \int_0^t \left[e^{\frac{i}{\hbar}(E_2 - E_1 + \hbar\omega)t'} + e^{\frac{i}{\hbar}(E_2 - E_1 - \hbar\omega)t'} \right] dt'$$

[two integrals are easy to do] (Ex.)

giving

$$a_2(t) = \frac{-e\mathcal{E}_0}{2} \overbrace{z_{21}}^{(\mu_z)_{21}} \left[\underbrace{\frac{e^{\frac{i}{\hbar}(E_2 - E_1 + \hbar\omega)t} - 1}{E_2 - E_1 + \hbar\omega}}_{\text{term ①}} + \underbrace{\frac{e^{\frac{i}{\hbar}(E_2 - E_1 - \hbar\omega)t} - 1}{E_2 - E_1 - \hbar\omega}}_{\text{term ②}} \right] \quad (22)$$

- Done! This is $a_2(t)$ due to $\hat{H}'$, given $a_2(0) = 0$ and $a_1(0) = 1$
- The rest is to extract the physics
- z_{21} or $(\mu_z)_{21}$ determines selection rules (generally $(\vec{\mu})_{21}$)
- term ① is to give stimulated emission, and term ② absorption

Physics in Eq. (22): $a_2(t) \sim \frac{\mathcal{E}_0}{2}(-e z_{21})\left[① + ②\right]$

- Look at term ②: dominates when $E_2 - E_1 \approx \overbrace{\hbar\omega}^{\text{positive}}$ [recall $a_1(0) = 1$]

  thus need $E_2 > E_1$ $\quad \overset{\omega}{\rightsquigarrow}$ $\quad 2 \text{ —— } E_2 \quad a_2(t)$ due to $\hat{H}'$

  $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 1 \text{ —— } E_1 \quad a_1(0) = 1$

∴ term ② represents absorption AND it is important when $\omega \approx \underbrace{\frac{E_2 - E_1}{\hbar}}$ (a condition on ω (or $\hbar\omega$))

- this is the common sense that the incident light should have $\hbar\omega$ that meets $E_2 - E_1$, to induce an upward transition by absorption
- Here, the condition emerges from QM (TDSE)
- Even we treated light "semi-classically", we still see $\hbar\omega \approx E_2 - E_1$ (absorption of a photon of energy $\hbar\omega$ in the transition)

When term ② dominates (near resonance), term ① is not important (way off resonance)

- Look at term ①: dominates when $E_1 - E_2 \approx \hbar\omega$ [recall $a_1(0) = 1$]

  thus need $E_1 > E_2$ ∴ downward transition ⇝ ω

  1 —— E_1 $a(0) = 1$

  2 —— E_2 $a_2(t)$ due to $\hat{H}'$

  term ① represents stimulated emission AND it is important when $\omega \approx \frac{E_1 - E_2}{\hbar}$ (i.e. incident light induces emission)

- Comes out from QM (but Einstein introduced effect in 1917 (before QM))

When term ① dominates (near resonance), term ② is not important (way off resonance)

(i) Absorption [term ② >> term ①]

neglect it

From Eq. (22),

$$a_2(t) = \frac{\mathcal{E}_0}{2}\underbrace{(\mu_z)_{21}}_{(-eZ_{21})}\left[\frac{e^{\frac{i}{\hbar}(E_2-E_1-\hbar\omega)t}-1}{E_2-E_1-\hbar\omega}\right]$$

$$= \mathcal{E}_0(-eZ_{21})\cdot\frac{\sin\frac{(E_2-E_1-\hbar\omega)t}{2\hbar}}{E_2-E_1-\hbar\omega}\cdot e^{\frac{i}{2\hbar}(E_2-E_1-\hbar\omega)t}$$

$|a_2(t)|^2 = ?$

E_2 —— $a_2(t) = ?$

$\hbar\omega$ ⇝

E_1 —— $a_1(0) = 1$

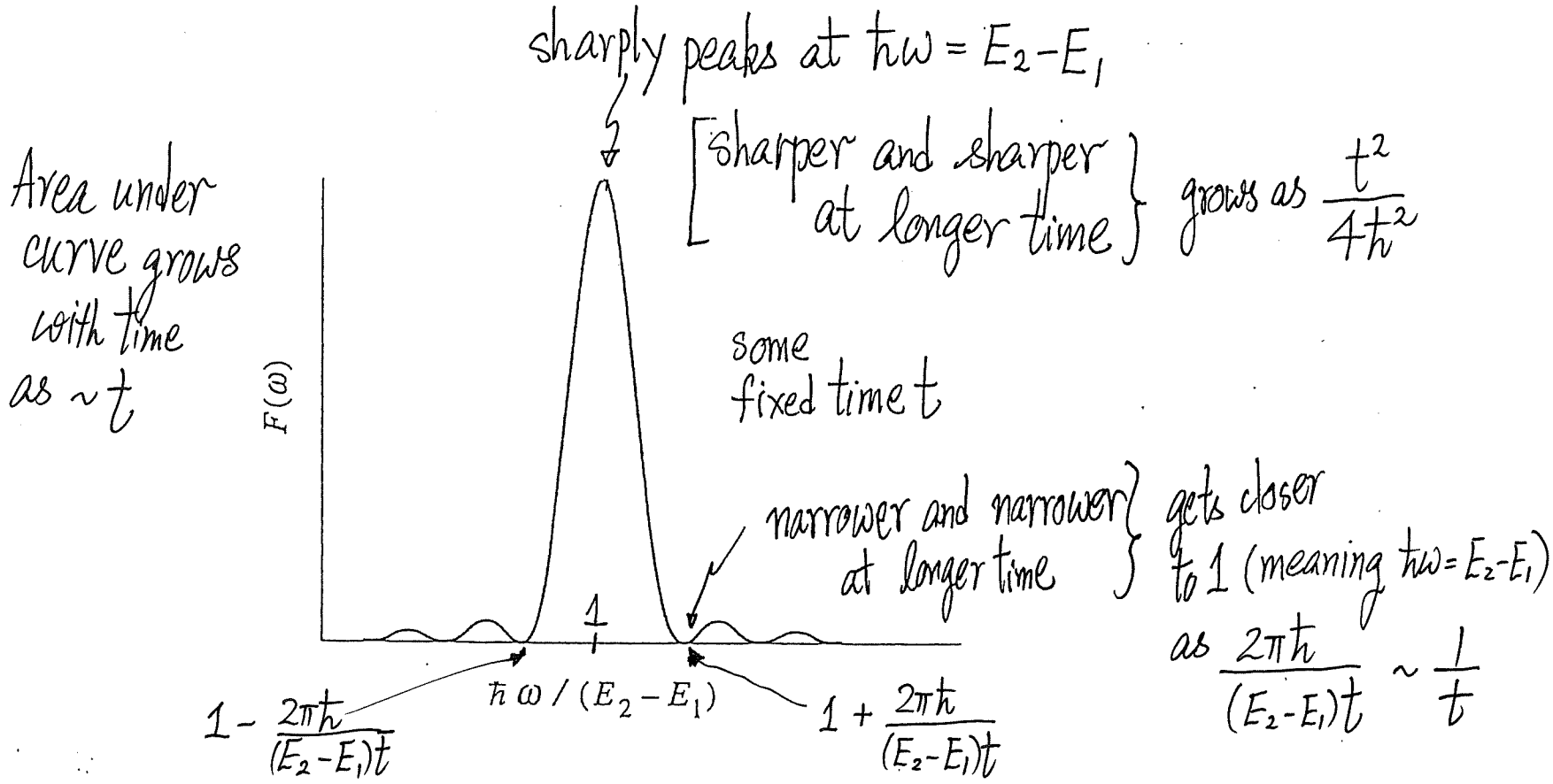
$$|a_2(t)|^2 = \mathcal{E}_0^2\, e^2 |Z_{21}|^2 \underbrace{\frac{\sin^2\left[\frac{(E_2-E_1-\hbar\omega)t}{2\hbar}\right]}{(E_2-E_1-\hbar\omega)^2}} \qquad (23)$$

Key Result

Prob. of finding system in state ψ_2 of energy E_2 at time t (given initially in state ψ_1 of energy E_1)

- gives condition on ω
- $|Z_{21}|^2$ or Z_{21} gives selection rule

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 $E_2 - E_1 = \hbar\omega = h\nu$.

- $F(\omega)$ sharply peaks at $\underbrace{\hbar\omega \approx E_2 - E_1}$ (otherwise $F(\omega) \sim 0$)
  "common sense" (out of QM)

  ∴ photon energy $\hbar\omega$ needs to hit $(E_2 - E_1)$ to induce <u>absorption</u>

- peak grows as $\sim t^2$ and width shrinks as $\sim \frac{1}{t} \Rightarrow$ Area under curve grows† as t

$$\Rightarrow |a_2(t)|^2 \propto t$$

∴ time part represented by $F(\omega)$ gives
- condition on ω (or $\hbar\omega$)
- $|a_2(t)|^2 \propto t$

---

† The behavior of $F(\omega)$ can be taken as $\frac{\pi}{2\hbar} t\,\delta(E_2 - E_1 - \hbar\omega) = \frac{\pi}{2\hbar^2} t\,\delta\left(\frac{E_2 - E_1}{\hbar} - \omega\right)$

(ii) Stimulated Emission [term ① >> term ②]

neglect it

From Eq. (22),

$$a_2(t) = \frac{\mathcal{E}_0}{2}\underbrace{(-e z_{21})}_{(\mu_z)_{21}} \left[\frac{e^{\frac{i}{\hbar}(E_2 - E_1 + \hbar\omega)t} - 1}{E_2 - E_1 + \hbar\omega}\right]$$

$\hbar\omega$ ⇝ E_1 —— $a_1(0) = 1$

E_2 —— $a_2(t) = ?$

$|a_2(t)|^2 = ?$

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

$$|a_2(t)|^2 = \mathcal{E}_0^2 e^2 \underbrace{|z_{21}|^2}_{\text{selection rule}} \underbrace{\frac{\sin^2\left[\frac{\hbar\omega - (E_1 - E_2)}{2\hbar}t\right]}{(\hbar\omega - (E_1 - E_2))^2}}_{\text{sharply peaks at } \hbar\omega = E_1 - E_2} \quad (24)$$

Key Result

and $|a_2(t)|^2 \propto t$

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

E_2 —— (higher)

E_1 —— (lower)

(Stimulated) Absorption (Eq. (23))

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

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

Stimulated Emission (Eq. (24))

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

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)!

(iii) Selection Rules

Eq. (20): $$i\hbar \frac{da_2(t)}{dt} = -\frac{1}{2}\vec{\mathcal{E}}_0 \cdot (\vec{\mu})_{21} \left[e^{\frac{i}{\hbar}(E_2 - E_1 + \hbar\omega)t} + e^{\frac{i}{\hbar}(E_2 - E_1 - \hbar\omega)t} \right]$$

Eq. (21): $$i\hbar \frac{da_2(t)}{dt} = \frac{e\mathcal{E}_0}{2} (z_{21}) \left[e^{\frac{i}{\hbar}(E_2 - E_1 + \hbar\omega)t} + e^{\frac{i}{\hbar}(E_2 - E_1 - \hbar\omega)t} \right]$$

Then Eqs. (23) & (24): $$|a_{1\to 2}(t)|^2 = e^2\mathcal{E}_0^2 |z_{21}|^2 \frac{\sin^2\left[\frac{\hbar\omega - (E_2 - E_1)}{2\hbar} \cdot t\right]}{[\hbar\omega - (E_2 - E_1)]^2}$$

If $(\vec{\mu})_{21} = 0$, or $z_{21} = 0$, then $1 \to 2$ transition is forbidden

not allowed ($\because a_2(t) = 0$)

$\therefore$ Conditions for $z_{21} \neq 0$ ($\vec{\mu}_{21} \neq 0$ generally) give selection rules

Selection Rules (work for both absorption & emission)

- $|Z_{21}|^2$ or Z_{21} determines whether transitions are allowed or forbidden
- Generally it is $\vec{\mu}_{21} \cdot \vec{\mathcal{E}}$ that matters (see Eq. (20))

OR $\int \psi_2^*(\vec{r})\,(-e\vec{r})\,\psi_1(\vec{r})\,d^3r \cdot \vec{\mathcal{E}}$ that matters (Spatial integral)

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

OR x_{21} (circularly polarized), y_{21} (circularly polarized), z_{21} that matter [Key idea]

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

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

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

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

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

$Z_{21} \neq 0$ 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 <u>θ-integral</u>

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

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

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

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

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

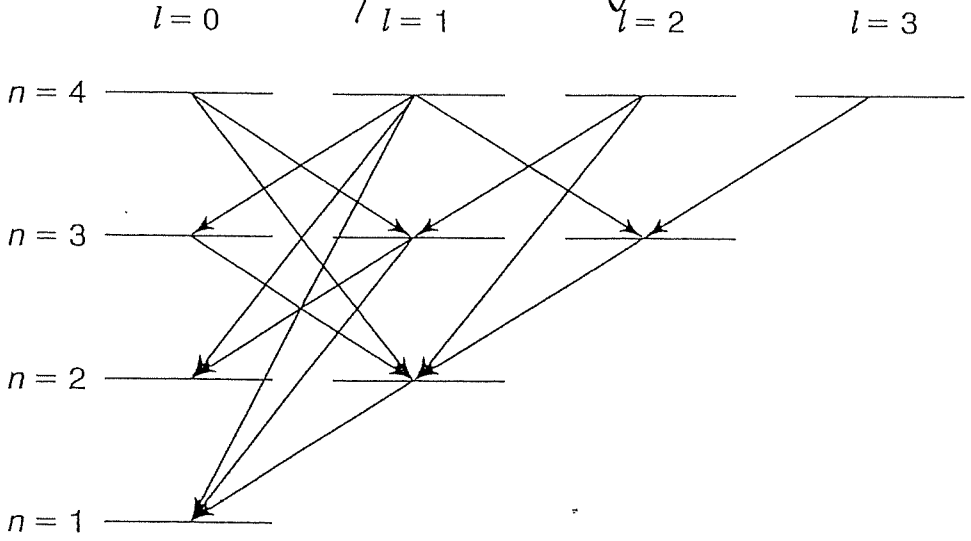
Similarly for y_{21}

$\therefore$ Different polarizations [linearly, circularly, unpolarized] take on different Δm_ℓ selection rules

Selection rules for unpolarized light

- $\Delta l = \pm 1$; $\Delta m_\ell = 0, \pm 1$ (for electric dipole mechanism) (25)
- Example

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



$(l=0)$ $(l=0)$

$2s \not\to 1s$

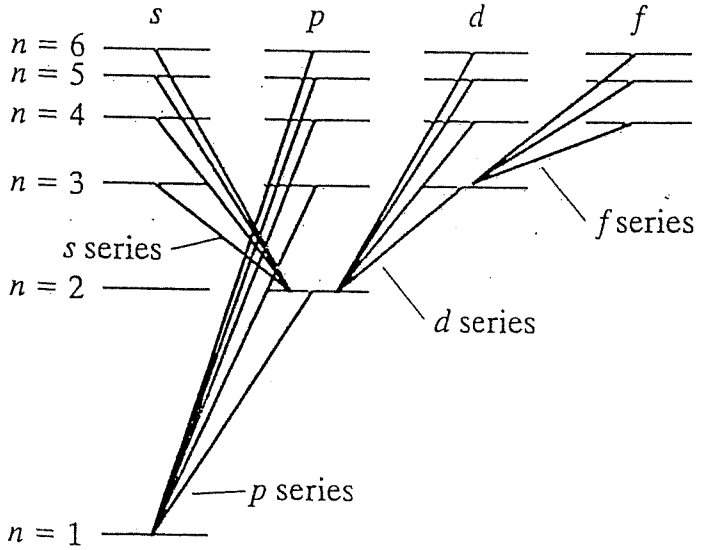
- 2s is a metastable state
  once there, stay there much longer
- Metastable states are crucial for designing laser

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

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.

Key Points

- QM works (time-dependent perturbation theory)
- Same theory works for stimulated absorption and stimulated emission
- Explains condition on ω [$\hbar\omega = E_2 - E_1$] and selection rules
  - condition on ω: $F(\omega)$
  - selection rules: matrix elements x_{21}, y_{21}, z_{21}
- Intensity (or transition rate) is related to $|\text{matrix element}|^2$
- $-\vec{\mu}\cdot\vec{\mathcal{E}}$ dipole mechanism captures key phenomena
- Same idea works for transitions in molecules/solids
- Selection rules are often determined by symmetry (parity) of $\psi_1(\vec{r})$ and $\psi_2(\vec{r})$

Remarks (Optional)

- Properties of Spherical Harmonics are key to selection rules

  e.g. θ, ϕ integrals in Z_{21}

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

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

- When a transition is "forbidden", it is forbidden by electric dipole transition

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

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