D. Poorman's[+] Time-dependent Perturbation Theory

TDSE $\quad i\hbar \dfrac{\partial \Psi}{\partial \underline{t}} = \hat{H}\Psi$ governs time evolution of Ψ

referring to $\hat{H}(\underline{t})$

[good for time-independent **AND** time-dependent $\hat{H}$]

- With $\Psi(x,0)$, what is $\Psi(x,\underline{\Delta t})$?

slightly later

$$\Psi(x,\Delta t) \approx \Psi(x,0) + \left.\frac{\partial \Psi}{\partial t}\right|_{t=0} \cdot \Delta t \qquad \text{(Taylor expansion)}$$

$$= \Psi(x,0) + \frac{1}{i\hbar}\left(\hat{H}\Psi\right)_{\underbrace{t=0}_{\text{meaning } \hat{H}(t=0)\Psi(x,0)}} \cdot \Delta t \quad (10) \quad \left(\text{Using TDSE } i\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi\right)$$

[+] Quickly getting at the key result, despite not in complete form

Let's say $\begin{cases} \hat{H} = \hat{H}_{atom} \text{ for } t<0 \quad \underline{\text{AND}} \quad \Psi(x,0) = \underbrace{\psi_i(x)}_{\text{an eigenstate of } \hat{H}_{atom} \text{ with energy } \varepsilon_i} \\ \hat{H} = \hat{H}_{atom} + \underbrace{\hat{H}'}_{\text{interaction enters (switched on)}} \text{ for } \underline{t \geq 0} \end{cases}$

- From (10), $$\Psi(x,\Delta t) \approx \psi_i(x) + \frac{1}{i\hbar}\Big(\hat{H}_{atom} + \underbrace{\hat{H}'}_{\text{takes part in evolving state (in addition to } \hat{H}_{atom})}\Big)\psi_i(x)\cdot\Delta t \qquad (11)$$

<u>Probability of finding atom in state ψ_f</u> --?

$$\text{Prob. amplitude} = \int_{-\infty}^{\infty} \psi_f^*(x)\,\Psi(x,\Delta t)\,dx$$

$$= \int_{-\infty}^{\infty} \cancelto{0}{\psi_f^*(x)\psi_i(x)}\,dx + \frac{1}{i\hbar}\varepsilon_i \int_{-\infty}^{\infty} \cancelto{0}{\psi_f^*(x)\psi_i(x)}\,dx\cdot\Delta t + \frac{\Delta t}{i\hbar}\int_{-\infty}^{\infty}\psi_f^*(x)\,\hat{H}'\,\psi_i(x)\,dx$$

$$= \Delta t \cdot \frac{1}{i\hbar}\int_{-\infty}^{\infty} \psi_f^*(x)\,\hat{H}'\,\psi_i(x)\,dx \qquad (12)$$

When the mathematics is done more accurately,† we have

- Without $\hat{H}'(t)$, $\psi_i(x)$ evolves to $e^{-iE_it'/\hbar}\psi_i(x)$ due to $\hat{H}_{atom}$ at time t'
- It is $\hat{H}'(t')$ that would bring in the mixing of other states

$$\frac{1}{i\hbar}\underbrace{\hat{H}'(t')e^{-iE_it'/\hbar}\psi_i(x)}_{\text{carries mixture of states other than }\psi_i}\cdot\Delta t' \qquad \text{(see Eq.(11))}$$

- Probability amplitude of finding atom in state ψ_f after $\hat{H}'(t)$ is on for time t'

$$a_f(t) = \frac{1}{i\hbar}\int_0^t\left[\int_{-\infty}^{\infty}\psi_f^*(x)\,e^{\frac{iE_ft'}{\hbar}}\,\hat{H}'(t')\,e^{\frac{-iE_it'}{\hbar}}\psi_i(x)\,dx\right]dt' \qquad (13)$$

Key Result (†can be derived formally from TDSE : Time-dependent Perturbation Theory]

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

- All results follow from analyzing Eq.(13)

$$\hat{H}'(t') = -\underset{\substack{\uparrow\\ \text{space}}}{\vec{\mu}}\cdot\vec{\mathcal{E}}_0\cos\omega\underset{\substack{\uparrow\\ \text{time}}}{t} = e\underset{\substack{\uparrow\\ \text{space}}}{\vec{r}}\cdot\vec{\mathcal{E}}_0\cos\omega\underset{\substack{\uparrow\\ \text{time}}}{t}$$

$$a_f(t) = -\underbrace{\left(\int \overset{\substack{\text{atomic state}\\ \downarrow}}{\psi_f^*(\vec r)}\,\overset{\substack{(-e\vec r)\\ \uparrow}}{\vec\mu}\,\overset{\substack{\text{atomic state}\\ \swarrow}}{\psi_i(\vec r)}\,d^3r\right)}_{}\cdot\underbrace{\left(\frac{1}{i\hbar}\vec{\mathcal{E}}_0\int_0^t e^{\frac{i}{\hbar}(E_f-E_i)t'}\cos\omega t'\,dt'\right)}_{} \tag{14}$$

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 $\hbar\omega$
- $\underbrace{\text{2 terms}}_{\text{stimulated absorption \& emission}}$ because $\cos\omega t' = \dfrac{e^{-i\omega t}+e^{i\omega t}}{2}$

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

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

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

(in general complex)

$\uparrow$ z-component of $\vec{\mu}_{fi}$

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

$\nearrow$ 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 $\hbar\omega$)

$$a_f(t) = (-e z_{fi}) \frac{\mathcal{E}_0}{2} \Bigg[\underbrace{\frac{e^{\frac{i}{\hbar}(E_f - E_i + \hbar\omega)t} - 1}{E_f - E_i + \hbar\omega}}_{\substack{\text{term ①} \\ \text{stimulated emission}}} + \underbrace{\frac{e^{\frac{i}{\hbar}(E_f - E_i - \hbar\omega)t} - 1}{E_f - E_i - \hbar\omega}}_{\substack{\text{term ②} \\ \text{(stimulated) absorption}}} \Bigg] \qquad (16)$$

$\uparrow$

initial condition

is $a_f(0) = 0$

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

- 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)
- $(-e z_{fi})\mathcal{E}_0$ in front is $(\mu_z)_{fi}\mathcal{E}_0$ [generally $(\vec{\mu})_{fi} \cdot \vec{\mathcal{E}}_0$]

(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),

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

$$\boxed{\underset{\uparrow}{|a_2(t)|^2} = \mathcal{E}_0^2\, e^2\, \underbrace{|z_{21}|}_{\uparrow}{}^2\;\underbrace{\frac{\sin^2\left[\frac{(E_2-E_1-\hbar\omega)t}{2\hbar}\right]}{(E_2-E_1-\hbar\omega)^2}}_{\text{requires } \underset{\substack{\uparrow\\ \text{final}}}{E_2}-\underset{\substack{\uparrow\\ \text{initial}}}{E_1}=\hbar\omega} \qquad (17)}$$

Prob. of finding atom in ψ_2 of energy E_2 at time t

$\neq 0$ (?) [allowed]

$= 0$ [forbidden]

(selection rule)

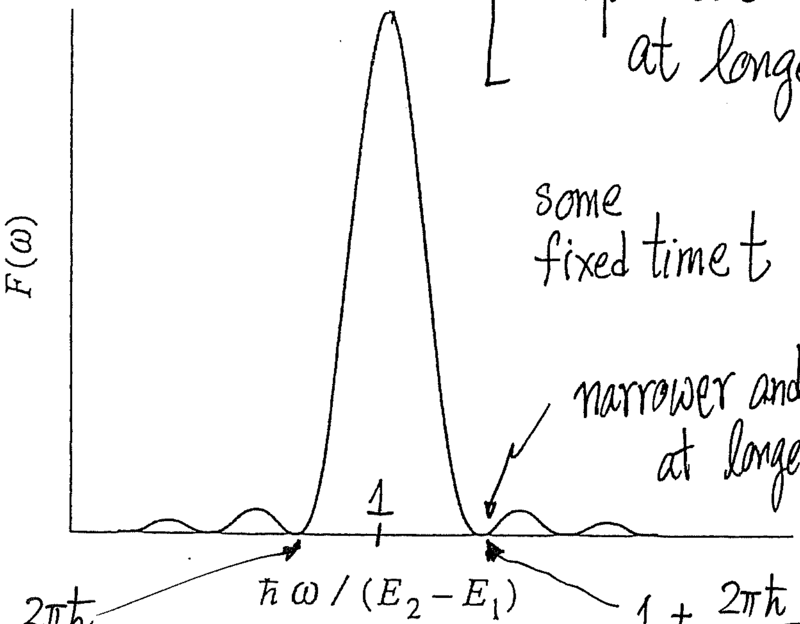
(Absorption)

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

Area under curve grows with time as $\sim t$

sharply peaks at $\hbar\omega = E_2 - E_1$

[sharper and sharper at longer time } grows as $\dfrac{t^2}{4\hbar^2}$ with time



some fixed time t

narrower and narrower at longer time } gets closer to 1 (meaning $\hbar\omega = E_2 - E_1$) as $\dfrac{2\pi\hbar}{(E_2 - E_1)t} \sim \dfrac{1}{t}$

$1 - \dfrac{2\pi\hbar}{(E_2 - E_1)t}$

$1 + \dfrac{2\pi\hbar}{(E_2 - E_1)t}$

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 $1 \to 2$ 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 $\sim \frac{1}{t}$ ⇒ Area under curve grows† as t

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

∴ 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 $\frac{\pi}{2\hbar} t\,\delta(E_2 - E_1 - \hbar\omega) = \frac{\pi}{2\hbar^2} t\,\delta\left(\frac{E_2 - E_1}{\hbar} - \omega\right)$

(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),

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

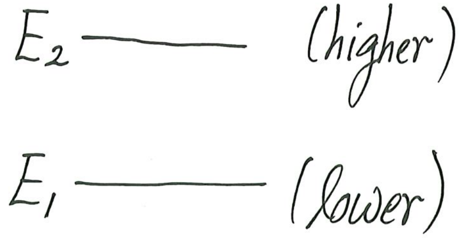
$$|a_2(t)|^2 = \mathcal{E}_0^2 e^2 |z_{21}|^2 \underbrace{\frac{\sin^2\left[\frac{\hbar\omega-(E_1-E_2)}{2\hbar}\cdot t\right]}{(\hbar\omega-(E_1-E_2))^2}}_{\text{sharply peaks at } \hbar\omega = E_1 - E_2} \qquad (18)$$

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

sharply peaks at $\hbar\omega = \underset{\text{initial}}{\overset{\text{higher}}{E_1}} - \underset{\text{final}}{\overset{\text{lower}}{E_2}}$

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

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



(Stimulated) Absorption (Eq. (17))

$$|a_{1\to 2}(t)|^2 = |a_{12}(t)|^2$$

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

Stimulated Emission (Eq. (18))

$$|a_{2\to 1}(t)|^2 = |a_{21}(t)|^2$$

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

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

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

$$|a_{1\to2}(t)|^2 \propto |z_{21}|^2 \quad ; \quad |a_{2\to1}(t)|^2 \propto |z_{12}|^2 = |z_{21}|^2 \quad (\vec{\mathcal{E}} \parallel \hat{z})$$

Generally, $(\vec{\mu})_{21}$ or $(\vec{r})_{21}$ determines whether $|a_{1\to2}|^2 = 0$ or $\neq 0$

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

OR

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

OR

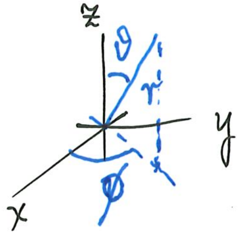
$$\underbrace{\underset{\substack{\uparrow \\ x\text{-polarized}}}{x_{21}} \;,\quad \underset{\substack{\uparrow \\ y\text{-polarized}}}{y_{21}}}_{\text{circularly polarized}} \;,\quad \underset{\substack{\uparrow \\ \vec{\mathcal{E}} \parallel \hat{z}\ (z\text{-polarized})}}{z_{21}} \qquad \text{matters}$$

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

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

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



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

∴ $\boxed{Z_{21} \neq 0 \text{ only for } m_\ell = m_\ell' \text{ OR } \underbrace{\Delta m_\ell = 0}_{\text{selection rule on } \Delta m_\ell \text{ for } z\text{-polarized } \vec{\mathcal{E}}}}$

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

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

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

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

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

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

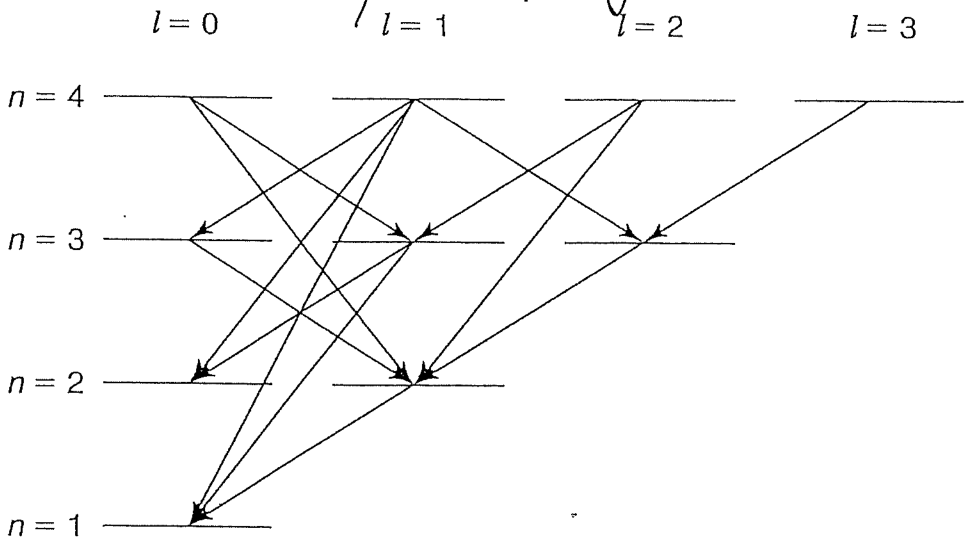
Similarly for y_{21}

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

Selection rules for unpolarized light

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

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



$\underset{(\ell=0)}{2s} \not\rightarrow \underset{(\ell=0)}{1s}$

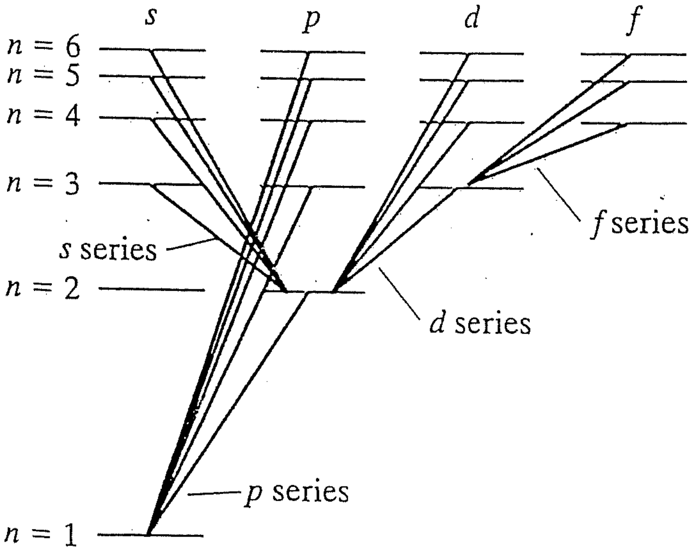
- 2s is $\underbrace{\text{a metastable state}}_{\text{once there, stay there much longer}}$
- Metastable states are crucial for designing laser

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 $\underbrace{\text{big}}_{\text{brightness of spectral lines}}$ or small

- 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} ← x, y, z behaves like $Y_{\underline{1}, \text{something}}$

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

  [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 $\Big(\underbrace{\text{involve } \hat{H}' \text{ twice}}_{\text{higher-order process}}\Big)$

(d) From $|a_{1\to 2}(t)|^2$ to Rate of Transition $\lambda_{1\to 2}$

Eq.(17):

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

single ω (monochromatic)

$$= \underbrace{\left(\frac{1}{2}\varepsilon_0\mathcal{E}_0^2\right)}_{} \frac{2}{\varepsilon_0} e^2 |z_{21}|^2 \left(\begin{array}{c}\text{shapely peaked at } \hbar\omega = E_2-E_1 \\ \text{\& area under curve grows} \sim t\end{array}\right)$$

$$= U_\omega \cdot \frac{2}{\varepsilon_0} e^2 |z_{21}|^2 \underbrace{\left(\quad \cdots \quad\right)}_{\text{peaks up light at the right } \hbar\omega\ (=E_2-E_1)}$$

U_ω: energy density [energy per unit volume] (~ intensity of incident light) monochromatic of angular frequency ω

ε_0: ε_0 in "$4\pi\varepsilon_0$"

After working things out carefully

$$|a_{1\to 2}(t)|^2 = \frac{2e^2}{\varepsilon_0}\underbrace{|z_{21}|^2}_{\text{selection rule}}\frac{\pi}{2\hbar^2}\cdot \overset{\text{linear in } t}{t}\cdot \underbrace{U(\omega_{21})}_{\propto \text{ how strong incident light of the right angular frequency}}$$

works† for non-monochromatic light

$U(\omega)d\omega$ = energy density in $\omega \to \omega + d\omega$

∝ how strong incident light of the right angular frequency [(stimulated) absorption, make sense]

$$\frac{|a_{1\to 2}(t)|^2}{t} \text{ is a quantity of unit } \frac{1}{\text{time}}$$

For stimulated emission, same argument gives

$$|a_{2\to 1}(t)|^2 = \frac{2e^2}{\varepsilon_0}|z_{21}|^2\frac{\pi}{2\hbar^2}\cdot t\cdot U(\omega_{21})$$

(same expression)

same $|z_{21}|^2$ enters

---

† Practically, the incident light has a spread in frequency. Up to last page, ω is taken as a discrete variable. Here, we go to a continuum description with $U(\omega)d\omega$ being energy density in interval $\omega \to \omega + d\omega$.

Make physical sense

involve atomic states and z (OR x & y) of electron in the middle

$$|a_{1\to 2}(t)|^2 = \underbrace{\frac{2e^2}{\varepsilon_0}\,\frac{\pi}{2\hbar^2}}_{\text{constants (from QM derivation)}} \cdot \underbrace{|z_{21}|^2}_{\text{selection rule}} \cdot \underbrace{U(\omega_{21})}_{\text{proportional to how strong the incident light is at the correct frequency}} \cdot t$$

proportional to time$^+$ t that light interacts with atom

$^+$ time t is often limited by factors such as collision with other atoms, thus don't be carried away that $|a_{1\to 2}(t)|^2$ can keep on increasing. Often, $|a_{1\to 2}(t)|^2$ is small.

- The Rate at which transition (1→2) occurs

≡ Transition Probability per unit time

(non-monochromatic)

$$\equiv \lambda_{\underset{\text{lower}}{1}\rightarrow\underset{\text{higher}}{2}} = \frac{|a_2(t)|^2}{t} = \frac{\pi e^2}{\varepsilon_0 \hbar^2} U(\omega_{21}) |z_{21}|^2 \quad (20) \quad (\text{for } \hat{z}\text{-polarized light})$$

averaging over polarizations and propagation directions†

Generally, Transition rate (absorption)

$$\boxed{\lambda_{1\rightarrow 2} = \frac{\pi e^2}{3\varepsilon_0 \hbar^2} U(\omega_{21}) |r_{21}|^2} \quad (21)$$

- $|r_{21}|^2 \equiv |\vec{r}_{21}|^2$ with $\vec{r}_{21} = \int \psi_2^*(\vec{r})\, \overset{(x\hat{i} + y\hat{j} + z\hat{k})}{\vec{r}}\, \psi_1(\vec{r})\, d^3r$ ← a vector (generally complex)
- $e^2|\vec{r}_{21}|^2 \equiv |\vec{\mu}_{21}|^2$ (reminds us that it is electric dipole moment that matters)

---

† Don't worry about the details from (20) to (21). They carry the same physics.

Following same argument,

Transition rate (stimulated emission)

$$\boxed{\lambda_{2\to1} = \frac{\pi e^2}{3\varepsilon_0\hbar^2} U(\omega_{21}) \, |r_{21}|^2} \quad (22)$$

$$\lambda_{\substack{1\to2 \\ 2\to1}} \propto U(\omega_{21}) \, |r_{21}|^2$$

"Applied QM common sense"

Between two states (one upper & one lower), $|r_{21}|^2$ in (21) & (22) is the same

∴ Between two states under the same condition [$U(\omega_{21})$ the same]

$$\boxed{\begin{array}{l}\text{Transition rate of Stimulated Absorption} \\ \quad = \underline{\text{Transition rate}}\ \text{of}\ \underline{\text{stimulated emission}}\end{array}} \quad (23)$$

- A result of QM (Applied QM common sense)
- QM gives absorption and stimulated emission

good

Given (23), if there are only 2 states (one lower & one higher), will it be possible to use light to excite to a situation where there are more atoms in state 2 than in state 1 in a gas of atoms?

Keywords: population inversion, 3-level & 4-level lasers

Another Applied QM common sense

Hint: Start with $\frac{dN_1}{dt}$ and $\frac{dN_2}{dt}$, $N_1 + N_2 = N$ = total # atoms

Remarks

- Eqs. (20), (21), (22) are special forms of the Fermi Golden Rule
- When there are many final states (~ degeneracy of energy E_2), add in different final states
- $$\mathrm{QM} \rightarrow \lambda_{1\rightarrow 2} \quad \text{or} \quad \underbrace{\lambda_{\text{initial}\rightarrow(\text{many final states})}}_{\text{related to spectroscopic } \underbrace{\text{absorption coefficient}}_{\text{measurable quantity}}}$$
- $$\frac{1}{\lambda} \text{ is } \underbrace{\text{a time}}_{\text{related to } \underbrace{\text{life time of an atomic state}}_{\text{measurable quantity}}}$$

- Absorption and Stimulated Emission are processes that can be readily explained within Schrödinger QM
- How about Spontaneous Emission? [No applied $U(\omega_{21})$?]