Special case: harmonic / constant perturbation

$$\hat{V}(t) = \hat{V}\sin\omega t \quad \text{for } t \geq 0$$

$$V_{ni} = \frac{1}{2i} V_{ni} (e^{i\omega t} - e^{-i\omega t}) \qquad V_{ni} = \langle n|\hat{V}|i\rangle \neq V_{ni}(t)$$

$$c_n^{(1)}(t) = -\frac{V_{ni}}{2\hbar}\int_0^t e^{i\omega_{ni}t'}(e^{i\omega t'} - e^{-i\omega t'})\,dt' =$$

$$= \frac{V_{ni}}{2\hbar i}\left[\frac{1-e^{i(\omega_{ni}+\omega)t}}{\omega_{ni}+\omega} - \frac{1-e^{i(\omega_{ni}-\omega)t}}{\omega_{ni}-\omega}\right] =$$

$$= \frac{V_{ni}}{\hbar}\left[-\frac{\sin\left(\frac{\omega_{ni}+\omega}{2}t\right)}{\omega_{ni}+\omega} e^{i\frac{(\omega_{ni}+\omega)t}{2}} + \frac{\sin\left(\frac{\omega_{ni}-\omega}{2}t\right)}{\omega_{ni}-\omega} e^{i\frac{(\omega-\omega_{ni})t}{2}}\right]$$

similar expression for $\hat{V}(t) = \hat{V}\cos\omega t$

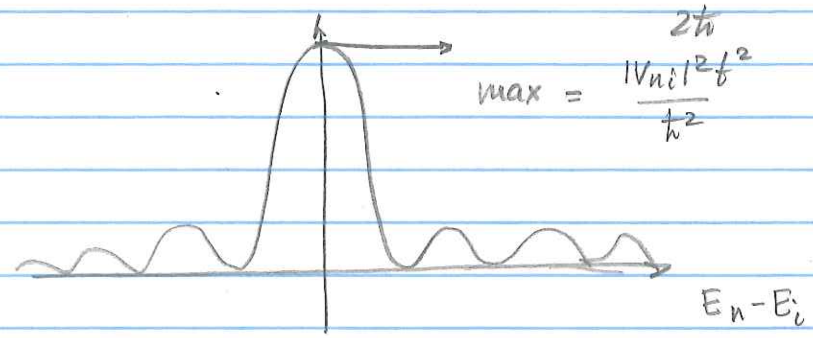
If $\omega = 0$ $\quad V(t) = \hat{V} = \text{const}$

$$c_n^{(1)}(t) = -\frac{V_{ni}}{\hbar}\int_0^t e^{i\omega_{ni}t}\,dt = i\frac{V_{ni}}{\hbar\omega_{ni}}(e^{i\omega_{ni}t} - 1) =$$

$$= -\frac{2V_{ni}}{\hbar\omega_{ni}} \sin\frac{\omega_{ni}t}{2}\, e^{i\omega_{ni}t/2}$$

$$P_{i\to n} = |c_n^{(1)}|^2 = \frac{4|V_{ni}|^2}{(E_n-E_i)^2}\sin^2\frac{(E_n-E_i)t}{2\hbar}$$

$$\text{or} \quad P_{i\to n} = \frac{|V_{ni}|^2}{\hbar^2}\left[\frac{\sin\frac{(E_n-E_i)t}{2\hbar}}{\frac{(E_n-E_i)}{2\hbar}}\right]^2$$



The central peak determines the most probable transition

width $\frac{\Delta E \cdot t}{2\hbar} \sim 1 \Rightarrow \Delta E \sim \frac{\hbar}{\Delta t}$ "Uncertainty relations"

The shorter is t, the brodder is the range of possible states

For longer times the probability of transitions b/w statates with the same energy $E_n = E_i$ grows as t^2

For large t (but such at $\left|\frac{V_{ni} t}{\hbar}\right| \ll 1$)

$$\lim_{\alpha \to \infty} \frac{\sin^2 \alpha x}{\alpha x^2} \to \pi \delta(x)$$

energy conservation

$$P_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \cdot t \; \delta(E_n - E_i)$$

Transition rate $\frac{dP_{i\to n}}{dt} = W_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i)$

Fermi's golden rule

Discrete spectrum

$$P_{i\to \text{anywhere}} = \sum_{n\neq i} |c_n^{(1)}|^2$$

Continuous spectrum

$$P_{i\to E_n = E} = \sum |c_n^{(1)}|^2 \cdot (\#\text{ states with } E \approx E_n) =$$

$$= \int \overline{|c_n^{(1)}|} \, \rho(E_n) \, dE_n$$

where $\rho(E_n) = \lim_{\Delta E \to 0} \frac{(\#\text{ of states b/w } E - \Delta E/2 \text{ and } E + \Delta E/2)}{\Delta E}$

Substituting the calculated expression for $|c_n^{(1)}|^2$ in case of constant potential

$$P(t) = \int \frac{4\,\overline{|V_{ni}|^2}}{(E_n-E_i)^2} \sin^2\frac{(E_n-E_i)t}{2\hbar}\, \rho(E_n)\, dE_n$$

for relatively large t $\left(\frac{\sin\frac{\Delta E\cdot t}{2\hbar}}{\Delta E}\right)^2 \longrightarrow t\,\delta(\Delta E)$

$$\underset{\text{(for large } t)}{P(t)} = \int \frac{2\pi}{\hbar}\, \overline{|V_{ni}|^2}\, t\, \delta(E_n-E_i)\, \rho(E_n)\, dE_n \approx$$

$$\approx \frac{2\pi}{\hbar}\, \overline{|V_{ni}|^2}\, t\, \rho(E_n)\Big|_{E_n \simeq E_i}$$

Transition rate

$$\left[\begin{array}{l} w_{i\to[n]} = \frac{2\pi}{\hbar}\, \overline{|V_{ni}|^2}\, \rho(E_n)_{E_n \simeq E_i} \\ \text{final state with } E_n \end{array}\right.$$

Fermi's Golden Rule

Here $\overline{|V_{ni}|}$ assumes averaging over all $[n]$ states. Often it is the case that for $E_n \approx E_{n'}$
$V_{in} \approx V_{in'}$

Back to the harmonic perturbation

$$\hat{V}(t) = \hat{V} e^{i\omega t} + \hat{V}^{+} e^{-i\omega t}$$

$$c_n^{(1)} = -\frac{i}{\hbar} \int_{-\infty}^{t} V_{ni}(t)\, e^{i\omega_{ni} t}\, dt$$

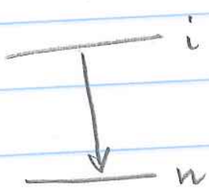
$$c_n^{(1)} = \frac{1}{\hbar} \Bigg[\underbrace{\frac{1 - e^{i(\omega_{ni}+\omega)t}}{\omega_{ni}+\omega}}_{\substack{\text{peaks near} \\ \omega \approx -\omega_{ni}}} V_{ni} + \underbrace{\frac{1 - e^{i(\omega_{ni}-\omega)}}{\omega_{ni}-\omega}}_{\substack{\text{peaks near} \\ \omega \approx \omega_{ni}}} V_{ni}^{*} \Bigg]$$

where $V_{ni} = \langle n | \hat{V} | i \rangle$

Following only the dominant contribution

$\omega \approx -\omega_{ni} = \omega_{in} > 0$

stimulated emission



$$c_n^{(1)} \approx \frac{1}{\hbar} \frac{1 - e^{i(\omega - \omega_{in})t}}{\omega - \omega_{in}} V_{ni}$$

$$|c_n^{(1)}|^2 \approx \frac{4 V_{ni}^2}{\hbar^2 (\omega - \omega_{in})^2} \sin^2\left(\frac{\omega - \omega_{in}}{2} t\right)$$

Following the same procedure as for the constant perturbation

$$W_{i \to n} = \frac{2\pi}{\hbar} V_{ni}^2\, \delta(E_n - E_i + \hbar\omega) \qquad \boxed{\text{emission rate}}$$

and for the degenerate / continuous spectrum

$$W_{i \to [n]} = \frac{2\pi}{\hbar} V_{ni}^2\, \rho(E_n) \Big|_{E_n \approx E_i - \hbar\omega}$$

$\omega \approx \omega_{ni} > 0$ stimulated absorption

$$|c_n^{(1)}|^2 \approx \frac{4|V_{ni}|^2}{\hbar^2(\omega-\omega_{ni})^2} \sin^2\left[\frac{\omega-\omega_{ni}}{2}t\right]$$

absorption rate

$$W_{i\to n} = \frac{2\pi}{\hbar}|V_{ni}|^2 \,\delta(E_n - E_i - \hbar\omega)$$

total rate

$$W_{i\to[n]} = \frac{2\pi}{\hbar}|V_{ni}|^2 \,\rho(E_n)\Big|_{E_n \approx E_i + \hbar\omega}$$

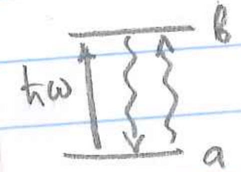
Conclusion: harmonic perturbation causes stimulated emission and absorption in units of $\hbar\omega$
Just what we'd expect for photons carrying $\hbar\omega$ quanta of energy!

For transitions to occure and satisfy the energy conservation, it is necessary to either
- Have a continuum of final states, to match $\Delta E = \hbar\omega$ for a fixed perturbation frequency ω

or

- perturbation must cover sufficiently wide spectrum of frequencies ω so that discrete transitions with the fixed $\Delta E_{nm} = \hbar\omega$ are possible

Also, it is easy to see that



$$\underset{\substack{\uparrow\\ \text{emission}\\ \text{rate}}}{\frac{W_{b\to a}}{\rho(E_a)}} = \underset{\substack{\uparrow\\ \text{absorption}\\ \text{rate}}}{\frac{W_{a\to b}}{\rho(E_b)}}$$

Harmonic perturbation nicely describes interaction of atoms with electromagnetic field

Vector potential $\vec{A} = 2A_0\,\underset{\substack{\uparrow\\ \text{polarization}}}{\vec{\varepsilon}}\cos\left(\frac{\omega}{c}\vec{n}\cdot\vec{r} - \omega t\right) =$

$= A_0\vec{\varepsilon}\left[e^{i(\frac{\omega}{c}\vec{n}\vec{r}-\omega t)} + e^{-i(\frac{\omega}{c}\vec{n}\vec{r}-\omega t)}\right]$

$$\hat{H} = \frac{\hat{p}^2}{2m} \underbrace{- \frac{e}{mc}\vec{A}\cdot\vec{p}}_{\text{interaction term}} + U(r) \qquad \text{where } \varphi = 0,\ \nabla\cdot\vec{A} = 0$$

$$\hat{V}_{int} = -\frac{e}{mc}\vec{A}\cdot\vec{p} = -\frac{e}{mc}A_0\vec{\varepsilon}\hat{\vec{p}}\left[\underbrace{e^{i(\vec{k}\vec{r}-\omega t)}}_{\text{absorption}} + \underbrace{e^{-i(\vec{k}\vec{r}-\omega t)}}_{\text{emission}}\right]$$

$\vec{k} = \frac{\omega}{c}\vec{n}$

$$V_{ni} = -\frac{e}{mc}A_0\langle n|\vec{\varepsilon}\hat{\vec{p}}e^{i\vec{k}\vec{r}}|i\rangle$$

$$W_{i\to n} = \frac{2\pi}{\hbar}|V_{ni}|^2\delta(E_n - E_i - \hbar\omega) =$$

$$= \frac{2\pi}{\hbar}\frac{e^2}{m^2c^2}|A_0|^2|\langle n|\vec{\varepsilon}\hat{\vec{p}}e^{i\vec{k}\vec{r}}|i\rangle|^2\delta(E_n - E_i - \hbar\omega)$$

Absorption cross-section

$$\sigma_{abs} = \frac{\text{Energy absorbed per unit time}}{\text{Energy flux}}$$

$$= \frac{\hbar\omega \cdot w_{i\to n}}{cU}$$

where U is energy density of e-m field

$$U = \frac{1}{2}\left(\frac{E_{max}^2}{8\pi} + \frac{B_{max}^2}{8\pi}\right) = \frac{1}{2\pi}\,\frac{\omega^2}{c^2}|A_0|^2$$

$$E_{max} = 2\frac{\omega}{c}A_0 = B_{max}$$

$$\sigma_{abs} = \frac{\cancel{\hbar}\omega \cdot \frac{2\pi}{\cancel{\hbar}}\,\frac{e^2}{m^2c^2}\cancel{|A_0|^2}\,|\langle n|\vec{\varepsilon}\vec{p}\,e^{i\vec{k}\vec{r}}|i\rangle|^2\,\delta(E_n-E_i-\hbar\omega)}{\frac{1}{2\pi}\,\frac{\omega^2}{c}\cancel{|A_0|^2}}$$

$$= \underbrace{\frac{4\pi^2}{\omega}\,\frac{e^2}{m^2c}}\,|\langle n|\vec{\varepsilon}\vec{p}\,e^{i\vec{k}\vec{r}}|i\rangle|^2\,\delta(E_n-E_i-\hbar\omega)$$

$$= \frac{4\pi^2\hbar}{m^2\omega}\underbrace{\left(\frac{e^2}{\hbar c}\right)}_{\approx\alpha = 1/137}|\langle n|\vec{\varepsilon}\vec{p}\,e^{i\vec{k}\vec{r}}|i\rangle|^2\,\delta(E_n-E_i-\hbar\omega)$$

or $\rho(E_n)$

Clearly, the rate of the stimulated emission will look identical, except for the argument of $\delta(E_n-E_i+\hbar\omega)$

The expression above is valid for all possible transitions (electric dipole, magnetic dipole, electric quadruple, etc.)

As we discussed before, for most light atoms we can use dipole approximation to describe electric dipole (strongest) transitions

$$e^{i\frac{\omega}{c}\vec{r}\vec{n}} \approx \underset{\substack{\uparrow \\ \text{electric} \\ \text{dipole}}}{1} + \frac{i\omega}{c}\underset{\substack{\uparrow \\ \text{electric} \\ \text{quadruple}}}{\vec{r}\cdot\vec{n}}$$

Then $\langle n|\vec{p}\vec{\varepsilon}e^{\pm i\vec{k}\vec{r}}|i\rangle \approx \langle n|\vec{p}\vec{\varepsilon}|i\rangle$

For the e-m wave propagating in z-direction $\vec{\varepsilon}$ must be $\perp \vec{e}_z$ $\rightarrow$ can choose $\vec{\varepsilon} = \vec{e}_x$

$$\langle n|\vec{p}|i\rangle = \frac{m}{i\hbar}\langle n|[\hat{x},\hat{H}_0]|i\rangle = im\omega_{ni}\langle n|x|i\rangle$$

$$\sigma_{\substack{abs \\ i\to n}} = \frac{4\pi^2\hbar}{\cancel{m^2}\omega}\alpha\,\cancel{m^2}\omega_{ni}^{\cancel{2}}\,|\langle n|x|i\rangle|^2\,\delta(\omega-\omega_{ni})$$

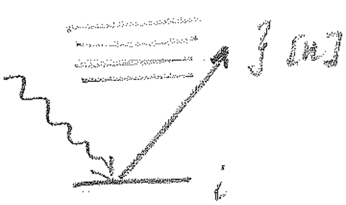
$$= 4\pi^2(\hbar\omega_{ni})\alpha\,|\langle n|x|i\rangle|^2\,\delta(\omega-\omega_{ni})$$

$$\hbar\omega\cdot\alpha = \cancel{\hbar}\omega\cdot\frac{e^2}{\cancel{\hbar}c} = \frac{e^2\cdot\omega}{c}$$

$\hbar$ - disappears!

Photoelectric effect

bound state $\longrightarrow$ continuum (ionization)



Initial state

$|i\rangle$ - non-degenerate, discrete

$[n]$ - continuum of free electrons, assume plane wave $|k\rangle$

$$\langle x|k\rangle = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\vec{k}\vec{r}}$$