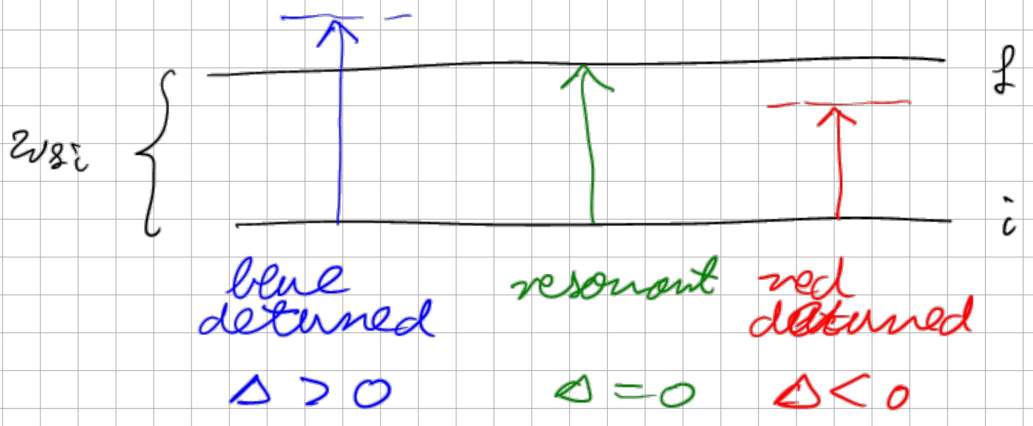
transition probability up to first order:

$$P_{i\to f}(t) = |c_f^{(1)}|^2 = \frac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{\hbar^2}\,\frac{\sin^2(\Delta t/2)}{\Delta^2}$$

detuning: $\Delta = \omega - \omega_{fi}$

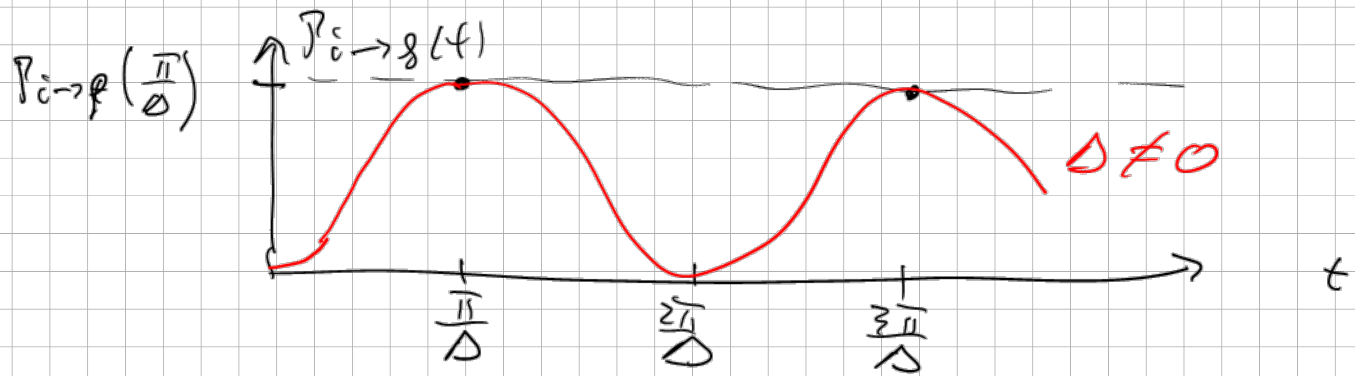


1) Time dependence:

a) non-resonant case: $\Delta \neq 0$

maximum: $\frac{\Delta t_{max}}{2} = \frac{\pi}{2} \Rightarrow t_{max} = \frac{\pi}{\Delta}$

$$\max_t P_{i\to f}(t) = P_{i\to f}\left(t_{max} = \frac{\pi}{\Delta}\right) = \frac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{\hbar^2\Delta^2} \quad (*)$$ is finite



b) resonant: $\Delta = 0$

$$P_{i\to f}(t) = \frac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{4\hbar^2}\, t^2 \quad (*)$$ increase in time

Validity condition for perturbative treatment:

a) $\Delta \neq 0$ $\quad \max_t P_{i\to f}(t) \ll 1 \overset{(*)}{\Longrightarrow} \frac{|\vec{d}_{fi}\cdot\vec{E}_0|}{\hbar} \ll |\Delta|$

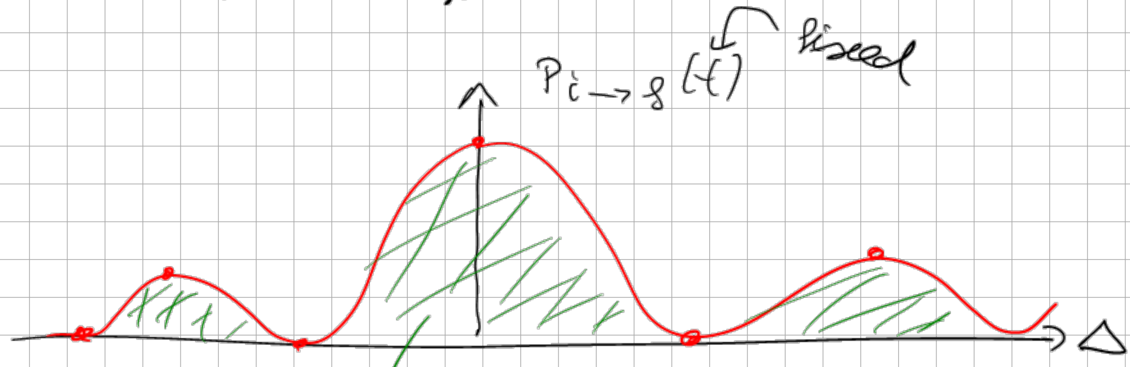
minimal value for detuning

b) $\Delta = 0$ $\quad P_{i\to f}(t) \ll 1 \Rightarrow t \ll \frac{2\hbar}{|\vec{d}_{fi}\cdot\vec{E}_0|}$

restriction for time

2.) Dependence of detuning:

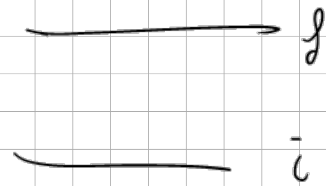
similar to slit diffraction



$$\int_{-\infty}^{+\infty} d\Delta \, \frac{\sin^2(\Delta t/2)}{\Delta^2} \overset{x=\frac{\Delta t}{2}}{=\!=\!=} \frac{t}{2}\int_{-\infty}^{+\infty} dx \, \frac{\sin^2 x}{x^2} = \frac{\pi t}{2}$$ (see Appendix E)

$$\lim_{t\to\infty} \frac{\sin^2(\Delta t/2)}{\Delta^2} = \frac{\pi t}{2}\cdot\delta(\Delta)$$

$$P_{i\to f}(t) \xrightarrow{t\to\infty} \frac{\pi t}{2}\,\frac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{\hbar^2}\,\delta(\omega-\omega_{fi})$$



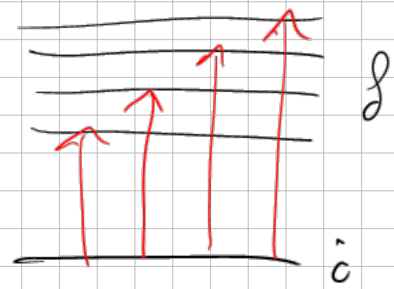
transition rate:

$$W_{i\to f} = \lim_{t\to\infty} \frac{P_{i\to f}(t)}{t} = \frac{\pi}{2}\,\frac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{\hbar^2}\,\delta(\omega-\omega_{fi})$$

Two extensions:

1) Summation over all final states:

$$W_{i\to[f]} = \frac{\pi}{2} \sum_{[f]} \frac{|\vec d_{fi}\cdot \vec E_0|^2}{\hbar^2}\,\delta(\omega-\omega_{fi})$$



Fermi's golden rule

2) Incoming light can have different frequency components:

$$\frac{P_{i\to f}(t)}{t} = \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} d\omega\, |\vec d_{fi}\cdot\vec E_0(\omega)|^2 \underbrace{\frac{\sin^2[(\omega-\omega_{fi})t/2]}{(\omega-\omega_{fi})^2 t}}_{\to \frac{\pi}{2}\delta(\omega-\omega_{fi})}$$

$$W_{i\to f}(t) \overset{t\to\infty}{\Longrightarrow} \frac{\pi}{2\hbar^2}|\vec d_{fi}\cdot\vec E_0(\omega_{fi})|^2$$

$\vec E_0(\omega)$ slowly varying

4.3 Interaction of Atom with Quantized Electric Field:

- Classical light field: transition probabilities for absorption and emission coincide
- Quantized light field:
  - > symmetry between absorption and emission is broken
  - > emission possible also when no photon is present, i.e. in vacuum
    - → spontaneous emission, which is of true quantum character

4.3.1 Einstein Elementary Processes:

Electric field in second quantization in vacuum:

$$\hat{\vec{E}}(\vec{x},t) = \sum_{\lambda=\pm 1} \underbrace{\int d^3k}_{\text{integration over continuous wave vectors}} \sqrt{\frac{\hbar\omega_{\vec{k}}}{2(2\pi)^3\varepsilon_0}}\; i\left\{ \vec{\varepsilon}(\vec{k},\lambda)\, e^{i(\vec{k}\vec{x}-\omega_{\vec{k}}t)}\, \hat{a}_{\vec{k},\lambda} + h.c. \right\}$$

1) Vacuum → cavity: finite volume V, discrete $\vec{k}$'s

$$\int d^3k \frac{1}{(2\pi)^{3/2}} \longrightarrow \sum_{\vec{k}} \frac{1}{\sqrt{V}}$$

2) dipole approximation:

$$\hat{\vec{E}}(\vec{x},t) \approx \hat{\vec{E}}(t) = \sum_{\lambda=\pm 1} \sum_{\vec{k}} \sqrt{\frac{\hbar\omega_{\vec{k}}}{2V\varepsilon_0}}\; i\left\{ \vec{\varepsilon}(\vec{k},\lambda)\, e^{-i\omega_{\vec{k}}t}\, \hat{a}_{\vec{k},\lambda} + h.c. \right\}$$

3) Limit ourselves to one mode: drop $\vec{k}$ and λ-dependencies

$$\hat{\vec{E}}(t) = i\,\vec{\varepsilon}_0 \left(\underbrace{e^{-i\omega t}}\,\hat{a} - \underbrace{e^{i\omega t}}\,\hat{a}^+ \right), \qquad \vec{\varepsilon}_0 = \sqrt{\frac{\hbar\omega}{2V\varepsilon_0}} \cdot \vec{\varepsilon}$$

Heisenberg picture

4) Heisenberg picture → Schrödinger picture

$$\vec{E} = i\,\vec{\varepsilon}_0 (\hat{a} - \hat{a}^+)$$

Interaction Hamiltonian: $\hat{H}^{(P)} = -\vec{d}\cdot\hat{\vec{E}} = -i\,\vec{d}\cdot\vec{\varepsilon}_0 (\hat{a} - \hat{a}^+)$

Unperturbed Hamiltonian:

first quantized   second quantized

$$\hat{H}^{(0)} = \underbrace{\hat{H}^{(0)}_{atom}}_{\text{as above}} + \underbrace{\hat{H}^{(0)}_{field}}_{=\hbar\omega\,\hat{a}^+\hat{a}}$$

unperturbed eigenvalue problem: $\hat{H}^{(0)}|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle$

$|\Psi^{(0)}\rangle = |\Psi^{(0)}_{atom}\rangle \, |\Psi^{(0)}_{field}\rangle$ direct product

$E^{(0)} = E^{(0)}_{atom} + E^{(0)}_{field}$ sum

initial state: $|i^{(0)}\rangle = |a\rangle \, |n\rangle$, $E_i^{(0)} = E_a + n\hbar\omega$

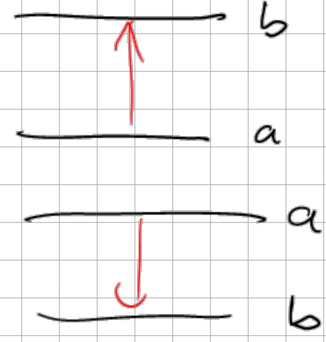
two possible final states:

1) photon absorption: $E_b > E_a$

$|f_1^{(0)}\rangle = |b\rangle \, |n-1\rangle$, $E^{(0)}_{f_1} = E_b + (n-1)\hbar\omega$

2) photon emission: $E_b < E_a$

$|f_2^{(0)}\rangle = |b\rangle \, |n+1\rangle$, $E^{(0)}_{f_2} = E_b + (n+1)\hbar\omega$



Applying perturbation theory:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \{ \hat{H}^{(0)} + \hat{H}^{(1)} \} |\Psi(t)\rangle$$

$$|\Psi(t)\rangle = c_i(t)\, |a\rangle |n\rangle \, e^{-\frac{i}{\hbar}[E_a + n\hbar\omega]t}$$
$$+ c_{f_1}(t)\, |b\rangle |n-1\rangle \, e^{-\frac{i}{\hbar}[E_b + (n-1)\hbar\omega]t}$$
$$+ c_{f_2}(t)\, |b\rangle |n+1\rangle \, e^{-\frac{i}{\hbar}[E_b + (n+1)\hbar\omega]t}$$

initial condition: $|\Psi(0)\rangle = |a\rangle |n\rangle$

coefficients in zeroth order:

$c_i(0) = c_i^{(0)}(t) = 1$, $c_{f_1}(0) = c_{f_1}^{(0)}(t) = 0$, $c_{f_2}(0) = c_{f_2}^{(0)}(t) = 0$

coefficients in first order: see last lecture

$$c^{(1)}_{f_{1,2}} = -\frac{i}{\hbar}\int_0^t dt'\, e^{\frac{i}{\hbar}E^{(0)}_{f_{1,2}i}t'}\, H^{(P)}_{f_{1,2}i} \quad \cancel{(\ast)}$$

1: absorption
2: emission

$$E^{(0)}_{f_1 i} = E^{(0)}_{f_1} - E^{(0)}_{i} = [E_b + (n-1)\hbar\omega] - [E_a + n\hbar\omega] = E_b - E_a - \hbar\omega$$

$$E^{(0)}_{f_2 i} = E^{(0)}_{f_2} - E^{(0)}_{i} = [E_b + (n+1)\hbar\omega] - [E_a + n\hbar\omega] = E_b - E_a + \hbar\omega$$

$$H^{(P)}_{f_1 i} = \langle f_1^{(0)}|\hat H^{(P)}|i\rangle = \langle b|\langle n-1|(-i)\,\vec d\cdot\vec\varepsilon_0(\hat a - \cancel{\hat a^+})|a\rangle|n\rangle$$

$$= -i\,\vec d_{ba}\cdot\vec\varepsilon_0\sqrt{n} \quad \text{photon absorption}$$

$$\hat a|n\rangle = \sqrt{n}\,|n-1\rangle$$

$$H^{(P)}_{f_2 i} = \langle f_2^{(0)}|\hat H^{(P)}|i\rangle = \langle b|\langle n+1|(-i)\,\vec d\,\vec\varepsilon_0(\cancel{\hat a} - \hat a^+)|a\rangle|n\rangle$$

$$= +i\,\vec d_{ba}\cdot\vec\varepsilon_0\sqrt{n+1} \quad \text{photon emission}$$

$$\hat a^+|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

dipole matrix element: $\vec d_{ba} = \langle b|\vec d|a\rangle$

induced emission

spontaneous emission

photon absorption

$\omega_{ba} > 0: \omega = \omega_{ba}$

photon emission

$\omega_{ba} < 0: \omega = -\omega_{ba} = |\omega_{ba}|$

Extreme special limit:

1) large photon number n: $\sqrt{n} \approx \sqrt{n+1}$

$\rightarrow$ classical case from last section

2) vacuum $n = 0$: spontaneous emission

Probability amplitude:

$$c_f^{(1)}(t) = c_{f_1}^{(1)}(t) + c_{f_2}^{(1)}(t)$$

$$= -\frac{i}{\hbar}\, i\, \vec{d}_{ba} \vec{E}_0 \left\{ \sqrt{n+1} \int_0^t dt'\, e^{i(\omega_{ba}+\omega)t'} - \sqrt{n} \int_0^t dt'\, e^{i(\omega_{ba}-\omega)t'} \right\}$$

atomic transition frequency $\omega_{ba} = \omega_b - \omega_a$

$$= -\frac{i}{\hbar} \vec{d}_{ba} \vec{\mathcal{E}}_0 \left\{ \sqrt{n+1}\, \underbrace{\frac{e^{i(\omega_{ba}+\omega)t} - 1}{\omega_{ba}+\omega}} - \sqrt{n}\, \underbrace{\frac{e^{i(\omega_{ba}-\omega)t} - 1}{\omega_{ba}-\omega}} \right\}$$

resonant: $\omega_{ba} + \omega = 0$
$\hat{=}$ emission

relevant: $\omega_{ba} - \omega = 0$
$\hat{=}$ absorption

$\omega \approx \omega_{ba}$: negligible — relevant

$\omega \approx -\omega_{ba}$: relevant — negligible

comparison with classical case:

$$c_f^{(1)}(t) \simeq \frac{1}{2\hbar} \vec{d}_{fi} \cdot \vec{E}_0 \frac{e^{i(\omega_{fi}^{(0)} - \omega)} - 1}{\omega_{fi}^{(0)} - \omega}$$

absorption

$\vec{E}_0 \;\hat{=}\; 2i\, \vec{\mathcal{E}}_0 \sqrt{n}$

emission

$\vec{E}_0 \;\hat{=}\; 2i\, \vec{\mathcal{E}}_0 \sqrt{n+1}$

Apply Fermi's golden rule to quantized electric field

$$W_{i\to f} \sim |\vec{E}_0|^2 \Rightarrow \boxed{\frac{W_{abs}}{W_{emiss.}} = \frac{n}{n+1}}$$

4.3.2 Derivation of spontaneous emission rate:

transition rate : Fermi's golden rule

$$W_{i\to f} = \frac{\pi}{2\hbar^2} |\vec{d}_{fi}\cdot\vec{E}_0|^2\, \delta(\omega-\omega_{fi})$$

$$\vec{E}_0 = 2i\,\vec{\varepsilon}_0, \quad \vec{\varepsilon}_0 = \sqrt{\frac{\hbar\omega}{2V\varepsilon_0}}\,\vec{\varepsilon}$$

$W_{spon.em.}$ = sum over all possible $\vec{k}, \lambda$

$$= \sum_{\vec{k}} \sum_{\lambda} \frac{\pi}{2\hbar^2}\, 4\, \frac{\hbar\omega_{\vec{k}}}{2V\varepsilon_0} |\vec{\varepsilon}(\vec{k},\lambda)\cdot\vec{d}_{fi}|^2\, \delta(\omega_{\vec{k}}-\omega_{fi})$$

$\sum_{\vec{k}} \to$ continuum $\to \int d^3k$; $V \to \frac{1}{(2\pi)^3}$

$$= \sum_{\lambda}\int_0^\infty d\omega\, \underbrace{\frac{\cancel{\omega^2}}{8\pi^3c^3}}_{\substack{\text{density of}\\ \text{states of photons}}} \int_0^\pi d\vartheta \sin\vartheta \int_0^{2\pi} d\varphi\, \frac{\pi\cancel{\omega}}{\hbar\varepsilon_0} |\vec{d}_{fi}\cdot\vec{\varepsilon}(\vec{k},\lambda)|^2\, \cancel{\delta(\omega-\omega_{fi})}$$

ω_{fi}^3

(see Lamb discussion)

completeness $\vec{\varepsilon}(\vec{k},\pm\lambda)$ and $\vec{k}/k$

$$(d_{fi})_k (d_{fi})_l \underbrace{\sum_\lambda \varepsilon_k(\vec{k},\lambda)\,\varepsilon_l(\vec{k},\lambda)}_{=\delta_{kl}-\frac{k_k k_l}{k^2}} = \vec{d}_{fi}^{\,2} - \frac{(\vec{d}_{fi}\cdot\vec{k})^2}{k^2}$$

without loss of generality: $\vec{d}_{fi} = d_{fi}\,\vec{e}_z$

$$W_{spon.em.} = \frac{\omega_{fi}^3\, d_{fi}^2}{8\pi^2\hbar\varepsilon_0 c^3}\underbrace{\int_0^\pi d\vartheta\,\sin\vartheta\int_0^{2\pi}d\varphi\,(1-\cos^2\vartheta)}_{=2\pi\cdot 4/3}$$

$$= \frac{\omega_{fi}^3\, d_{fi}^2}{3\pi\hbar\varepsilon_0 c^3} \sim \underline{\omega_{fi}^3\, d_{fi}^2}$$

dependence on initial/final atomic state

4.3.3 Calculation:

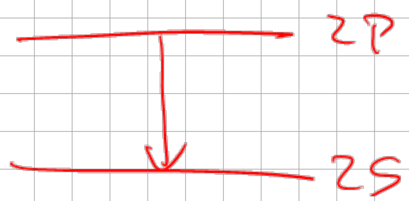
First estimate: $d_{fi}\sim e\, a_B$, $\omega_{fi}\sim \frac{c}{\lambda_c}\alpha^2$ Appendix C

$$\alpha = \frac{\lambda_c}{2\pi a_B} = \frac{e^2}{4\pi\hbar\varepsilon_0 c}\approx\frac{1}{137}$$

$W_{sp.em.}\sim \omega_{fi}\cdot\underbrace{\alpha^3}_{10^{-6}}$ ⇒ electron encircles nucleus 10^6 times before it does a spont. emiss.

$$\text{lifetime } \tau\sim\frac{1}{W_{sp.em.}}=\frac{10^6}{10^3\,\mathrm{THz}}\sim \underline{\underline{1\,\mathrm{ns}}}$$

Next time:



⇒ $\underline{\tau = 0.2\,\mathrm{ns}}$