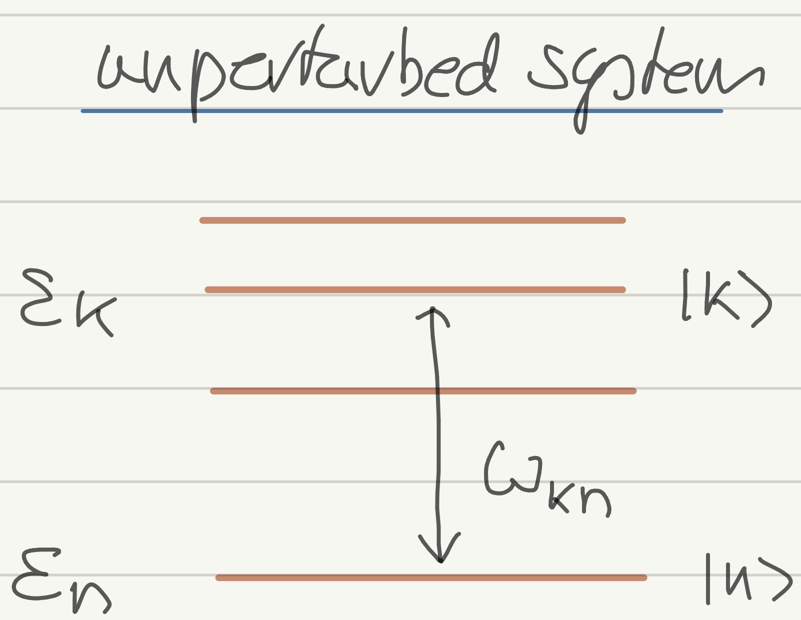
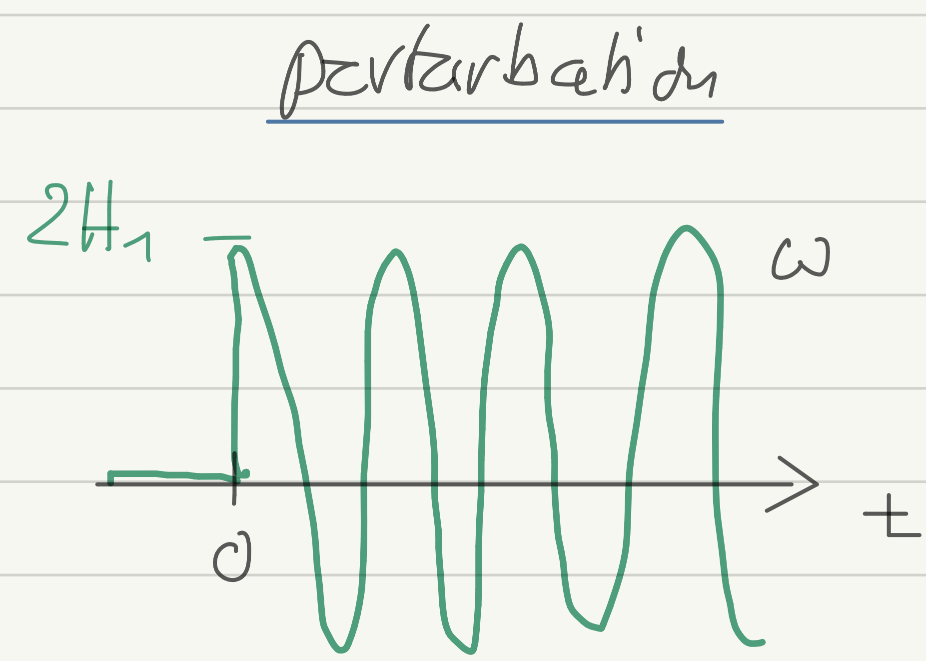
I.2 Harmonic perturbation and Fermi's golden rule

As an important application of time-dependent perturbation theory we will discuss a time-dependent perturbation with frequency ω switched on at $t=0$.

$$H_1(t) = \begin{cases} 0 & t<0 \\ 2H_1\cos(\omega t) & t>0 \end{cases} \qquad \omega>0 \tag{27}$$

Note that any time dependent perturbation can be Fourier-decomposed into frequency components





$|\psi(t=0)\rangle = |n\rangle$ first-order perturbation

$$c_k^{(1)}(t) = -\frac{i}{\hbar} H_{1kn} \int_0^t d\tau\, e^{i\omega_{kn}\tau} \underbrace{\left(e^{i\omega\tau} + e^{-i\omega\tau}\right)}_{2\cos\omega\tau} \tag{28}$$

initial condition: $\quad C_n^{(0)}(0) = 1 \qquad C_{k\neq n}^{(0)}(0) = 0$

$$C_k^{(1)}(t) = -\frac{H_{1kn}}{\hbar}\left[\frac{e^{i(\omega_{kn}-\omega)t}-1}{\omega_{kn}-\omega} + \frac{e^{i(\omega_{kn}+\omega)t}-1}{\omega_{kn}+\omega}\right]$$

using $e^{i\theta}-1 = 2ie^{i\frac{\theta}{2}}\sin\frac{\theta}{2} \Rightarrow$

(29) $$C_k^{(1)}(t) = -\frac{2iH_{1kn}}{\hbar}\left[e^{i(\omega_{kn}-\omega)\frac{t}{2}}\frac{\sin(\omega_{kn}-\omega)\frac{t}{2}}{\omega_{kn}-\omega} + e^{i(\omega_{kn}+\omega)\frac{t}{2}}\frac{\sin(\omega_{kn}+\omega)\frac{t}{2}}{\omega_{kn}+\omega}\right]$$

if $\omega_{kn} > 0 \quad \Rightarrow$ only first term in (29) relevant

$\quad\;\; \omega_{kn} < 0 \quad \Rightarrow$ only second term in (29) relevant

relevant timescale $\quad (\omega_{kn} \mp \omega)^{-1}$

(A) short time limit $\qquad (\omega_{kn} > 0)$

$$(\omega_{kn}-\omega)t \lesssim \mathcal{O}(1)$$

(30) $$C_k^{(1)}(t) \simeq -\frac{iH_{1kn}t}{\hbar}$$

$$(31) \qquad \boxed{P_{n\to k}(t) \simeq \frac{|H_{1kn}|^2 t^2}{\hbar^2}} \qquad \text{transition probability}$$

On short time scales the transition probability to discrete states is quadratic in time. This is different from an exponential law predicted by a rate equation:

from (31)

and $P_n + P_n = 1$

$$P_n(t) \cong 1 - \frac{|H_{1n}|^2}{\hbar^2} t^2 + \dots$$

rate equation

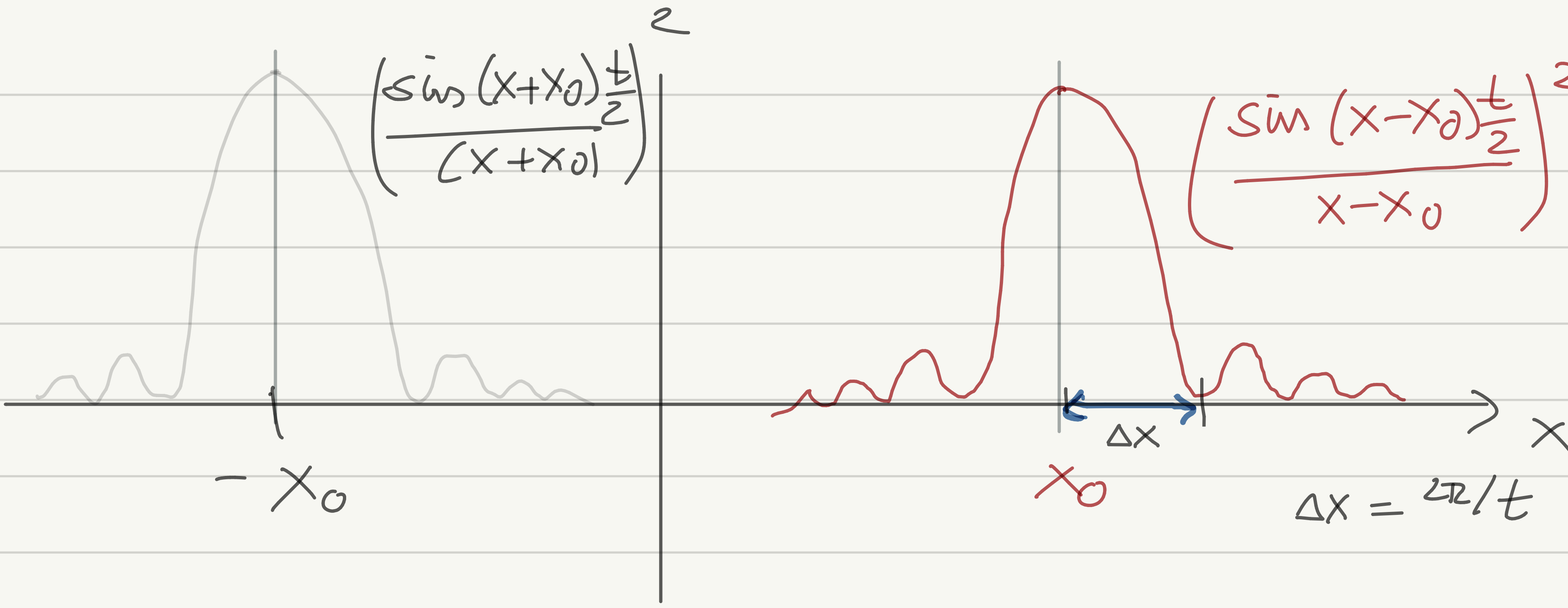
$$\dot{P}_n = -\Gamma P_n \qquad P_n(t) \cong 1 - \Gamma t + \dots$$

This leads to some interesting phenomena such as the quantum Zeno effect, i.e. the inhibition of transitions by frequent projections (projective measurements)

(B) Long-time limit $\quad (\omega_{kn} > 0)$

$$C_k^{(1)}(t) = -\frac{2i H_{1kn}}{\hbar} e^{i(\omega_{kn}-\omega)\frac{t}{2}} \frac{\sin(\omega_{kn}-\omega)\frac{t}{2}}{\omega_{kn}-\omega}$$

$$(32) \qquad |C_k^{(1)}(t)|^2 = \frac{4 H_{1kn}^2}{\hbar^2} \left| \frac{\sin(\omega_{kn}-\omega)\frac{t}{2}}{\omega_{kn}-\omega} \right|^2$$



it holds

(33) $$\boxed{\frac{2}{\pi}\lim_{t\to\infty}\frac{\sin^2(xt/2)}{x^2 t} = \delta(x)}$$

so in the long-time limit $(\omega_{kn}-\omega)t \gg 1$

(34) $$\boxed{P_{n\to k}(t) = \frac{2\pi}{\hbar^2}\, t\, |H_{1kn}|^2\,\delta(\omega_{kn}-\omega)}$$

i.e. in contrast to short times the transition probability scales linear in t

A linear dependence corresponds to a solution of a rate equation

(35) $$\frac{dp_k}{dt} = W_{n\to k}\, p_n \qquad \frac{dp_n}{dt} = -W_{n\to k}\, p_n$$

$W_{n\to n}$: transition probability per time (rate)

(36) $$\boxed{W_{n\to k} = \frac{P_{n\to k}}{t} = \frac{2\pi}{\hbar^2}|H_{1kn}|^2\,\delta(\omega_{kn}\mp\omega)}$$

"+" for $\omega_{kn}<0$

If there is an (approximate) continuum of states

$$W_{n\to k} \longrightarrow \overline{W}_{n\to k} = \int_{E_k-\frac{\Delta E}{2}}^{E_k+\frac{\Delta E}{2}} dN \; W_{n\to k}$$

- dN is infinitesimal number of states in the energy interval

$$E_k - \frac{\Delta E}{2} \leq E \leq E_k + \frac{\Delta E}{2}$$

density of states $\qquad g(E_k)$

(37) $$dN = g(E_k)\, dE_k$$

$$\overline{W}_{n\to k} = \frac{2\pi}{\hbar^2} \int_{E_k-\Delta E/2}^{E_k+\Delta E/2} dE_k' \; g(E_k') \, |H_{1kn}|^2 \, \delta\!\left(\frac{E_k'-E_n}{\hbar} - \omega\right)$$

(here $E_k' \, E_n > 0$)

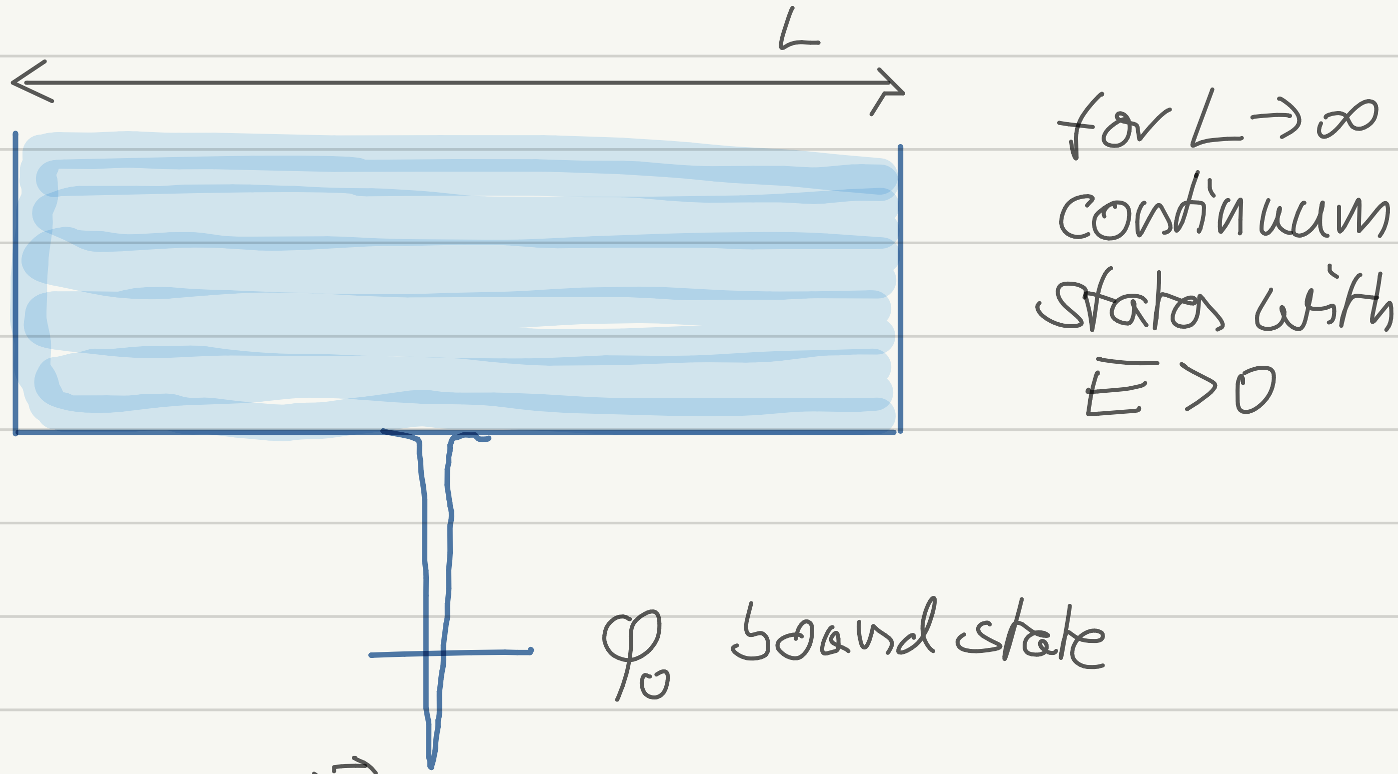
(38) $$\boxed{\overline{W}_{n\to n} = \frac{2\pi}{\hbar^2} g(E_n + \hbar\omega) \, |H_{1kn}|^2}$$

Fermi's golden rule

- remark: typically for a continuum of states $g(E)$ diverges but $g(E)|H_{1kn}|^2$ is finite example

$V = L^3$

with periodic boundary conditions



continuum states $\quad e^{i\vec{k}\cdot\vec{r}} / \sqrt{V}$

bound state $\quad \varphi_0(\vec{r})$

$$H_{1kn} \sim \int d^3r \, \frac{e^{-i\vec{k}\vec{r}}}{\sqrt{V}} H_1 \varphi_0 \sim \frac{1}{\sqrt{V}}$$

i.e. $|H_{1kn}|^2 \sim \frac{1}{V}$

in an excercise you will show that the number of states with energy between 0 and E is

$$N_V(E) = \alpha E^{3/2}$$

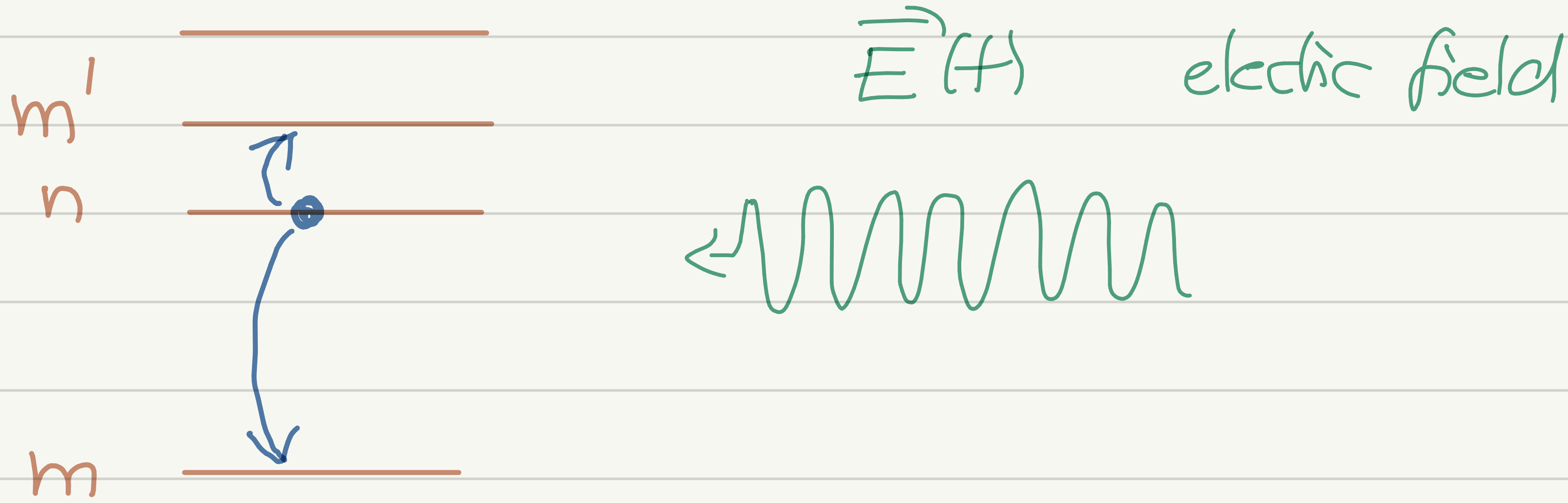
$$\Rightarrow \quad g_V(E) = \frac{dN_V(E)}{dE} = \frac{3}{2} \alpha E^{1/2} V$$ diverges in limit $V \to \infty$

but

$$g_V(E) |H_{1kn}|^2 \sim \frac{3}{2} \alpha E^{1/2} V \cdot \frac{1}{V}$$ constant

I.3 Emission and Absorption of Radiation from an Atom

An important application of Fermi's golden rule is the absorption and emission of energy by an atom in an external electro-magnetic field



interaction Hamiltonian of a (Valence) electron in a central potential with elm. field

$$(39) \qquad H = \frac{1}{2m_0}\left(\hat{\vec{p}} - e\vec{A}(\vec{r},t)\right)^2 + V(\vec{r}) = H_0 + H_1$$

$$H_0 = \frac{1}{2m_0}\hat{\vec{p}}^{\,2} + V(\vec{r}) \qquad \text{bare atom states}$$

$$H_1 = -\frac{e}{2m_0}\left(\underbrace{\hat{\vec{p}}\cdot\vec{A} + \vec{A}\cdot\hat{\vec{p}}}\right) + \cancel{\frac{e^2}{2m}\vec{A}^2} \qquad \text{often negligible}$$

$\vec{A}, \hat{\vec{p}}$ do not commute

Coulomb (radiation) gauge

$$(40) \qquad \mathrm{div}\,\vec{A} = 0 \quad \Rightarrow \quad [\hat{\vec{p}}, \vec{A}] \sim \mathrm{div}\,\vec{A} = 0$$

in Coulomb gauge momentum and vector potential commute i.e.

$$\boxed{H_1 = -\frac{e}{m_0}\hat{\vec{p}}\cdot\vec{A}(\vec{r},t)} \tag{41}$$

consider monochromatic plane wave of frequency ω

$$\vec{A}(\vec{r},t) = a\,\vec{e}\,e^{i(\vec{k}\cdot\vec{r}-\omega t)} + a^*\vec{e}\,e^{-i(\vec{k}\cdot\vec{r}-\omega t)} \tag{42}$$

where $|\vec{k}| = \frac{\omega}{c}$ $\quad \vec{e}$ polarization unit vector

(A) <u>stimulated emission</u> $\quad E_n > E_m$

only $\omega_{mn}-\omega$ term relevant

$$|H_{1mn}|^2 = |\langle m|H_1|n\rangle|^2 = \tag{43}$$

$$= \left(\frac{e}{m_0}\right)^2 |a|^2 \, |\langle m| e^{i\vec{k}\cdot\vec{r}}\,\vec{e}\cdot\hat{\vec{p}}\,|n\rangle|^2$$

to proceed we apply some approximations

$$\lambda = \frac{2\pi}{k} \gg \text{size of atom}$$

dipole approximation

$$\Rightarrow \quad e^{i\vec{k}\cdot\vec{r}} \approx 1 \tag{44}$$

what is $\langle m|\vec{e}\cdot\hat{\vec{p}}|n\rangle$?

use $\quad [H_0, \hat{\vec{x}}] = \frac{\hbar}{i}\frac{\vec{p}}{m_0}$

thus

$$\langle m|\vec{p}\,|n\rangle = \frac{i m_0}{\hbar}\langle m|[H_0, \vec{e}\cdot\vec{x}]|n\rangle$$

(45) $$= \frac{i m_0}{\hbar}(E_m - E_n)\langle m|\vec{e}\cdot\vec{x}\,|n\rangle$$

$$= i m_0 \,\omega_{mn}\langle m|\vec{e}\cdot\vec{x}\,|n\rangle$$

substitution into (43) using

(46) $$\vec{d} = \underset{\substack{\uparrow \\ \text{(electr charge)}}}{e}\,\vec{x}$$ dipole operator of atom

(47) $$|H_{1\,mn}|^2 = \underbrace{\omega_{mn}^2}_{\text{square of transition frequency}}\ \underbrace{|a|^2}_{\text{elm. field amplitude squared}}\ \underbrace{|\langle m|\vec{e}\cdot\vec{d}\,|n\rangle|^2}_{\text{dipole matrix element squared}}$$

Fermi's golden rule for monochromatic elm. wave

(48) $$W_{n\to m} = \frac{2\pi}{\hbar^2}\,\omega_{mn}^2\,|a|^2\,|\langle m|\vec{e}\cdot\vec{d}\,|n\rangle|^2\,\delta(\omega_{mn}-\omega)$$

lets express this in terms of the energy density of the radiation field

(49) $$\mathcal{S} = \frac{1}{c}|\underset{\substack{\uparrow \\ \text{Poynting vector}}}{\vec{S}}| = \varepsilon_0|\vec{E}|^2 = \varepsilon_0\left|\frac{\partial\vec{A}}{\partial t}\right|^2 = 2\varepsilon_0|a|^2\omega^2$$

$$W_{n\to m} = \frac{\pi}{\hbar^2 \varepsilon_0} \mathcal{g} \, |\langle m | \vec{e} \cdot \vec{d} \, | n \rangle|^2 \, \delta(\omega_{mn} - \omega)$$

Assume that we have an incoherent superposition of light with all frequencies ω

(50) $$\mathcal{g} \longrightarrow \int d\omega \, u(\omega)$$

(51) $$W_{n\to m} = \frac{4\pi^2}{\hbar^2} \frac{u(\omega_{mn})}{4\pi\varepsilon_0} \, |\langle m | \vec{e} \cdot \vec{d} \, | n \rangle|^2$$

So far we have assumed that all e/m. waves have the same polarization. If we assume a random polarization

(52) $$\mathcal{g} \to \int d\omega \, \underbrace{\frac{1}{4\pi} \int d^2\Omega_{\vec{e}}}_{\text{orientation arevage over } \vec{e}} \, u(\omega) \cdots$$

using $\vec{e} \cdot \vec{d} = d \cos\vartheta$

$$\frac{1}{4\pi} \int d^2\Omega_{\vec{e}} \, |\langle n | \vec{e} \cdot \vec{d} \, | m \rangle|^2$$

(53) $$= \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta \, \sin\vartheta \, \cos^2\vartheta \, |\langle n | \vec{d} \, | m \rangle|^2$$

$$= \frac{1}{2} \int_{-1}^{1} d\xi \, \xi^2 \, |\langle n | \vec{d} \, | m \rangle|^2 = \frac{1}{3} |\langle n | \vec{d} \, | m \rangle|^2$$

this gives

$$\boxed{\begin{aligned} W_{n\to m} &= \frac{4\pi^2}{3\hbar^2}\,\frac{u(\omega_{mn})}{4\pi\varepsilon_0}\,|\langle m|\vec{d}\,|n\rangle|^2 \\ &= B_{nm}\, u(\omega_{mn}) \end{aligned}} \tag{54}$$

B_{nm} Einstein coefficient of stimulated emission

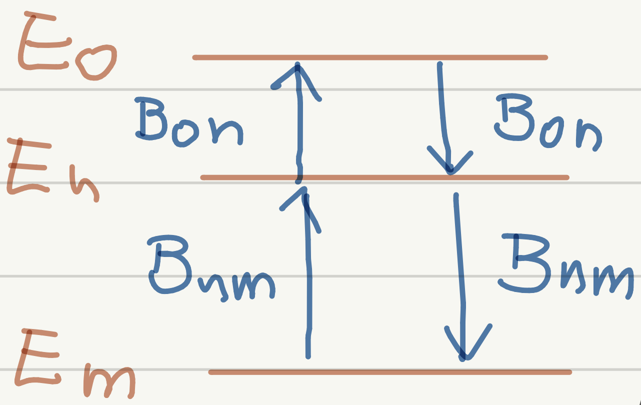
(B) Stimulated Absorption

The same arguments can be made exchanging the roles of initial and final state

$$\boxed{\begin{aligned} W_{m\to n} &= B_{mn}\, u(\omega_{mn}) \\ B_{mn} &= B_{nm} \end{aligned}} \tag{55}$$

(C) Spontaneous Emission

Einstein concluded that the picture of stimulated emission and absorption cannot be complete as equal rates from low energy to high energy states and vice versa would preclude a stationary state in the interaction between atoms and thermal radiation in contrast to observation!

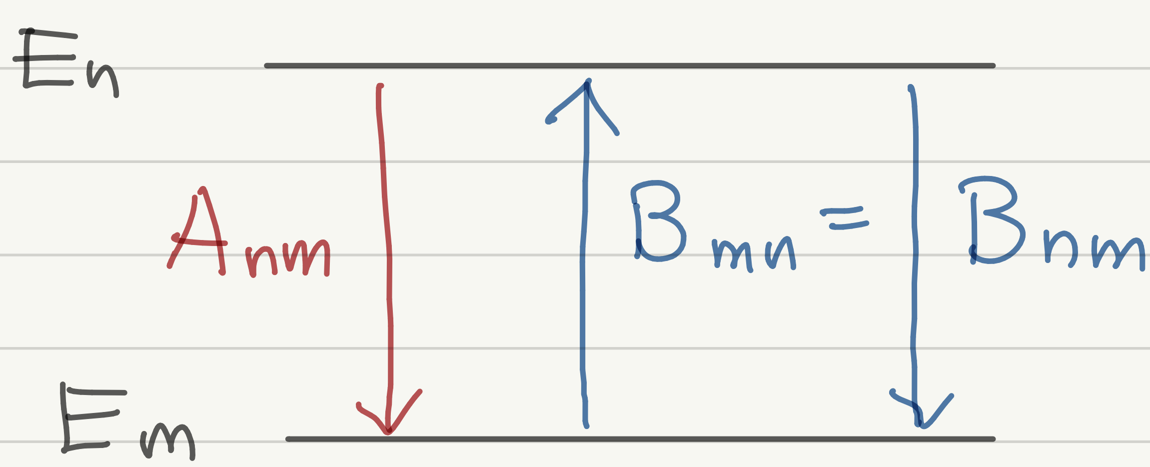


p_n: probability to be in state n

$$(56) \qquad \dot{p}_n = \underbrace{\sum_{m \neq n}^{N} B_{mn} p_m}_{\text{in}} - \underbrace{\sum_{k \neq n}^{N} B_{kk} p_k}_{\text{out}}$$

in stationary state $\dot{p}_n = 0 \Rightarrow p_n^{ss} = \frac{1}{N}$ ↯

$\Rightarrow$ he concluded there must be an additional emission process



from statistical physics

$$(57) \qquad p_n^{ss} = C e^{-\beta E_n} \qquad \beta = \frac{1}{k_B T}$$

and Planck

$$u(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1}$$

$$(58) \qquad \Rightarrow \boxed{\frac{A_{nm}}{B_{nm}} = \frac{\hbar \omega^3}{\pi^2 c^3}}$$

Einstein coefficient of spontaneous emission