● Consider at the initial time ($t=0$), the system is governed by H_0 (time-independent, unperturbated), and stays in one eigenstate ψ_k. Since $t>0$, we apply an external perturbation H', (which may be time-dependent) and check its time evolution.

we still use the basis for H_0: $H_0 \psi_n = E_n \psi_n$, and use this set of basis to expand

$$\psi(t) = \sum_n C_n(t) \, e^{-iE_nt/\hbar} \, \psi_n , \qquad (*)$$

and the initial condition is that $C_n(0) = \delta_{nk}$.

● Plug (*) into the time-dependent Schrödinger Eq

$$i\hbar \frac{\partial}{\partial t} \psi(t) = (H_0 + H'(t)) \psi(t)$$

$$i\hbar \sum_n \dot{C}_n(t) \, e^{-iE_nt/\hbar} \, \psi_n + \sum_n C_n(t) E_n \, e^{-iE_nt/\hbar} \, \psi_n$$

$$= \sum_n C_n(t) \, \cancel{E_n} \, e^{-iE_nt/\hbar} \, \psi_n + \sum_n C_n(t) \, e^{-iE_nt/\hbar} \, H'(t) \psi_n$$

do the inner product with the $\psi_{k'}$ $\Rightarrow$

$$i\hbar \dot{C}_{k'}(t) \, e^{-iE_{k'}t/\hbar} = \sum_n C_n(t) \, e^{-iE_nt/\hbar} \langle \psi_{k'} | H'(t) | \psi_n \rangle$$

$$\begin{cases} i\hbar \dot{C}_{k'}(t) = \sum_n C_n(t) \, e^{i(E_{k'}-E_n)t/\hbar} \langle \psi_{k'} | H'(t) | \psi_n \rangle \\ \\ C_{k'}(0) = \delta_{nk\,k'} \end{cases}$$

zero-th order, we ignore $H'(t) = 0 \Rightarrow C_n^{(0)} = \delta_{nk}$. Plug in this solution into time-evolution Eq,

$$i\hbar \dot{C}_{k'}^{(1)}(t) = e^{i(E_{k'} - E_k)t/\hbar} \langle \psi_{k'} | H'(t) | \psi_k \rangle$$

$$C_{k'}^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{k'k}t} H'_{k'k} \, dt \; , \text{ where } \omega_{k'k} = \frac{E_{k'} - E_k}{\hbar}$$

$$\Rightarrow C_{k'}(t) \simeq \delta_{kk'} + \frac{1}{i\hbar} \int_0^t e^{i\omega_{k'k}t} H'_{k'k} \, dt$$

for the transition $k' \neq k \Rightarrow$ probability

$$\boxed{P_{k' \leftarrow k}(t) = |C_{k'}(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t H'_{k'k} e^{i\omega_{k'k}t} dt \right|^2}$$

Discussion

① if H' has certain symmetry, such that $\langle \psi_{k'} | H' | \psi_k \rangle = 0$, then $P_{k' \leftarrow k} = 0$ at 1st order. We say such a transition <u>is forbidden</u>. But <u>selection rule</u> at high orders, such a transition is still possible, but much weaker.

② ∫ If initial state has degeneracy, we need to do average over initial states according to its density matrix. For example, for a thermal ensemble, we just averge evenly over the degenerate initial states.

     If final states have degeneracy, we will sum over the final states.

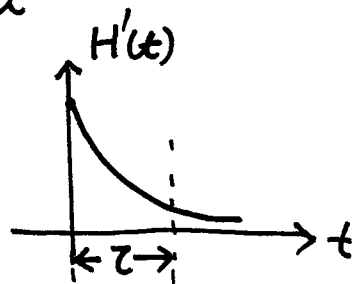Example ① consider the perturbation $H'(t) = F e^{-t/\tau}$. At long time $t \gg \tau$, let us calculate the probility in the state $\psi_{k'}$.

$$C_{k'}(t) = \frac{1}{i\hbar} \int_0^t H'_{k'k}(t) \, e^{i\omega_{k'k}t} \, dt$$

$$H'_{k'k} = \langle \psi_{k'} | F e^{-t/\tau} | \psi_k \rangle = F_{k'k} \, e^{-t/\tau}$$

$$\Rightarrow \quad C_{k'}(t) = \frac{1}{i\hbar} F_{k'k} \int_0^t e^{\left(i\omega_{k'k} - \frac{1}{\tau}\right)t} \, dt$$

$$= F_{k'k} \, \frac{e^{\left(i\omega_{k'k} - 1/\tau\right)t} - 1}{-\hbar\omega_{k'k} - i\hbar/\tau}$$

$H'(t)$

as $t \gg \tau \quad \Rightarrow \quad C_{k'}(t) = F_{k'k} \, \frac{1}{\hbar\omega_{k'k} + i\hbar/\tau}$

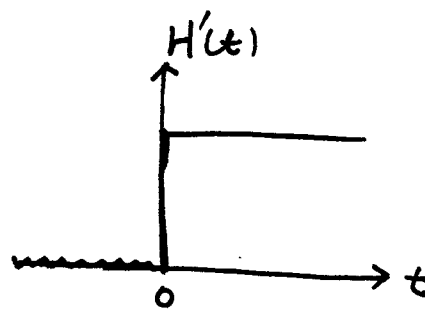thus $P_{k' \leftarrow k} = \frac{|F_{k'k}|^2}{(E_{k'} - E_k)^2 + (\hbar/\tau)^2}$ ← Lorentzian

this conclusion is valid in the case of $P_{k' \leftarrow k} \ll 1$.

② a constant pertubation

$H'(t)$

$$P_{k' \leftarrow k} = \frac{1}{\hbar^2} |H'_{k'k}|^2 \left| \int_0^t e^{i\omega_{k'k}t} \, dt \right|^2$$

$$= \frac{1}{\hbar^2} |H'_{k'k}|^2 \left| \frac{e^{i\omega_{k'k}t} - 1}{\omega_{k'k}} \right|^2$$

$$= \frac{1}{\hbar^2} |H'_{k'k}|^2 \, \frac{\sin^2(\omega_{k'k}t/2)}{(\omega_{k'k}/2)^2}$$

This expression makes sense if $P_{k' \leftarrow k} \ll 1$. This can be justified in the case of $\boxed{t \ll \dfrac{\hbar}{|H_{kk'}|}}$. Let us consider the limit that $|H_{kk'}| \to 0$ such that t can approach a long time. For state k' with $\omega_{k'k} t \gg$ their average transition probability $\overline{P_{k' \leftarrow k}} = \dfrac{2}{\hbar^2} \dfrac{|H_{k'k}|^2}{\omega_{k'k}^2}$, which does not increase with time. But for states with $\omega_{k'k} t \ll 1$,
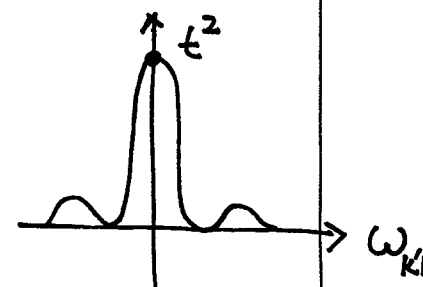
$$P_{k' \leftarrow k} = \frac{1}{\hbar^2} |H_{k'k}|^2 t^2,$$ which increases with t quadratically.

Let us consider if there are many possibility for the final states, and we are interested in the sum of transition probability in a certain energy interval. Then we need

$$\sum_{k'}' P_{k' \leftarrow k} = \frac{1}{\hbar^2} \rho(E_{k'}) dE_{k'} |H_{k'k}|^2 \frac{\sin^2(\omega_{k'k} t/2)}{(\omega_{k'k}/2)^2}$$

For a fixed but large value of t,

$$\frac{\sin^2 \omega_{k'k} t/2}{(\omega_{k'k}/2)^2} \xrightarrow{t \to \infty} 2t \pi \delta(\omega_{k'k})$$

in this sense, we have

$$P_{k' \leftarrow k} = \frac{1}{\hbar^2} |H'_{k'k}|^2 2\pi t \, \delta(\omega_{k'k})$$

$$= \frac{2\pi t}{\hbar} |H'_{k'k}|^2 \delta(E_{k'} - E_k)$$

Although the peak value increase as t^2, but the width shrink as $1/t$.

the meaning of δ-function should be understood correctly. It doesn't mean infinity, but a distribution whose peak value $\propto t^2$, but width $\overbrace{\text{over } \omega_{k'k}}$ shrinks $\propto 1/t$. As $t \to +\infty$, the transition concentrates to states with energy conservation. For a distribution of final states we have

$$\int dE_{k'} \, \rho(E_k) \; P_{k \leftarrow k} = \frac{2\pi t}{\hbar} \int dE_{k'} \underbrace{|H_{k'k}|^2}_{\rho(E_k')} \delta(E_{k'} - E_k)$$

$\uparrow$ density of states

It means that the total probability of transition is proportional to

$t \quad \Rightarrow \quad \boxed{\text{transition rate: } \frac{2\pi}{\hbar} \int dE_{k'} \overbrace{|H_{k'k}|^2}^{\rho(E_{k'})} \delta(E_{k'} - E_k) \\ \text{This is Fermi golden rule.}}$

§ light absorption and semi-classical theory

We will consider the interaction between atomic levels and radiation fields. The atomic levels are ~~treated~~ quantum mechanically, while we ~~treat~~ the E-M field classically. A more advance treatment will be the quantization of E-M field. For this purpose, let us consider the periodical perturbation.

$$H' = W\cos\omega t = W(e^{i\omega t} + e^{-i\omega t})/2$$

Repeat the process presented before, we have

$$C_{k'}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{k'k}t} H'_{k'k}\, dt \qquad \text{for } k' \neq k$$

$$= \frac{W_{k'k}}{2i\hbar} \int_0^t \left[e^{i(\omega_{k'k} + \omega)t} + e^{i(\omega_{k'k} - i\omega)t} \right] dt$$

$$= -\frac{W_{k'k}}{2i\hbar} \left\{ \frac{e^{i(\omega_{k'k} + \omega)t} - 1}{\omega_{k'k} + \omega} + \frac{e^{i(\omega_{k'k} - \omega)t} - 1}{\omega_{k'k} - \omega} \right\}$$

assume $\omega > 0$, and $\omega_{k'k} > 0$ usually the $\omega_{k'k}$ for two different levels is large. ω for light (say, 5000 Å, $\omega \sim 4\times10^{15}s^{-1}$), we will neglect the contribution from the first term.

$$\Rightarrow C_{k'}(t) = -\frac{W_{k'k}}{2i\hbar} \frac{e^{i(\omega_{k'k} - \omega)t} - 1}{\omega_{k'k} - \omega}$$

$$P_{k' \leftarrow k}(t) = \frac{|W_{k'k}|}{4\hbar^2} \frac{\sin^2(\omega_{k'k} - \omega)t/2}{[(\omega_{k'k} - \omega)/2]^2}.$$

again as t goes large, we have

The transition Rate

$$W_{k' \leftarrow k} = \frac{\pi}{4\hbar^2} |W_{k'k}|^2 \delta\left[\frac{\omega_{k'k} - \omega}{2} \right]$$

$$= \frac{\pi}{2\hbar} |W_{k'k}|^2 \delta\left[E_{k'} - E_k - \hbar\omega \right]$$

Consider the monochromatic light

$$\vec{E} = \vec{E}_0 \cos(\omega t - \vec{k}\cdot\vec{r}).$$

The wavelength of light ~ 1 μm thus in the scale of atomic length we can think $\vec{E}$ is uniform by neglecting $\vec{k}\cdot\vec{r}$.

$$W = -e\,\vec{E}_0\cdot\vec{r}\,\cos\omega t$$

define $\vec{D} = e\ \vec{r}$

The transition from state $k \to k'$ ($E_k < E_{k'}$). The transition rate

$$\omega_{K \leftarrow K} = \frac{\pi}{2\hbar}\left| \vec{D}_{k'k}\cdot\vec{E}_0 \right|^2 \delta(E_{k'} - E_k - \hbar\omega)$$

if we use unpolarized light, then the angle between $\vec{D}_{k'k}$ and $\vec{E}_0$ is random $\Rightarrow$ averager over angle $\overline{\cos^2\theta} = 1/3$

$$\Rightarrow \omega_{k' \leftarrow k} = \frac{\pi}{6\hbar}\left| \vec{D}_{k'k} \right|^2 E_0^2\, \delta(E_{k'} - E_k - \hbar\omega)$$

If for no-monochromatic light, the spectra density $\rho(\omega)\,d\omega$ represents the energy density of E-M wave.

$$\rho(\omega)\,d\omega = \frac{1}{8\pi}\overline{E^2 + B^2} = \frac{1}{4\pi}\overline{E^2} = \frac{1}{8\pi}E_0^2$$

Replace $E_0^2 \underset{\text{with}}{\frown} 8\pi\rho(\omega)\,d\omega$ in the transition rate $\Rightarrow$

$$\int d\omega\, 8\pi\rho(\omega)\cdot\frac{\pi}{6\hbar}\left| \vec{D}_{k'k} \right|^2 \delta(E_{k'} - E_k - \hbar\omega)$$

$$= \frac{8\pi^2}{6\hbar}\cdot\frac{1}{\hbar}\,\rho(\omega_{kk})\left| \vec{D}_{k'k} \right|^2 = \frac{4\pi^2 e^2}{3\hbar^2}\left| \vec{r}_{k'k} \right|^2 \rho(\omega_{k'k})$$

The matrix elements $\quad r_{k'k}$:

$$x = \frac{r}{2} \sin\theta \left(e^{i\varphi} + e^{-i\varphi} \right)$$

$$y = \frac{r}{2i} \sin\theta \left(e^{i\varphi} - e^{-i\varphi} \right)$$

$$z = r \cos\theta$$

and

$$\cos\theta \, Y_{\ell m} = \sqrt{\frac{(\ell+1)^2 - m^2}{(2\ell+1)(2\ell+3)}} \; Y_{\ell+1, m}$$

$$+ \sqrt{\frac{\ell^2 - m^2}{(2\ell-1)(2\ell+1)}} \; Y_{\ell-1, m}$$

$$e^{\pm i\varphi} \sin\theta \, Y_{\ell m} = \pm \sqrt{\frac{(\ell \pm m + 1)(\ell \pm m + 2)}{(2\ell+1)(2\ell+3)}} \; Y_{\ell+1, m\pm}$$

$$\mp \sqrt{\frac{(\ell \mp m)(\ell \mp m - 1)}{(2\ell-1)(2\ell+1)}} \; Y_{\ell-1, m\pm 1}$$

$$k' \sim |n'\ell'm'\rangle \, , \quad k \sim |n\ell m\rangle$$

$$z_{k'k} : \quad \ell' = \ell \pm 1, \quad m' = m$$

$$x_{k'k}, \, y_{k'k} : \quad \ell' = \ell \pm 1, \quad m' = m \pm 1$$

$\left. \right\}$ dipole transition selection rule.

§ ~~Einstein's spontaneous emission theory~~

● If initially, the atomic system is in the excited state, in non-relativistic QM, it is a stationary state, and it will not decay. But in fact, the excited stated has finite life time due to spontaneous emission. This is because the interaction between electrons and E-M modes. Einstein proposed a model to describe spontaneous emission.

Suppose that the atom is in the light field with the intensity $\rho(\omega)$, then transition rate from $k \to k'$ state (assume $E_{k'} > E_k$) is

$$W_{K \leftarrow k} = B_{k' \leftarrow k} \, \rho(\omega_{k'k}), \quad \text{where } B_{K \leftarrow k} = \frac{4\pi^2 e^2}{3\hbar^2} |\vec{r}_{k'k}|^2$$

is called the absorbtion coefficient.

● for the stimulated emission from $k' \to k$,

we also have

$$W_{k \leftarrow k'} = B_{k \leftarrow k'} \, \rho(\omega_{k'k}) \quad \text{where } B_{k \leftarrow k'} = \frac{4\pi^2 e^2}{3\hbar^2} |\vec{r}_{k'k}|^2$$

clearly, we have $B_{k' \leftarrow k} = B_{k \leftarrow k'}$, which are independent on the light intensity.

Let us consider a thermo equilibrium system: there're n_k atoms at E_k level, and $n_{k'}$ atoms lie at the $E_{k'}$ level. In the equilibrium, we have

$$\frac{n_k}{n_{k'}} = e^{(E_{k'} - E_k)/k_B T} = e^{\hbar \omega_{k'k}/k_B T}$$

we must introduce a new term of spontaneous emission for the higher energy state. Otherwise since $n_k > n_{k'}$, we cannot reach equilibrium.

$$n_k \, B_{k' \leftarrow k} \, \rho(\omega_{k'k}) = n_{k'} \left[B_{k \leftarrow k'} \, \rho(\omega_{k'k}) + A_{k \leftarrow k'} \right].$$

$$\Rightarrow \rho(\omega_{k'k}) = \frac{A_{k \leftarrow k'}}{B_{kk'}} \frac{1}{n_k/n_{k'} - 1} = \frac{A_{k \leftarrow k'}}{B_{kk'}} \frac{1}{e^{\hbar \omega_{k'k}/kT} - 1}$$

Consider the atom ensemble is in an isolated cavity with temperature T, then we can use black body ρ radiation spectra.

$$\rho(\omega) = \frac{\hbar \omega^3}{c^2 2\pi^2} \frac{1}{2\pi} \frac{1}{e^{\hbar \omega/kT} - 1} \cdot \frac{4\pi}{c}$$

$$= \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega/kT} - 1}$$

$$\Rightarrow \frac{A_{k \leftarrow k'}}{B_{kk'}} = \frac{\hbar \omega_{kk}^3}{\pi^2 c^3} \Rightarrow \boxed{A_{kk'} = \frac{4 e^2 \omega_{k'k}^3}{3 \hbar c^3} \, |r_{k'k}|^2}$$

$$\frac{4}{3} \frac{c}{a} \alpha^4 \left(\frac{\omega_{k'k}}{e^2/a} \right)^3 \left| \frac{r_{k'k}}{a} \right|^2$$

$$\text{where} \quad \alpha = \frac{e^2}{\hbar c}$$

Example: The spontaneous emission of the 1st excited state.

There are 2s and 2p states. The transition from $2s \to 1s$ is forbidden. We only consider the transition from $2p \to 1s$.

$$A_{1s \leftarrow 2p} = \frac{4e^2}{3\hbar c^3} \omega^3_{1s,2p} |\langle 1s | \vec{r} | 2p \rangle|^2$$

$$\omega_{1s,2p} = \frac{me^4}{2\hbar^3}\left(1 - \frac{1}{2^2}\right) = \frac{3me^4}{8\hbar^3}$$

$$|\langle 1s | \vec{r} | 2p \rangle|^2 = |\langle 1s | x | 2p \rangle|^2 + |\langle 1s | y | 2p \rangle|^2 + |\langle 1s | z | 2p \rangle|^2$$

$|2p\rangle$ can take any of $|2p_z\rangle$, $|2p_x\rangle$, and $|2p_y\rangle$.

By symmetry, all of these three give rise to the same $|\langle 1s | \vec{r} | 2p \rangle|^2$

If we calculate the life time of the 2p state, we need to do average over the 3 2p states. We can choose any of them, say, the $2p_z$ state.

$$\psi_{210} = R_{21}(r)\, Y_{10}(\Omega) = \frac{1}{4\sqrt{2\pi}} \frac{r}{a^{5/2}} e^{-r/2a} \cos\theta \qquad a = \frac{\hbar^2}{me^2}$$

$$\psi_{100} = R_{10}(r)\, Y_{00}(\Omega) = \frac{1}{\sqrt{\pi}a^{3/2}} e^{-r/a} .$$

$$\langle 100 | x | 210 \rangle = \langle 100 | y | 210 \rangle = 0 \qquad (\text{why?})$$

$$\langle 100 | z | 210 \rangle = \frac{1}{4\sqrt{2}\pi a^4} \int_0^\infty r^4 e^{-3r/2a}\, dr \int \cos\theta\, d\Omega$$

$$\xcancel{\int \cos\theta\, d\Omega = 2\pi \int_0^\pi \frac{\sin 2\theta}{2}\, d\theta} = \frac{1}{3\sqrt{2}\,a^4}\left(\frac{2a}{3}\right)^5 \int_0^\infty x^4 e^{-x}\, dx$$

$$= \frac{2^5 a}{3\sqrt{2}} \frac{24}{3^5} = \frac{2^{\frac{15}{2}}}{3^5} a$$

$$A_{1s,2p} = \frac{4e^2}{3\hbar c^3} \frac{3^3}{8^3} \left(\frac{me^4}{\hbar^3}\right)^3 \cdot \frac{2^{15}}{3^{10}} a^2$$

$$= \frac{2^8}{3^8} \frac{e^{14} m^3 a^2}{\hbar^{10} c^3} = \frac{2^8}{3^8} \frac{c}{a} \left(\frac{e^2}{\hbar c}\right)^4 \simeq \left(\frac{1}{137}\right)^4 \frac{(2)^8}{3^8} \left(\frac{c}{a}\right)$$

$$\simeq 1.1 \times 10^{-10} \left(\frac{c}{a}\right) \simeq 1.1 \times 10^{-10} \frac{3 \times 10^8}{0.5 \times 10^{-10}} \simeq 6.27 \times 10^8 \, s^{-1}$$

$$\tau = \frac{1}{A_{1s,2p}} \simeq 1.6 \times 10^{-9} \, s$$