- Consider at the initial time ($t=0$), the system is govened 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

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

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

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

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

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

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

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 $k' \neq k \Rightarrow$ probility

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

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
selection rule
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.

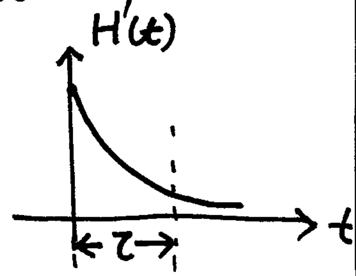
Example 1 consider the perturbation $H'(t) = F e^{-t/\tau}$. At long time $t \gg \tau$, let us calculate the probility in the state $\psi_{k'}$.

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

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

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

$$= F_{k'k} \frac{e^{[i\omega_{k'k} - 1/\tau]t} - 1}{-\hbar\omega_{k'k} - i\hbar/\tau}$$

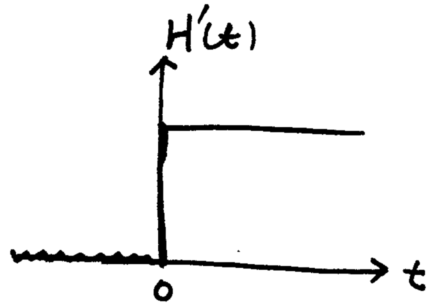


as $t \gg \tau$ $\quad \Rightarrow \quad C_{k'}(t) = F_{k'k} \dfrac{1}{\hbar\omega_{k'k} + i\hbar/\tau}$

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

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

2 a constant pertubation



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

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

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

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

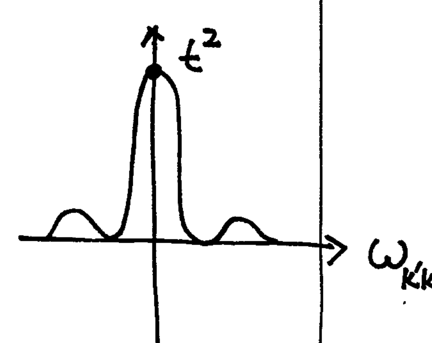
$P_{k'\leftarrow k} = \frac{1}{\hbar^2}|H_{k'k}|^2 t^2$, which increases with t quadratically.

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 vaule 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

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

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

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

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

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

density of states

It means that the total propabity of transition is proportional to t $\Rightarrow$

$$\boxed{\text{transition rate: } \frac{2\pi}{\hbar} \int dE_{k'} \overbrace{|H_{k'k}|^2}^{\rho(E_{k'})} \delta(E_{k'} - E_k) \quad \text{This is Fermi golden rule.}}$$

§ light absorpation 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 $\omega_{k'k} > 0$, and usually the $\omega_{k'k}$ for two different levels is large, ω for light (say, 5000Å, $\omega \sim 4\times10^{15}s^{-1}$), we will neglet 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

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

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

Consider the monochromatic light

$\vec{E} = \vec{E}_0 \cos(\omega t - \vec{k}\cdot\vec{r})$. The wavelength of light $\sim 1\mu m$ 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 with $8\pi\rho(\omega)\,d\omega$ in the transition rate $\Rightarrow$

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

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

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

$$\left.\begin{aligned} x &= \frac{r}{2}\sin\theta\,(e^{i\varphi}+e^{-i\varphi}) \\ y &= \frac{r}{2i}\sin\theta\,(e^{i\varphi}-e^{-i\varphi}) \\ z &= r\cos\theta \end{aligned}\right\}$$

and

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

$$e^{\pm i\varphi}\sin\theta\, Y_{lm} = \pm\sqrt{\frac{(l\pm m+1)(l\pm m+2)}{(2l+1)(2l+3)}}\, Y_{l+1,m\pm 1} \mp \sqrt{\frac{(l\mp m)(l\mp m-1)}{(2l-1)(2l+1)}}\, Y_{l-1,m\pm 1}$$

$k' \sim |n'l'm'\rangle$, $k \sim |nlm\rangle$

$$\left.\begin{aligned} z_{k'k}&: \; l'=l\pm 1,\; m'=m \\ x_{k'k}, y_{k'k}&: \; l'=l\pm 1,\; m'=m\pm 1 \end{aligned}\right\}$$ dipole transition selection role.

*

§ 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

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

is called the absorbtion coefficient.

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

we also have

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

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.

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

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

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

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

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

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

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

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

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 $2p \to 1s$.

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

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

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

$|2p\rangle$ 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 $\left|\langle 1s|\vec{r}|2p\rangle\right|^2$

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.

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

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

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

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

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

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

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

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

$$\simeq 1.1\times10^{-10}\left(\frac{c}{a}\right) \approx 1.1\times10^{-10}\,\frac{3\times10^8}{0.5\times10^{-10}} \simeq 6.27\times10^8\,s^{-1}$$

$$\tau = 1/A_{1s,2p} \approx 1.6\times10^{-9}\,s$$