Lecture #1

The variational method (Ritz theorem)

- This is another of approximation methods, which has numerous applications.
- Consider an arbitrary physical system with time-independent Hamiltonian. We assume that the energy spectrum is discrete and non-degenerate:

$$H|\varphi_n\rangle = E_n|\varphi_n\rangle \quad , \quad n=0,1,2,\ldots$$

Although H is known, E_n and $|\varphi_n\rangle$ are not $\Rightarrow$ we need to diagonalize H in order to find E_n and then determine the eigenstates.

- Consider an arbitrary ket $|\psi\rangle = \sum_{n=0}^{\infty} C_n|\varphi_n\rangle$

Then $\langle\psi|H|\psi\rangle = \sum_{n=0}^{\infty} C_n^* \langle\varphi_n|E_n C_n|\varphi_n\rangle =$

$$= \sum_{n=0}^{\infty} |C_n|^2 E_n \geq E_0 \sum_{n=0}^{\infty} |C_n|^2 \; ; \quad \langle\psi|\psi\rangle = \sum_{n=0}^{\infty}|C_n|^2$$

E_0 — the lowest energy

Then, the mean value of the Hamiltonian H (2)
in the state $|\Psi\rangle$ is;

$$\langle H \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq \frac{E_0 \sum_n |C_n|^2}{\sum_n |C_n|^2} = E_0$$

For the equality (i.e. $\langle H \rangle = E_0$) $\Rightarrow$ it is necessary that $\underbrace{C_n = 0}_{\text{for all } n\text{'s}}$ except C_0 (i.e. $n=0$)

Then, $|\Psi\rangle$ is an eigenvector of H with the eigenvalue E_0.

This property is the basis for a method of approximate determination of E_0.

We choose kets $|\Psi(\alpha)\rangle$ which depend on a certain number of parameters $\{\alpha\}$, calculate mean value of H, i.e. $\langle H \rangle(\alpha)$ in these states and minimize $\langle H \rangle(\alpha)$ with respect to $\{\alpha\}$ to find (approximately) the energy of the ground state E_0

The kets $|\Psi(\alpha)\rangle$ are called trial kets,

the method $\Rightarrow$ variational method

α - Ritz parameter

Example 1D harmonic oscillator

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

Let's see how close to the exact solution we can get with the variational method.

(a) Try $\psi_\alpha(x) = e^{-\alpha x^2}$, $\alpha > 0$

(that's a very good, completely unbiased :)) try)

Then $\langle \psi_\alpha | H | \psi_\alpha \rangle = \int_{-\infty}^{\infty} e^{-\alpha x^2}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \right.$

$\left. + \frac{1}{2}m\omega^2 x^2\right] e^{-\alpha x^2} dx = -\frac{\hbar^2}{2m}(-2\alpha)\int_{-\infty}^{\infty} e^{-2\alpha x^2}\cdot(1 -$

$- 2\alpha x^2)\, dx + \frac{1}{2}m\omega^2 \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{\hbar^2}{m}\alpha \cdot \underbrace{\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx}_{= \sqrt{\frac{\pi}{2\alpha}}} +$

$\left(-\frac{2\hbar^2\alpha^2}{m} + \frac{1}{2}m\omega^2\right)\underbrace{\int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} dx}_{= -\frac{\partial}{\partial(2\alpha)}\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx} \ominus$

$$-\frac{\partial}{\partial(2\alpha)}\int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = -\frac{\partial}{\partial(2\alpha)}\sqrt{\frac{\pi}{2\alpha}} = \frac{\sqrt{\pi}}{2}\frac{1}{(2\alpha)^{3/2}}$$

$$\ominus \left(\frac{\hbar^2}{m}\alpha - \frac{\cancel{2}\hbar^2\alpha^{\cancel{2}}}{2m}\frac{1}{\cancel{2\alpha}} + \frac{1}{2}\frac{m\omega^2}{2}\cdot\frac{1}{2\alpha}\right)\cdot\sqrt{\frac{\pi}{2\alpha}} = \left(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right)\sqrt{\frac{\pi}{2\alpha}}$$

So, we get a pretty good agreement with the exact value of E_0 even with an arbitrary trial function.

However, it gets tricky to find an "approximate" eigenstate (which would show a good agreement with a "true" eigenstate) $\Rightarrow$ see pp. 1154–1155 of Cohen-Tannoudji.

<u>Summary</u>:

There is no infallible method for knowing to what energy level the variational method gives an approximate value. In practice, one chooses trial functions with a simple analytical form and a very limited number of oscillations. Therefore, there is a good chance that we get the energy of the <u>ground state</u> or, more precisely, an <u>upper limit</u> of the energy. Unfortunately, there is no reliable method for evaluating the order of magnitude of the error.

$$\langle \Psi_\alpha | \Psi_\alpha \rangle = \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = \sqrt{\frac{\pi}{2\alpha}}$$

Then, $\langle H \rangle(\alpha) = \dfrac{\langle \Psi_\alpha | H | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle} = \dfrac{\hbar^2 \alpha}{2m} + \dfrac{m\omega^2}{8\alpha}$

Now let's find the minimum of $\langle H \rangle(\alpha)$:

$$\left.\frac{\partial \langle H \rangle(\alpha)}{\partial \alpha}\right|_{\alpha=\alpha_0} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha_0^2} = 0 \Rightarrow$$

$\alpha_0 = \dfrac{m\omega}{2\hbar}$ (since we specified before that $\alpha > 0$) $\Rightarrow$

$$\langle H \rangle(\alpha_0) = \frac{\hbar^2}{2m} \cdot \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \cdot \frac{2\hbar}{m\omega} = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2}$$

So, an "approximate" value of the lowest energy $E_0 = \dfrac{\hbar\omega}{2}$ is actually an exact result.

What if our choice of the "trial" function is not as good? $\Rightarrow$ Let's try $\Psi_a(x) = \dfrac{1}{x^2+a}$, $a > 0$

$$\langle \Psi_a | H | \Psi_a \rangle (a) = \int_{-\infty}^{\infty} \frac{1}{x^2+a} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right) \frac{1}{x^2+a} dx =$$

$$= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left(\frac{-2}{(x^2+a)^2} + \frac{16x^2}{2(x^2+a)^3} \right) \frac{dx}{x^2+a} + \frac{1}{2} m\omega^2 \underbrace{\int_{-\infty}^{\infty} \frac{x^2 dx}{(x^2+a)^2}}_{= \frac{\pi}{2\sqrt{a}}} =$$

$$= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left(\frac{6}{(x^2+a)^3} - \frac{\cancel{16}^{8} a}{\cancel{2}(x^2+a)^4} \right) dx + \frac{1}{2} m\omega^2 \left(\int_{-\infty}^{\infty} \frac{dx}{x^2+a} - a \int_{-\infty}^{\infty} \frac{dx}{(x^2+a)^2} \right) =$$

$$= -\frac{\hbar}{2m}\left(-\cancel{2}\cdot\frac{3\pi}{\cancel{8}_4 a^{5/2}} + \frac{\pi}{2a^{5/2}}\right) + \frac{1}{2}m\omega^2\cdot\frac{\pi}{2\sqrt{a}} =$$

$$= -\frac{\hbar^2}{2m}\frac{\pi}{a^{5/2}}\left(-\frac{1}{4}\right) + \frac{m\omega^2\pi}{4\sqrt{a}}$$

$$\langle \psi_a | \psi_a \rangle = \int_{-\infty}^{\infty}\frac{dx}{(x^2+a)^2} = \frac{\pi}{2a\sqrt{a}}$$

$$\langle H \rangle = \frac{\langle \psi_a | H | \psi_a \rangle}{\langle \psi_a | \psi_a \rangle} = \frac{\frac{\hbar^2}{8m}\frac{\pi}{a^{5/2}} + \frac{m\omega^2\pi}{4\sqrt{a}}}{\frac{\pi}{2a\sqrt{a}}} =$$

$$= \frac{\hbar^2}{4ma} + \frac{m\omega^2 a}{2}$$

$$\frac{\partial\langle H \rangle}{\partial a} = -\frac{\hbar^2}{4ma^2} + \frac{m\omega^2}{2}\Big|_{a=a_0} = 0 \Rightarrow a_0 = \frac{\hbar}{\sqrt{2}\,m\omega}$$

Then $\langle H \rangle(a_0) = \frac{\hbar^2}{4m}\frac{\sqrt{2}\,m\omega}{\hbar} + \frac{m\omega^2}{2}\cdot\frac{\hbar}{\sqrt{2}\,m\omega} = \hbar\omega\left(\frac{\sqrt{2}}{4}+\frac{1}{2\sqrt{2}}\right)$

$$= \hbar\omega\,\frac{\sqrt{2}\cdot\sqrt{2}+2}{4\sqrt{2}} = \hbar\omega\cdot\frac{4}{4\sqrt{2}} = \frac{\hbar\omega}{\sqrt{2}}$$

So, the minimal value of ground state energy obtained using the trial function $\psi_a = \frac{1}{x^2+a}$ is $\frac{\hbar\omega}{\sqrt{2}}$, while the exact value is $\frac{\hbar\omega}{2}$ $\Rightarrow$ so the error (per quantum) is $\frac{\hbar\omega}{\hbar\omega}\left(\frac{1}{\sqrt{2}}-\frac{1}{2}\right)$

$$= \frac{2-\sqrt{2}}{2\sqrt{2}} \approx \frac{2-1.4}{2\cdot 1.4} = \frac{0.6}{2.8} \approx 21\%$$

Lecture #2

Time-dependent potentials: the interaction picture

Recall from Phys 651 ⇒ Schrödinger vs Heisenberg picture

Schrödinger	Heisenberg
$\vert\alpha, t_0; t\rangle_S =$	time-indep: $\vert\alpha, t_0; t\rangle_H = \vert\alpha, t_0\rangle$
$= \underbrace{\hat{U}(t_0, t)}_{\text{propagator}} \vert\alpha, t_0\rangle$; propagator $\Leftarrow e^{-\frac{i}{\hbar}H(t-t_0)}$, $+f(t)$	$A_H(t) = \hat{U}^+(t, t_0) A_S \hat{U}(t, t_0)$
$A_S(t) = A_S(0)$ ← time-independent	$\dfrac{dA_H(t)}{dt} = \dfrac{1}{i\hbar}[A_H, H]$

Intermedial (or interaction, or Dirac) picture

Both a state ket and an observable are time-dependent ⇒ useful for ⇒

$$H = \underbrace{H_0}_{\text{time-independent}} + V(t)$$

(2)

$\Rightarrow$ define $|\alpha, t_0; t\rangle_{\underset{\substack{\uparrow \\ \text{interaction}}}{I}} = e^{iH_0(t-t_0)/\hbar} |\alpha, t_0; t\rangle_S$

$$|\alpha, t_0; t_0\rangle_I = |\alpha, t_0; t_0\rangle_S$$

Consider $t_0 = 0$ for simplicity $\Rightarrow$

$$A_I = e^{\frac{iH_0 t}{\hbar}} A_S e^{-\frac{i}{\hbar}H_0 t}$$

$$\frac{dA_I}{dt} \underset{\substack{\uparrow \\ \text{show!}}}{=} \frac{1}{i\hbar}[A_I, H_0]$$

$$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = i\hbar\frac{\partial}{\partial t}\left(e^{\frac{i}{\hbar}H_0 t}|\alpha, t_0; t\rangle_S\right)$$

$$= -H_0 e^{\frac{i}{\hbar}H_0 t}|\alpha, t_0; t\rangle_S + \underbrace{e^{\frac{i}{\hbar}H_0 t}}\,\underbrace{i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_S}_{= \left(H_{0(S)} + V_{(S)}(t)\right)|\alpha, t_0; t\rangle_S} =$$

$$= e^{\frac{i}{\hbar}H_0 t}\underbrace{V_S(t)}_{e^{-\frac{i}{\hbar}H_0 t} V_I e^{\frac{i}{\hbar}H_0 t}}|\alpha, t_0; t\rangle_S \Rightarrow$$

$$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = V_I|\alpha, t_0; t\rangle_I \qquad (2.1)$$

Consider $H_0|n\rangle = E_n|n\rangle$

Let's say the system is in some initial state $|i\rangle$

Now apply some time-dependent potential $V(t)$, so the total Hamiltonian is

$$H = H_0 + V(t)$$

What is the probability that at some time t the system will be found in some state $|f\rangle$, where $f \neq i$? $\Rightarrow$ use interaction picture $\Rightarrow$

$$|\alpha, t_0; t\rangle_I = \sum_n \underbrace{c_n(t)}_{\uparrow \text{ due to } V(t)!} |n\rangle \Rightarrow \quad \text{Eq. (2.1)}$$

$$i\hbar \frac{\partial}{\partial t} |\alpha, t_0; t\rangle_I = V_I |\alpha, t_0; t\rangle_I \Rightarrow \text{multiply by } \langle n|$$

$$i\hbar \frac{\partial}{\partial t} \underbrace{\langle n|\alpha, t_0; t\rangle_I}_{= c_n(t)} = \sum_m \langle n|V_I|m\rangle \underbrace{\langle m|\alpha, t_0; t\rangle_I}_{= c_m(t)}$$

$$\langle n|V_I|m\rangle = \langle n|e^{\frac{i}{\hbar}H_0 t} V(t) e^{-\frac{i}{\hbar}H_0 t}|m\rangle =$$

$$= e^{\frac{i}{\hbar}(E_n - E_m)t} \langle n|V(t)|m\rangle = V_{nm} e^{\frac{i}{\hbar}(E_n - E_m)t}$$

So, $$i\hbar \frac{d C_n(t)}{dt} = \sum_m V_{nm} e^{i\omega_{nm} t} C_m(t) \Rightarrow$$

$$\omega_{nm} = \frac{E_n - E_m}{\hbar}$$

$$i\hbar \begin{pmatrix} \dot{C}_1(t) \\ \dot{C}_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} V_{11} & V_{12} e^{i\omega_{12} t} & \cdots \\ V_{21} e^{i\omega_{21} t} & V_{22} & \cdots \\ \cdots & \cdots & V_{33} \quad \cdots \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \end{pmatrix} \qquad (2.2)$$

So, to find a probability to end up in some state $|n\rangle$ after time t due to $V(t)$ $\Rightarrow$ need to solve Eqs. (2.2) and then find $|C_n(t)|^2$.

Note: in most cases (2.2) is not solvable exactly!

$\Downarrow$ But there are exceptions! $\Rightarrow$

$\Downarrow$ use time-dependent perturbation theory

Two-level systems (NMR, Spin Magn Reson, Maser, ...)

$H_0 |n\rangle = E_n |n\rangle$, $n = 1, 2$

E_2

E_1

$$H_0 = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2|$$

Apply $V(t) = \gamma e^{i\omega t} |1\rangle\langle 2| + \gamma e^{-i\omega t} |2\rangle\langle 1|$; $\gamma, \omega > 0$ and real (2.3)

physical content: oscillating (with ω) electric or magnetic fields

Say, at $t=0 \Rightarrow \underbrace{c_1(0) = 1}_{}$, $c_2(0) = 0$

only level E_1 is populated

What happens at $t > 0$?

Eqs. (2.2) $\Rightarrow$

$$i\hbar \frac{dc_1}{dt} = V_{11} c_1 + V_{12} e^{i\omega_{12} t} c_2$$

$$i\hbar \frac{dc_2}{dt} = V_{21} e^{i\omega_{21} t} c_1 + V_{22} c_2$$

$V_{11} = V_{22} = 0$; $V_{12} = V_{21}^* = \gamma e^{i\omega t} \Rightarrow$

from (2.3)

$$i\hbar \frac{dc_1(t)}{dt} = \gamma e^{i(\omega+\omega_{12})t} c_2(t) \quad \Rightarrow$$

$$i\hbar \frac{dc_2(t)}{dt} = \gamma e^{-i(\omega+\omega_{12})t} c_1(t)$$

$$i\hbar \frac{d^2c_1}{dt^2} = i(\omega+\omega_{12}) \underbrace{\gamma e^{i(\omega+\omega_{12})t} c_2(t)}_{= i\hbar \frac{dc_1}{dt}} +$$

$$+ \gamma e^{i(\omega+\omega_{12})t} \underbrace{\dot{c}_2(t)}_{\frac{1}{i\hbar}\gamma e^{-i(\omega+\omega_{12})t} c_1(t)} \quad \Rightarrow$$

$$i\hbar \ddot{c}_1 = -\hbar(\omega+\omega_{12})\dot{c}_1 - \frac{i}{\hbar}\gamma^2 c_1 \quad \Rightarrow$$

$$\ddot{c}_1 - i(\omega+\omega_{12})\dot{c}_1 + \frac{\gamma^2}{\hbar^2} c_1 = 0 \underset{\text{solve!}}{\Longrightarrow} c_1 = ?$$

Or $$i\hbar \frac{d^2c_2}{dt^2} = -i(\omega+\omega_{12}) \cdot i\hbar \frac{dc_2}{dt} + \gamma \cancel{e^{-i(\omega+\omega_{12})t}} \cdot \frac{1}{i\hbar}\gamma \cancel{e^{i(\omega+\omega_{12})t}} c_2(t);$$

$$\ddot{c}_2(t) + i(\omega+\omega_{12})\dot{c}_2(t) + \frac{\gamma^2}{\hbar^2} c_2(t) = 0 \underset{\text{solve!}}{\Longrightarrow}$$

$$|c_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\frac{\gamma^2}{\hbar^2} + (\omega+\omega_{12})^2/4} \sin^2\left[\sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega+\omega_{12})^2}{4}}\; t\right]$$

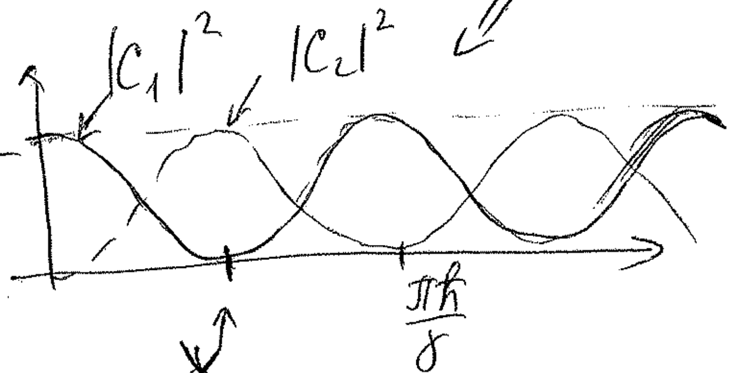
Denote $\Omega = \sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega+\omega_{12})^2}{4}}$ (Rabi frequency)

If $\omega \approx \omega_{21} = \frac{E_2 - E_1}{\hbar} \Rightarrow \omega + \omega_{12} = \omega - \omega_{21} \approx 0 \Rightarrow$

resonance condition

$\Omega = \frac{\gamma}{\hbar} \Rightarrow |C_2(t)|^2 \approx \sin^2 \Omega t$

$|C_1(t)|^2 + |C_2(t)|^2 = 1 \Rightarrow |C_1(t)|^2 \approx \cos^2 \Omega t$



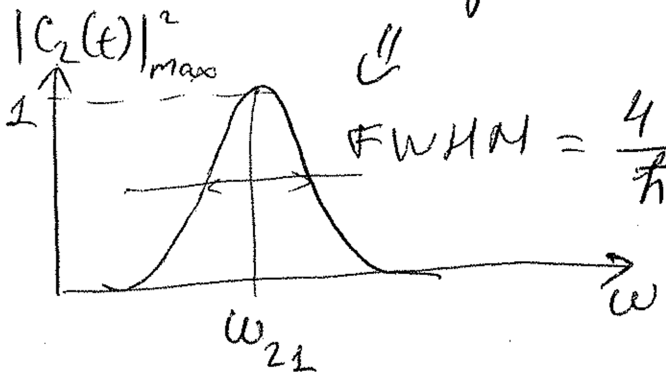
$\frac{\gamma}{\hbar} t_1 = \frac{\pi}{2}$

$\Downarrow$

$t_1 = \frac{\pi\hbar}{2\gamma}$

$\Rightarrow$ $V(t)$ causes transitions from $|1\rangle$ to $|2\rangle$ (absorption) and then from $|2\rangle$ to $|1\rangle$ (emission) (or spin flips if $|1\rangle = |+\rangle$, $|2\rangle = |-\rangle$)

Far away from resonance $\Rightarrow$ $\underbrace{|C_2(t)|^2_{max}}_{= \frac{\gamma^2/\hbar^2}{\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4}}} \neq 1 \Rightarrow$ modulation depth is reduced!



FWHM $= \frac{4\gamma}{\hbar}$

<u>Reading assignment:</u> Sakurai 5.5

Lecture #3

Time-dependent perturbation theory

Consider a physical system described by H_0 $\Rightarrow$

$H_0 |n\rangle = E_n |n\rangle$ (assume for simplicity discrete and non-degenerate spectrum)

At $t=0$, a perturbation $\lambda V(t)$ is applied, so that
$\lambda \ll 1$

$H(t) = H_0 + \lambda V(t)$

If the system is initially in some stationary state $|i\rangle$, i.e. $|\Psi(t=0)\rangle = |i\rangle$, what is the probability to find the system in the state $|f\rangle$ after time t? $\Rightarrow$ i.e. find

$$P_{i\to f}(t) = |\langle f | \Psi(t)\rangle|$$

Need to solve

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = [H_0 + \lambda V(t)] |\Psi(t)\rangle \quad (3.1)$$

with the initial condition $|\Psi(t=0)\rangle = |i\rangle$

Problem: for most $V(t)$, Eq. (3.1) cannot be solved exactly $\Rightarrow$ need approximation methods! (2)

Choose $\{|n\rangle\}$ basis and expand $|\Psi(t)\rangle$:

$$|\Psi(t)\rangle = \sum_n b_n(t)\,|n\rangle, \quad b_n(t) = \langle n|\Psi(t)\rangle \qquad (3.2)$$

Also introduce

$$\langle n|V(t)|k\rangle = V_{nk}(t);$$

$$\langle n|H_0|k\rangle = E_n\,\delta_{nk}$$

Multiply Eq. (3.1) by $\langle n|$:

$$i\hbar\frac{\partial}{\partial t}\langle n|\Psi(t)\rangle = \langle n|H_0|\Psi(t)\rangle +$$

$$+\lambda\langle n|V(t)|\Psi(t)\rangle \underset{\text{Eq. }(3.2)}{\Longrightarrow}$$

$$i\hbar\frac{db_n(t)}{dt} = E_n b_n(t) + \lambda\sum_k V_{nk}(t)\,b_k(t) \qquad (3.3)$$

Present $b_n(t) = C_n(t)\,e^{-\frac{i}{\hbar}E_n t}$ and substitute $\Rightarrow$

$$i\hbar\frac{dC_n(t)}{dt} = \lambda\sum_k V_{nk}(t)\,C_k(t)\,e^{i\omega_{nk}t} \qquad (3.4)$$

$$\omega_{nk} = \frac{E_n - E_k}{\hbar}$$

same as we got in Lecture #2 using interaction picture.

Unfortunately, the system of Eqs (3.4) can be ③
solved exactly only in the simplest cases $\Rightarrow$ need approx.
expand $C_n(t)$ in powers of λ:

$$C_n(t) = C_n^{(0)}(t) + \lambda C_n^{(1)}(t) + \lambda^2 C_n^{(2)}(t) + \ldots$$

and plug into (3.4) $\Rightarrow$

$$i\hbar\left(\frac{dC_n^{(0)}(t)}{dt} + \lambda\frac{dC_n^{(1)}(t)}{dt} + \lambda^2\frac{dC_n^{(2)}(t)}{dt} + \ldots\right) =$$

$$= \lambda\sum_k V_{nk}(t)\left(C_k^{(0)}(t) + \lambda C_k^{(1)}(t) + \lambda^2 C_k^{(2)}(t) + \ldots\right) \cdot e^{i\omega_{nk}t};$$

Collect the terms with equal
powers of λ:

$$\lambda^0: \quad \frac{dC_n^{(0)}}{dt} = 0 \Rightarrow C_n^{(0)} = \text{const} = \delta_{ni}$$

$$\lambda: \quad i\hbar\frac{dC_n^{(1)}}{dt} = \sum_k V_{nk}(t)\, C_k^{(0)}(t)\, e^{i\omega_{nk}t}$$

$$\vdots \qquad\qquad \vdots$$

$$\lambda^r: \quad i\hbar\frac{dC_n^{(r)}}{dt} = \sum_k V_{nk}(t)\, C_k^{(r-1)}(t)\, e^{i\omega_{nk}t}$$

$$i\hbar\frac{dC_n^{(1)}}{dt} = \sum_k V_{nk}(t)\,\delta_{ki}\, e^{i\omega_{nk}t} = V_{ni}(t)\, e^{i\omega_{ni}t}$$

$\Rightarrow$

$$\Rightarrow \quad C_n^{(1)}(t) = \frac{1}{i\hbar}\int_0^t V_{ni}(t')\, e^{i\omega_{ni}t'}\,dt'$$

Then substitute $C_n^{(1)}(t)$ into the equation for $\frac{dC_n^{(2)}}{dt}$, etc. to find higher-order terms.

The transition probability

$$\mathcal{P}_{if}(t) = |\langle f|\Psi(t)\rangle|^2 = |\langle f|\sum_n b_n(t)|n\rangle|^2$$

$$= |\sum_n b_n(t)\delta_{nf}|^2 = |b_f(t)|^2 = |C_f(t)|^2 =$$

$$= |C_f^{(0)}(t) + \lambda C_f^{(1)}(t) + \ldots|^2$$

Assuming that $i \neq f \Rightarrow C_f^{(0)} = 0$

To the first-order,

$$\mathcal{P}_{if}(t) = |\lambda\, C_f^{(1)}(t)|^2 = \frac{\lambda^2}{\hbar^2}\left|\int_0^t V_{fi}(t')\, e^{i\omega_{fi}t'}\,dt'\right|^2$$

(3.5)

Alternative approach to derivation of (3,5) $\Rightarrow$

Consider time evolution of a state ket in the interaction picture $\Rightarrow$ $|\alpha, t_0; t\rangle_I = U_I(t,t_0) \cdot |\alpha, t_0; t_0\rangle_I$;

To find $U_I(t,t_0)$ $\Rightarrow$

$\uparrow$ propagator in the interaction picture

$\Rightarrow$ solve $i\hbar \frac{d}{dt} U_I(t,t_0) = V_I(t)\, U_I(t,t_0)$

(Recall $A_I = e^{\frac{i}{\hbar}H_0 t} A_S\, e^{-\frac{i}{\hbar}H_0 t}$, $A = V$)

with the initial condition $U_I(t_0,t_0) = 1$ $\Rightarrow$

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\, U_I(t',t_0)\, dt' = \quad (3.6)$$

$$= 1 - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t') \left[1 - \frac{i}{\hbar}\int_{t_0}^{t'} V_I(t'')\, U_I(t'',t_0)\, dt''\right] dt' =$$

$$= 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_I(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, V_I(t')\, V_I(t'') +$$

$$+ \ldots \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \ldots \int_{t_0}^{t^{(n-1)}} dt^{(n)}\, V_I(t')\, V_I(t'') \ldots V_I(t^{(n)}) + \ldots$$

$\nearrow$ Dyson series $\Rightarrow$ can compute to any order (finite)

Let's say we know $U_I(t,t_0)$.
Then, if the system is at $t=t_0$ in the state $|i\rangle$, which is an eigenstate of H_0 $\Rightarrow$

$$\underbrace{|i,t_0;t\rangle_I}_{\textstyle \| \atop \textstyle \sum_n c_n(t)|n\rangle} = U_I(t,t_0)\underbrace{|i\rangle_I}_{\textstyle \| \atop \textstyle |i,t_0;t_0\rangle_I}$$

$|n\rangle$ ← eigenstates of H_0

Then, $c_n(t) = \langle n|U_I(t,t_0)|i\rangle$

the probability of transition from $|i\rangle$ to $|n\rangle$ is

$$P_{i\to n} = |c_n(t)|^2 = |\langle n|U_I(t,t_0)|i\rangle|^2 \overset{\text{Eq. (3.6) (Dyson series)}}{=}$$

$$= \left|\delta_{ni} + \left(-\frac{i}{\hbar}\right)\int_{t_0}^{t} \underbrace{e^{i\omega_{ni}t'}V_{ni}(t')}_{\langle n|V_I|i\rangle = e^{i\omega_{ni}t}V_{ni}(t)}dt' + \ldots\right|^2,$$

which is the same as Eq. (3.5)!

QM III
hys 653

Lecture # 4

①

Time-dependent perturbation: special cases

Last time: if the system is in some initial state $|i\rangle$, a perturbation $V(t)$ is turned on at $t=0$, the probability that the system will make a transition to state $|f\rangle$ after time t:

$$\mathcal{P}_{i\to f}(t) \underset{\substack{\uparrow \\ \text{to the} \\ \text{1st order;} \\ i\neq f}}{=} \frac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t'}\, V_{fi}(t')\,dt'\right|^2,$$

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

$$V_{fi} = \langle f|V(t)|i\rangle$$

Special cases:

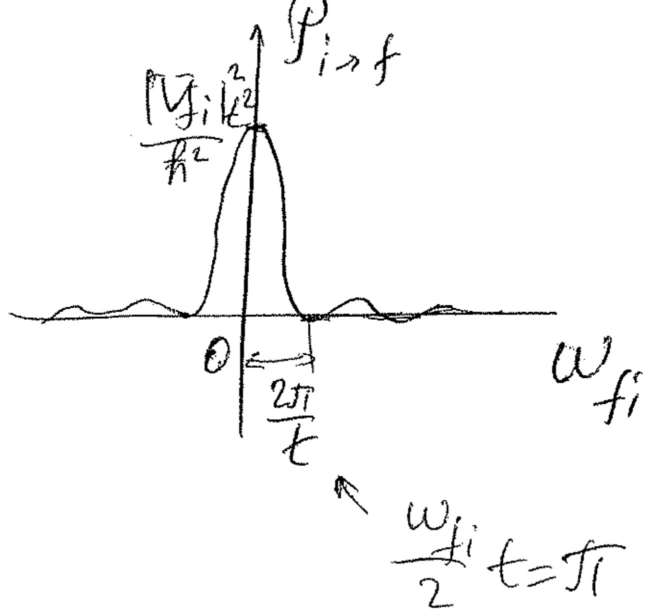
(a) $V(t) \neq$ function of time (so, at $t=0$, some time-independent perturbation is applied)

↑ but can be function of $\vec{X}, \vec{P}, \vec{S}, \ldots$

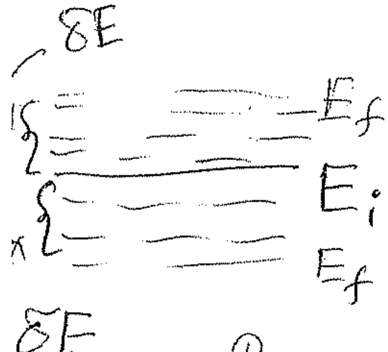
$$\mathcal{P}_{i\to f}(t) = \frac{1}{\hbar^2}|V_{fi}|^2 \cdot \Big|\underbrace{\int_0^t e^{i\omega_{fi}t'}dt'}_{=\frac{1}{i\omega_{fi}}(e^{i\omega_{fi}t}-1)}\Big|^2 =$$

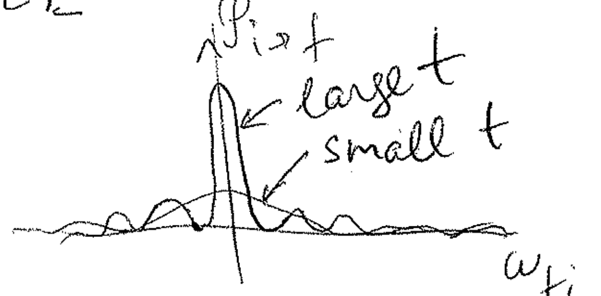
$$= \frac{4|V_{fi}|^2}{\hbar^2\omega_{fi}^2}\sin^2\frac{\omega_{fi}}{2}t = \frac{|V_{fi}|^2}{\hbar^2}\left(\frac{\sin\frac{\omega_{fi}t}{2}}{\frac{\omega_{fi}}{2}}\right)^2$$

Analysis for a fixed t $\Rightarrow$



So, the largest probability of transitions is for states with $|\omega_{fi}| < \frac{2\pi}{t}$, i.e. transitions will be made preferentially to states whose energy is situated in a band of width $\delta E \simeq \frac{2\pi\hbar}{t}$ about the energy of the initial state





At small t $\Rightarrow$ more chances of finding the system at some state with E_f very different from E_i

At large t $\rightarrow$ the function acts as a $\delta(\omega_{fi})$ $\Rightarrow$ the most likely outcome is transitions between degenerate levels ($E_f \simeq E_i$) $\leftarrow$ "energy conservation"

At $\omega_{fi}=0 \Rightarrow \mathcal{P}_{i\to f}=\frac{|V_{fi}|^2}{\hbar^2}t^2$ ③

Problem: $t\to\infty \Rightarrow \mathcal{P}_{i\to f}\to\infty \Rightarrow >1!$

$\Downarrow$

1st-order approximation is valid at

$$t \ll \frac{\hbar}{|V_{fi}|}$$

At fixed $\omega_{fi}\neq 0 \Rightarrow \mathcal{P}_{i\to f}=\frac{4|V_{fi}|^2}{\hbar^2\omega_{fi}^2}\sin^2\frac{\omega_{fi}t}{2}$

$\Downarrow$

oscillates between 0 and $\frac{4|V_{fi}|^2}{\hbar^2\omega_{fi}^2}$

as $\omega_{fi}\uparrow$ (i.e. $|E_f-E_i|\gg 0$) $\Leftrightarrow$

$\Downarrow$

amplitude of oscillations $\downarrow$

(b) $V(t)=V_0\sin\omega t$

$\uparrow$ time-independent observable

$$\mathcal{P}_{i\to f}(t)=\frac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t'}\left(e^{i\omega t'}-e^{-i\omega t'}\right)dt'\right|^2\cdot\frac{|V_{0fi}|^2}{4}$$

$=$

(4)

$$= \frac{|V_{0fi}|^2}{4\hbar^2}\left|\frac{e^{i(\omega_{fi}+\omega)t}-1}{i(\omega_{fi}+\omega)} - \frac{e^{i(\omega_{fi}-\omega)t}-1}{i(\omega_{fi}-\omega)}\right|^2 =$$

$$= \frac{|V_{0fi}|^2}{4\hbar^2}\left|e^{i\frac{\omega_{fi}+\omega}{2}t}\,\frac{\sin\frac{\omega_{fi}+\omega}{2}t}{\frac{\omega_{fi}+\omega}{2}} - e^{i\frac{\omega_{fi}-\omega}{2}t}\cdot\frac{\sin\frac{\omega_{fi}-\omega}{2}t}{\frac{\omega_{fi}-\omega}{2}}\right|^2 \quad (4.1)$$

$\Rightarrow$ two terms with possible <u>resonant</u> behavior $\Rightarrow$

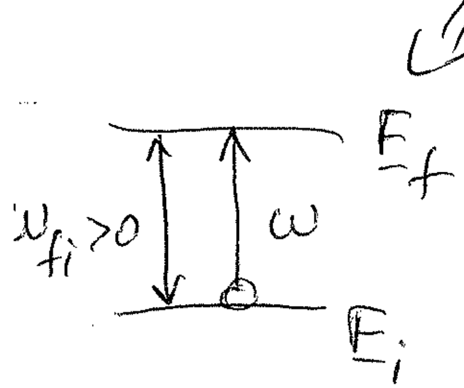
either at $\omega_{fi}+\omega=0$

or $\omega_{fi}-\omega=0$

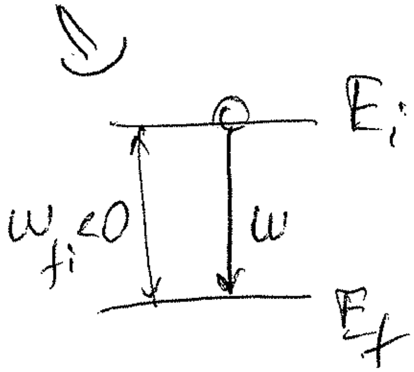
note that both terms can't be resonant at the same time

Let's specify that $\omega>0$. Then, the <u>resonant</u> conditions are $\omega=\omega_{fi}$ $(\omega_{fi}>0)$

$\omega=-\omega_{fi}$ $(\omega_{fi}<0)$



$\Rightarrow$ resonant absorption at $\omega\approx\omega_{fi}$

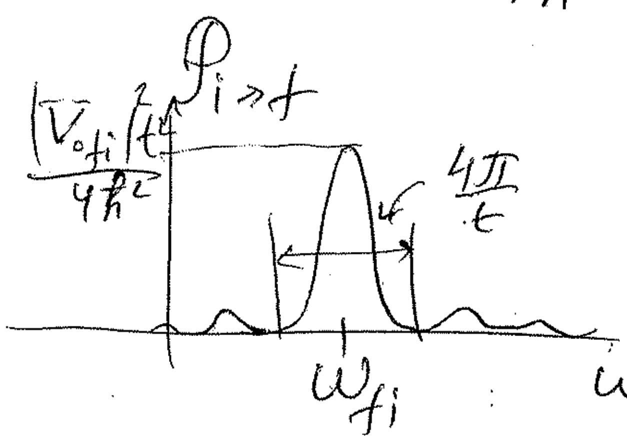


$\Rightarrow$ resonant emission at $\omega\simeq-\omega_{fi}$

Consider resonant absorption $\Rightarrow$

$$P_{i\to f} = \frac{|V_{0fi}|^2}{4\hbar^2}\,\frac{\sin^2\frac{\omega_{fi}-\omega}{2}t}{\left(\frac{\omega_{fi}-\omega}{2}\right)^2} \Rightarrow$$

very similar to constant perturbation (except $\omega_{fi} \to \omega_{fi}$



analysis is similar to the case of constant perturbation

most probable transitions are for $E_f - E_i \sim \hbar\omega$

$t \ll \frac{\hbar}{|V_{0fi}|}$, to keep the approximation valid

Another thing: since we neglected one of the terms in (4.1), we assumed that

$$\frac{1}{\frac{\omega_{fi}+\omega}{2}} \ll \frac{1}{\frac{\omega_{fi}-\omega}{2}} \Rightarrow \text{let's say } \omega_{fi} = \omega + \underbrace{\Delta\omega}_{\text{small!}}$$

Then, $\omega_{fi} + \omega \simeq 2\omega \Rightarrow \underbrace{2\omega}_{\approx\omega_{fi}} \gg \underbrace{\Delta\omega}_{\sim\frac{4\pi}{t}} \Rightarrow$

$$|\omega_{fi}| \gg \frac{2\pi}{t} \Rightarrow t \gg \frac{2\pi}{\omega} \quad (4.2)$$

So, overall, the result is valid if

$$\frac{\hbar}{|V_{0fi}|} \gg \frac{2\pi}{\omega_{fi}} \Rightarrow \underline{\hbar\omega_{fi} \gg |V_{0fi}|}$$

compare with the condition for validity of non-degen. time-independent perturbation theory!!

Note:

It is reasonable to expect the condition similar to (4.2) for validity of $P_{i\to f}$, since if $t < \frac{1}{\omega} \Rightarrow$ the perturbation $V_0 \sin\omega t$ would not have time to oscillate $\Rightarrow V_0 \sin\omega t \xrightarrow[t\to 0]{} V_0\omega t$

$\Downarrow$

linear perturbation

$\Downarrow$

different $P_{i\to f}$!

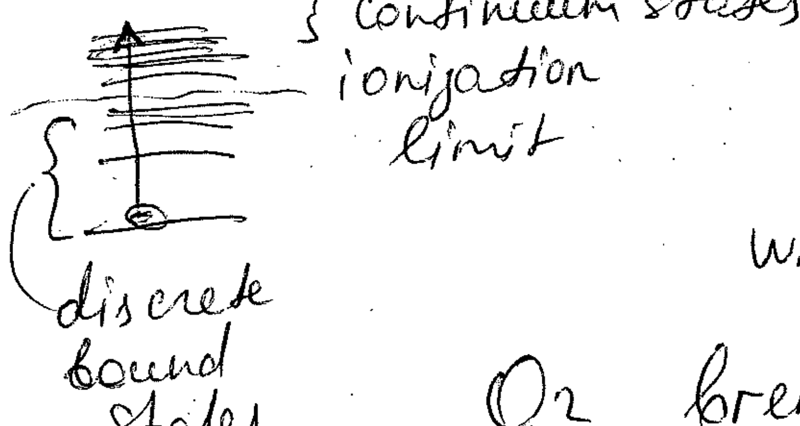
Lecture #5

Transitions between continuum states

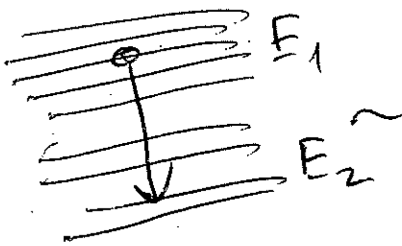
So far we've considered an unperturbed operator that has only a <u>discrete</u> spectrum $\Rightarrow$

$$H_0 |\varphi_n\rangle = E_n |\varphi_n\rangle$$

What if we deal with ionization of atoms as a consequence of the perturbation field of a charged particle which is passing by



Or bremsstrahlung of charged particles as a result of acceleration or deceleration in the field of other particles



$$\rightsquigarrow \hbar\omega = E_1 - E_2$$

Consider general case $\Rightarrow$ H_0 has both discrete and continuous spectrum $\Rightarrow$

$$H_0 \Psi_n(\vec{r}) = E_n \Psi_n(\vec{r}) \quad \text{and} \quad H_0 \Psi_\alpha(\vec{r}) = E_\alpha \Psi_\alpha(\vec{r})$$

discrete index — continuous index

Stationary solutions of the Schrödinger equation: $\Psi_{n,\alpha}(\vec{r},t) = \Psi_{n,\alpha}(\vec{r}) e^{-\frac{i}{\hbar}E_{n,\alpha} t}$

Normalization: $\int \Psi_{n'}^*(\vec{r},t)\Psi_n(\vec{r},t)\,dV = \delta_{n'n}$

$$\int \Psi_\alpha^*(\vec{r},t)\Psi_{\alpha'}(\vec{r},t)\,dV = \delta(\alpha-\alpha')$$

$$\int \Psi_\alpha^*(\vec{r},t)\Psi_n(\vec{r},t)\,dV = 0$$

Closure: $\sum_n |\Psi_n\rangle\langle\Psi_n| + \int d\alpha\, |\Psi_\alpha\rangle\langle\Psi_\alpha| = 1$

At $t=0 \Rightarrow$ introduce perturbation $V(t)$ $\Rightarrow$

$$i\hbar\frac{\partial\Psi}{\partial t} = (H_0 + V(\vec{r},t))\Psi$$

From Lecture # 3 $\Rightarrow$

$$\Psi(\vec{r},t) = \sum_n C_n(t) e^{-\frac{i}{\hbar}E_n t}\Psi_n(\vec{r}) + \int d\alpha\, C_\alpha(t) e^{-\frac{i}{\hbar}E_\alpha t}\Psi_\alpha(\vec{r}), \qquad (6.1)$$

$$\sum_n |C_n(t)|^2 + \int d\alpha\, |C_\alpha(t)|^2 = 1$$

Substitute Eq. (6.1) into Shrödinger equation $\Rightarrow$

$$i\hbar\left(\sum_n \frac{dc_n(t)}{dt} e^{-\frac{i}{\hbar}E_n t}\psi_n(\vec{r}) + \int d\alpha \frac{dc_\alpha(t)}{dt} e^{-\frac{i}{\hbar}E_\alpha t}\cdot \psi_\alpha(\vec{r})\right) = \sum_n c_n(t) e^{-\frac{i}{\hbar}E_n t} V(\vec{r},t)\psi_n(\vec{r}) +$$

$$+\int d\alpha\, c_\alpha(t) e^{-\frac{i}{\hbar}E_\alpha t} V(\vec{r},t)\psi_\alpha(\vec{r}); \qquad (6.2)$$

Multiply (6.2) by $e^{\frac{i}{\hbar}E_{n'}t}\psi^*_{n'}(\vec{r})$ and integrate over $\vec{r} \Rightarrow$

$$\underline{i\hbar\frac{dc_{n'}(t)}{dt}} = \sum_n c_n(t) e^{-\frac{i}{\hbar}(E_n - E_{n'})t} V_{n'n} +$$

$$+\int d\alpha\, c_\alpha(t) e^{\frac{i}{\hbar}(E_{n'}-E_\alpha)t} V_{n'\alpha} =$$

$\omega_{n'n} = \frac{E_{n'}-E_n}{\hbar}$

$\omega_{n'\alpha} = \frac{E_{n'}-E_\alpha}{\hbar}$

$$\underline{= \sum_n c_n(t) e^{i\omega_{n'n}t} V_{n'n}(t) + \int d\alpha\, c_\alpha(t) e^{i\omega_{n'\alpha}t} V_{n'\alpha}(t)} \qquad (6.3)$$

Similarly, if (6.2) is multiplied by $e^{\frac{i}{\hbar}E_{\alpha'}t}\psi^*_{\alpha'}(\vec{r})$ and integrated over $\vec{r} \Rightarrow$

get $$i\hbar \frac{dC_{\alpha'}(t)}{dt} = \sum_n C_n(t) e^{i\omega_{\alpha' n} t} V_{\alpha' n}(t) + \int C_\alpha(t) e^{i\omega_{\alpha'\alpha} t} V_{\alpha'\alpha}(t)\, d\alpha \qquad (6.3)$$

Recall Lecture #3 $\Rightarrow$ $C_n(t) = C_n^{(0)} + \lambda C_n^{(1)} + \ldots$

$C_\alpha(t) = C_\alpha^{(0)} + \lambda C_\alpha^{(1)} + \ldots$

From Eqs. (6.3) $\Rightarrow$

<u>0th order</u>: $i\hbar \frac{dC_{n'}^{(0)}}{dt} = 0$; $i\hbar \frac{dC_{\alpha'}^{(0)}}{dt} = 0$ $\Rightarrow$

$C_{n'}^{(0)}, C_{\alpha'}^{(0)}$ are constants

<u>1st order</u>: $$i\hbar \frac{dC_{n'}^{(1)}}{dt} = \sum_n C_n^{(0)} e^{i\omega_{n'n} t} V_{n'n}(t) + \int d\alpha\, C_\alpha^{(0)} e^{i\omega_{n'\alpha} t} V_{n'\alpha}(t) ;$$

$$i\hbar \frac{dC_{\alpha'}^{(1)}}{dt} = \sum_n C_n^{(0)} e^{i\omega_{\alpha' n} t} V_{\alpha' n}(t) + \int d\alpha\, C_\alpha^{(0)} e^{i\omega_{\alpha'\alpha} t} V_{\alpha'\alpha}(t) ;$$

$- - - -$

Let's specify that at $t=0$ our system is in a state k of the discrete spectrum $\Rightarrow$ ⑤

$$C_{n'}^{(0)} = \delta_{n'k} \ ; \ C_{\alpha'}^{(0)} = 0$$

Then, $i\hbar \dfrac{dC_{n'}^{(1)}}{dt} = e^{i\omega_{n'k}t} V_{n'k}(t)$

$$i\hbar \frac{dC_{\alpha'}^{(1)}}{dt} = e^{i\omega_{\alpha'k}t} V_{\alpha'k}(t)$$

transitions between bound states $\Rightarrow$ Lecture #3

transitions between bound and unbound states

$\Downarrow$

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

very similar to what we had for the case of discrete spectrum!

What's different? $\Longrightarrow$ the probability of transition is now $P_{k\to\alpha} = \int d\alpha\, |C_\alpha(t)|^2$, not just $|C_\alpha(t)|^2$!

$\alpha \updownarrow n$

$k \neq \alpha$, 1st order

What is $d\alpha$? $\Longrightarrow$

$$\Big\}\ B(E) \Longrightarrow d\alpha = \underbrace{\rho_\alpha(E)}_{\text{density of states}}\, \underset{\text{energy}}{dE}$$

$B(E)$: domain in which the electron ends up after the transition

So, $\mathcal{P}_{i \to f} = \int_{B(E)} |C_\alpha^{(1)}(t)|^2 \rho_\alpha(E)\, dE =$

i: discrete state K; f: continuum state α

$$= \int_{B(E)} \frac{1}{\hbar^2} \left| \int_0^t V_{\alpha K}(t')\, e^{i\omega_{\alpha K} t'}\, dt' \right|^2 \rho_\alpha(E)\, dE$$

probability of transition from state K to an "energy region" $B(E)$ in the continuum

If the initial state is in continuum too $\Rightarrow$

$C_K(0) = 0, \quad C_{\alpha'}(0) = \delta(\beta - \alpha') \Rightarrow$

$$\mathcal{P}_{\beta \to \alpha} = \frac{1}{\hbar^2} \int_{B(E)} \left| \int_0^t V_{\alpha\beta}(t')\, e^{i\omega_{\alpha\beta} t'}\, dt' \right|^2 \rho_\alpha(E)\, dE$$

Notes on "sudden" change versus "adiabatic" change in the Hamiltonian

(a) consider a system whose H changes abruptly over a small time interval ε. What is the change in the state vector as $\varepsilon \to 0$?

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = H(t)\,|\psi(t)\rangle \;;$$

Say, $t \in \left[-\frac{\varepsilon}{2}, \frac{\varepsilon}{2}\right]$ ↑ change at $t=0$

$$\underbrace{|\psi(\tfrac{\varepsilon}{2})\rangle}_{|\psi_{\text{after change}}\rangle} - \underbrace{|\psi(-\tfrac{\varepsilon}{2})\rangle}_{|\psi_{\text{before change}}\rangle} = -\frac{i}{\hbar}\int_{-\varepsilon/2}^{\varepsilon/2} H(t)\,|\psi(t)\rangle\, dt$$

If $H(t)$ is not a δ-function $\Rightarrow$ $\varepsilon \to 0 \Rightarrow$

$$|\psi_{\text{after}}\rangle = |\psi_{\text{before}}\rangle$$

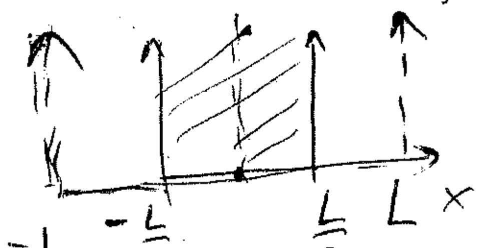
(b) now let's say that $H(t)$ changes very slowly from $H(0)$ to $H(\tau)$ in a time τ. If the system starts out at $t=0$ in an eigenstate $|n(0)\rangle$ of $H(0)$, where will it end up at time τ?

$\Rightarrow$

adiabatic theorem : if the rate of change of H

is "slow enough", the system will end up (8)
in the corresponding eigenket $|n(\tau)\rangle$ of $H(\tau)$

Recall one of the HW problems from Phys. 651:



Particle in the box of length L.
Then, the box expands to $2L$.
If the particle is initially in its ground state, where is it going to end up after the change?

"sudden"

$\mathcal{P}(n=1, \text{old} \to n=1, \text{new}) = \left(\frac{8}{3\pi}\right)^2 \sim 81\%$

(the rest is $\to n=2, \ldots$ new)

"adiabatic" $\Rightarrow \mathcal{P}(n=1, \text{old} \to n=1, \text{new}) \stackrel{\text{after time } \tau}{=} 1$

But: how slow is slow?! $\Rightarrow$ introduce "natural time scale" for a system $T \sim \frac{1}{\omega_{fi}} \sim \frac{1}{\omega_i}$ if $\omega_{fi} \neq 0$ (non-degen.)

Particle-in-the-box $\Rightarrow E_n^0 = \frac{\hbar^2\pi^2}{2mL^2} n^2$

$T \sim \frac{mL^2}{\hbar} \Rightarrow$ so $\tau \gg T$ is <u>slow</u>

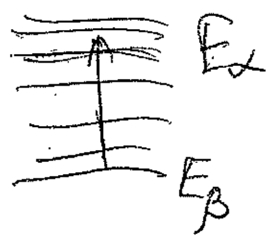
<u>Note</u>: the adiabatic theorem suggests that at $\tau \gg T$ time-dependent perturb. theory $\Rightarrow$ time-indep. one!

Lecture #6

Fermi's golden rule

Consider a transition between two continuum states α and β $\Rightarrow$ the transition probability ($\alpha \neq \beta$, 1st order) $\Rightarrow$

$$\mathcal{P}_{\beta\to\alpha} = \frac{1}{\hbar^2}\int_{B(E)} \left| \int_0^t \tilde{V}_{\alpha\beta}(t')\, e^{i\omega_{\alpha\beta}t'}\, dt' \right|^2 \rho_\alpha(E)\, dE$$



Consider a "constant" perturbation, i.e.

$$V(\vec{r},t) = \begin{cases} V(\vec{r}), & 0 \le t \le T \\ 0 & \text{otherwise} \end{cases}$$

Then

$$\tilde{V}_{\alpha\beta}(t') = \int \psi_\alpha^* V(\vec{r})\, \psi_\beta\, dV \equiv V_{\alpha\beta}$$

$$\mathcal{P}_{\beta\to\alpha} = \frac{1}{\hbar^2}\int_{B(E)} |V_{\alpha\beta}|^2 \rho_\alpha(E) \underbrace{\left| \int_0^T e^{i\omega_{\alpha\beta}t'}\, dt' \right|^2}_{= \frac{\sin^2 \frac{\omega_{\alpha\beta}T}{2}}{\left(\frac{\omega_{\alpha\beta}}{2}\right)^2}} dE =$$

$$= \frac{1}{\hbar^2}\int_{B(E)} |V_{\alpha\beta}|^2 \rho_\alpha(E) \frac{\sin^2 \frac{\omega_{\alpha\beta}T}{2}}{\left(\frac{\omega_{\alpha\beta}}{2}\right)^2}\, dE \quad (7.1)$$

Note that if $\rho_\alpha(E) = \delta(E - E_f) \Rightarrow$ Eq. (7.1)

$\Downarrow$

discrete states $\Rightarrow$ Eq. on p. 2, Lec. #4

Let $B(E) = \left[E_f - \frac{\varepsilon}{2}, E_f + \frac{\varepsilon}{2}\right]$, $\varepsilon \to 0$

$\Downarrow$

$\rho_\alpha(E)$, $V_{\alpha\beta}(E)$ are practically E-independent

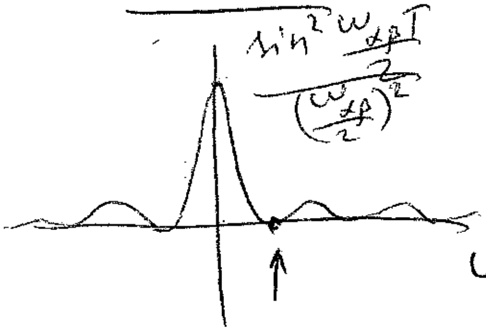
$\Downarrow$

Then, Eq. (7.1) $\Rightarrow$

$$\mathcal{P}_{\beta \to B(E)} = \frac{1}{\hbar^2} |V_{\alpha\beta}|^2 \rho_\alpha(E_f) \int_{E_f - \frac{\varepsilon}{2} < E < E_f + \frac{\varepsilon}{2}} \frac{\sin^2 \frac{\omega_{\alpha\beta}}{2} T}{(\omega_{\alpha\beta}/2)^2} dE$$

$$\omega_{\alpha\beta} = \frac{E - E_\beta}{\hbar}$$

Recall:

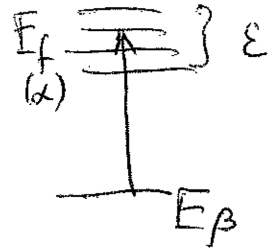


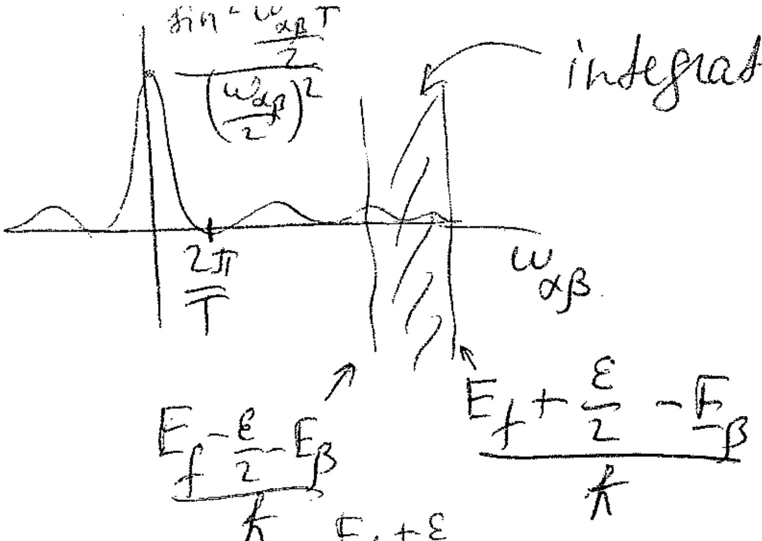
$\frac{\omega_{\alpha\beta} T}{2} = \pi \Rightarrow \underbrace{|\omega_{\alpha\beta}| \le \frac{2\pi}{T}}_{}$ $\leftarrow$ largest probability

(a) $\underbrace{\hbar \omega_{\alpha\beta} \gg \varepsilon}_{} \gg \frac{2\pi\hbar}{T}$

$\Downarrow$

energy non-conserving transitions





integration over this region

$\Rightarrow$ in this case

$$\int_{B(E)} \frac{\sin^2\frac{\omega_{\alpha\beta}T}{2}}{\left(\frac{\omega_{\alpha\beta}}{2}\right)^2}\, dE \simeq$$

$$\simeq 2\hbar^2 \int_{E_f-\frac{\varepsilon}{2}}^{E_f+\frac{\varepsilon}{2}} \frac{dE}{(E-E_\beta)^2}$$

average

$$\overline{\frac{\sin^2\frac{\omega_{\alpha\beta}T}{2}}{\left(\frac{\omega_{\alpha\beta}}{2}\right)^2}}^{\,T} \simeq \frac{1}{2\left(\frac{\omega_{\alpha\beta}}{2}\right)^2}$$

Then, $\mathcal{P}_{\beta\to B(E)} = \frac{1}{\hbar^2}|V_{\alpha\beta}|^2\rho_\alpha(E_f)\cdot 2\hbar^2\cdot$

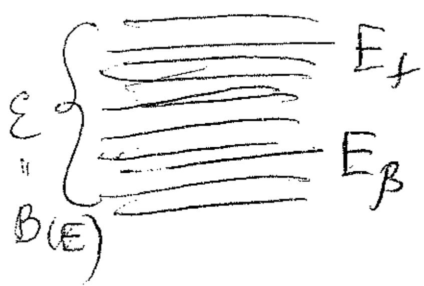
$$\cdot\int_{E_f-\frac{\varepsilon}{2}}^{E_f+\frac{\varepsilon}{2}} \frac{dE}{(E-E_\beta)^2} = 2|V_{\alpha\beta}|^2\rho_\alpha(E_f)\left[\frac{1}{E_f-\frac{\varepsilon}{2}-E_\beta}-\frac{1}{E_f+\frac{\varepsilon}{2}-E_\beta}\right]$$

$$= 2|V_{\alpha\beta}|^2\rho_\alpha(E_f)\frac{\varepsilon}{(E_f-E_\beta)^2-\frac{\varepsilon^2}{4}} \approx \underline{\frac{2\varepsilon|V_{\alpha\beta}|^2\rho(E_f)}{(E_f-E_\beta)^2}}$$

$\hbar\omega_{\alpha\beta} \gg \varepsilon$

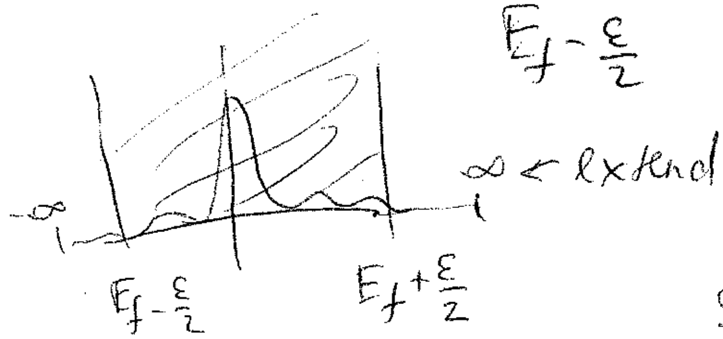
does <u>not</u> depend on time

(b) now let $E_f - E_\beta \approx \mathcal{E} \gg \frac{2\pi\hbar}{T}$



In this case

$$\int_{E_f - \frac{\varepsilon}{2}}^{E_f + \frac{\varepsilon}{2}} \frac{\sin^2 \frac{\omega_{\alpha\beta} T}{2}}{\left(\frac{\omega_{\alpha\beta}}{2}\right)^2} dE \approx \int_{-\infty}^{+\infty} \frac{\sin^2 \frac{\omega_{\alpha\beta} T}{2}}{\left(\frac{\omega_{\alpha\beta}}{2}\right)^2} dE \simeq$$



$$\simeq \hbar \int_{-\infty}^{+\infty} \frac{\sin^2 \frac{\omega T}{2}}{\left(\frac{\omega}{2}\right)^2} d\omega = 2\pi\hbar T$$

$\omega_{\alpha\beta} \approx \omega$

HW!

Then, $\mathcal{P}_{\beta \to B(E)} = \frac{1}{\hbar^2} |V_{\alpha\beta}|^2 \rho_\alpha(E_f) \cdot 2\pi\hbar T =$

$$= \underline{\frac{2\pi}{\hbar} |V_{\alpha\beta}|^2 \rho_\alpha(E) T}$$

note $E \approx E_f$ since $\omega_{\alpha\beta} \approx 0$

$\Downarrow$

<u>energy-conserving</u>

<u>transition</u>

Introduce transition probability per unit time $\Rightarrow$

$$p_{\beta \to B(E)} = \frac{d\mathcal{P}_{\beta \to B(E)}}{dt} = \frac{2\pi}{\hbar} |V_{\alpha\beta}|^2 \rho_\alpha(E) \quad (7.2)$$

Fermi's Golden rule

for energy-conserving transitions $\Rightarrow$ time-indep probability per unit time

For energy non-conserving

$\Downarrow$

$\mathcal{P}_{\beta \to B(E)}$ is time-independent $\Rightarrow$ $p_{\beta \to B(E)} = 0$

Validity of Eq. (7.2) $\Rightarrow$ T is long enough to guarantee that $\varepsilon \gg \frac{2\pi\hbar}{T}$. From another side T is short enough to justify the 1st-order pert. theory, i.e. $\omega_{\alpha\beta} t \big|_{t=T} \ll 1$.

What if we have another perturbation? $\Rightarrow$

$V(t) = V e^{-i\omega t}$ $\Rightarrow$ Lecture #4 $\Rightarrow$

$$\mathcal{P}_{i \to f} = \frac{1}{\hbar^2} |V_{if}|^2 \left| \int_0^t e^{i(\omega_{fi} - \omega)t'} dt' \right|^2 =$$

$$= \frac{|V_{if}|^2}{\hbar^2} \underbrace{\frac{\sin^2 \frac{\omega_{fi}-\omega}{2} t}{\left(\frac{\omega_{fi}-\omega}{2}\right)^2}}$$

What if the perturbation is applied from $-\frac{T}{2}$ to $\frac{T}{2}$ and $T \to \infty$? $\Rightarrow$

$$\mathcal{P}_{i\to f} = \frac{1}{\hbar^2} |V_{if}|^2 \Big| \underbrace{\int_{-\frac{T}{2}}^{\frac{T}{2}} e^{i(\omega_{fi}-\omega)t'} dt'}_{\Downarrow\, T\to\infty \atop 2\pi\,\delta(\omega_{fi}-\omega)} \Big|^2 =$$

$$= \frac{4\pi^2}{\hbar^2} |V_{if}|^2 \underbrace{\delta(\omega_{fi}-\omega)\,\delta(\omega_{fi}-\omega)} = \underbrace{\frac{2\pi}{\hbar^2} |V_{if}|^2 \delta(\omega_{fi}-\omega) \cdot \lim_{T\to\infty} T}$$

$$\lim_{T\to\infty} \underbrace{\delta(\omega_{fi}-\omega)}_{\substack{\downarrow \\ 0 \text{ unless} \\ \omega_{fi}=\omega}} \frac{1}{2\pi} \int_{-\frac{T}{2}}^{\frac{T}{2}} \underbrace{e^{i(\omega_{fi}-\omega)t}}_{= 1} dt =$$

$$= \underbrace{\delta(\omega_{fi}-\omega) \lim_{T\to\infty} \frac{T}{2\pi}}$$

Average transition rate $\Rightarrow$

$$\underbrace{P_{i\to f} = \frac{d\mathcal{P}}{dt} = \frac{2\pi}{\hbar} |V_{if}|^2 \delta\left(E_f^{(0)} - E_i^{(0)} - \hbar\omega\right)}$$

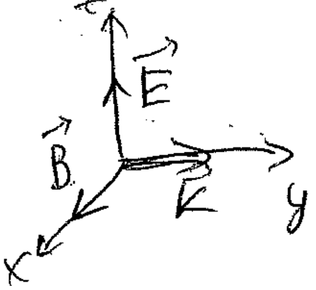
QM III
Phys 653

Lecture #9

Interaction of radiation with matter

Consider a plane electromagnetic wave, with wave vector $\vec{k}$ (say, $\vec{k} \parallel Oy$)

and angular frequency $\omega = ck$



Introduce vector potential $\vec{A}$ =>

$$\vec{A}(\vec{r},t) = \left(A_0 e^{i(ky-\omega t)} + A_0^* e^{-i(ky-\omega t)}\right)\vec{e}_z$$

$\vec{e}_z$: unit vector $\parallel Oz$

Then, $\vec{E} = -\frac{\partial}{\partial t}\vec{A}(\vec{r},t) =$

$$= i\omega\left(A_0 e^{i(ky-\omega t)} - A_0^* e^{-i(ky-\omega t)}\right)\vec{e}_z$$

$$\vec{B} = \vec{\nabla}\times\vec{A}(\vec{r},t) = ik\left(A_0 e^{i(ky-\omega t)} - A_0^* e^{-i(ky-\omega t)}\right)\vec{e}_x$$

$$\begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ 0 & 0 & A \end{vmatrix}$$

Set $i\omega A_0 = \frac{E_0}{2}$

$ikA_0 = \frac{B_0}{2}$ =>

imaginary

$$\frac{E_0}{B_0} = \frac{\omega}{k} = c \Rightarrow \vec{E}(\vec{r},t) = E_0\vec{e}_z\cos(ky-\omega t)$$

$$\vec{B}(\vec{r},t) = B_0\vec{e}_x \cos(ky-\omega t)$$

(Here we assumed the Coulomb gauge $\varphi = 0$

a.k.a. radiation, transverse $\qquad \vec{\nabla}\cdot\vec{A} = 0$

(2)

How do we describe interaction between matter & E&M field? $\Rightarrow$ full treatment

$\Downarrow$

need relativistic QM!

For now $\Rightarrow$ simplified version:

$$H = H_{matter} + H_{EM} \quad , \quad \mathcal{E} = \mathcal{E}_{matter} \otimes \mathcal{E}_{EM}$$

total Hamiltonian for the combined matter-field system; space

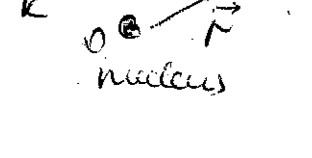
$$H_{EM} = \sum_{\lambda} \hbar\omega_\lambda \underbrace{a_\lambda^+ a_\lambda}_{\text{number operator}} \Leftrightarrow \text{Adv. QM!}$$

$$H_{matter} = \sum_{i} \frac{1}{2m_i}\left[p_i - \frac{q_i}{c}\vec{A}(\vec{r}_i,t)\right]^2 +$$

particles

$$+ \sum_{i<j} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} - \sum_i \vec{\mu}_i \cdot \vec{B}(\vec{r}_i,t)$$

Consider the simplest case $\Rightarrow$ H like atom with a single electron $\Rightarrow q = -|e|$, $\vec{\mu} = \frac{e}{mc}\vec{S}$ and assume that nucleus is very heavy



$$H_{matter} = \frac{1}{2m}\left[\vec{p} + \frac{e}{c}\vec{A}(\vec{r},t)\right]^2 - \frac{Ze^2}{|\vec{r}|} + \frac{e}{mc}\vec{S}\cdot\vec{B}_{(\vec{r},t)}$$

$$H = \underbrace{\frac{\vec{p}^2}{2m} - \frac{Ze^2}{|\vec{r}|} + \sum_\lambda \hbar\omega_\lambda a_\lambda^\dagger a_\lambda}_{H_0} +$$

$$+ \underbrace{\frac{e}{mc}\vec{p}\cdot\vec{A}(\vec{r},t)}_{1} + \underbrace{\frac{e}{mc}\vec{S}\cdot\vec{B}(\vec{r},t)}_{2} + \underbrace{\frac{e^2}{2mc^2}\vec{A}(\vec{r},t)^2}_{3}$$

perturbation $V(\vec{r},t)$

if $\vec{A}=0 \Rightarrow 0 \Rightarrow$ (interaction Hamiltonian)

Estimate relative orders of magnitude $\Rightarrow$

$$V_1 = \frac{e}{mc}\vec{p}\cdot\vec{A} \sim \frac{e}{mc}\, p\, A_0$$

p: momentum of the electron

$$V_2 = \frac{e}{mc}\vec{S}\cdot\vec{B} \sim \frac{e}{mc}\hbar\,(k A_0)$$

k: wave vector of the EM wave

$\Delta p \Delta x \sim \hbar$

$\sim a_0$ for an atom

$$\frac{V_2}{V_1} \sim \frac{\hbar k}{p} = \frac{\hbar}{p}\cdot\frac{2\pi}{\lambda} \sim \frac{a_0}{Z\lambda} \ll 1$$

λ: wavelength of light

$a_0 = 0.5\,\text{Å}$

$\lambda \sim 500\,\text{nm}$ visible light

So, V_1 dominates!

$V_3 \sim \vec{A}^2$ and in most cases can be neglected (unless dealing with amplified laser sources!)

Consider $V_{①} = \frac{e}{mc} \vec{p} \cdot \vec{A}(\vec{r},t) = \frac{e}{mc} p_z \cdot$
$\cdot \left[A_0 e^{i(ky-\omega t)} + A_0^* e^{-i(ky-\omega t)} \right]$

(Recall $V = \underbrace{V_0 e^{i\omega t}}_{\text{emission}} + \underbrace{V_0^+ e^{-i\omega t}}_{\text{absorption}}$)

Example

Transition rate in the case of absorption $\Rightarrow$

$$\underbrace{P_{i \to f}}_{\text{discrete}} = \frac{2\pi}{\hbar} \left(\frac{e}{mc} \right)^2 |A_0|^2 \left| \langle f | e^{iky} p_z | i \rangle \right|^2 ,$$

$$E_f = E_i + \hbar\omega$$

Approximations:

The region of interaction between EM wave and an atom is confined to $\sim a_0 \Rightarrow$

$$ky \sim \frac{2\pi}{\lambda} \cdot a_0 << 1 \Rightarrow$$

$$e^{iky} \simeq 1 + iky - \frac{1}{2} k^2 y^2 + \ldots$$

If consider $e^{iky} \simeq 1 \rightarrow$ electric dipole approximation

$\Rightarrow$

$$V_{1} \approx \underbrace{V_{DE}}_{\text{electric dipole}} = \frac{e}{mc} P_z \underbrace{\left(A_0 e^{-i\omega t} + A_0^* e^{i\omega t}\right)}_{\Uparrow} =$$

$A_0 = \dfrac{E_0}{2i\omega}$

p. 1

$$= -\frac{eE_0}{mc\omega} P_z \sin\omega t$$

So, what is $\langle f | V_{DE} | i \rangle$? $\Rightarrow$

$$\langle f | \frac{-eE_0}{mc\omega} P_z \sin\omega t | i \rangle = -\frac{eE_0}{m\omega} \sin\omega t \langle f | P_z | i \rangle =$$

$$= -ie\frac{\omega_{fi}}{\omega} E_0 \sin\omega t \langle f | z | i \rangle$$ ← looks familiar!

$$\underbrace{\left\langle \frac{dz}{dt} \right\rangle}_{\frac{P_z}{m}} = \frac{i}{\hbar} \langle \overbrace{[H_0, z]}^{= -i\hbar \frac{P_z}{m}} \rangle$$ ← time evolution of expectation values (Phys 657)

consider only $H_{0,\text{matter}}$

$$\langle f | [z, H_0] | i \rangle = \frac{i\hbar}{m} \langle f | P_z | i \rangle =$$

$$= \langle f | z \underbrace{H_0 | i}_{E_i |i\rangle} \rangle - \langle \underbrace{f | H_0}_{E_f \langle f|} z | i \rangle =$$

$$= -(E_f - E_i) \langle f | z | i \rangle = -\hbar\omega_{fi} \langle f | z | i \rangle$$

$$\langle f | P_z | i \rangle = i m \omega_{fi} \langle f | z | i \rangle$$

Consider $\langle f|z|i\rangle \Rightarrow$ if it's not $\neq 0$

transition $|i\rangle \Rightarrow |f\rangle$ is allowed in electric dipole approximation

$$|i\rangle \Rightarrow R_{n_i l_i}(r)\, Y_{l_i}^{m_i}(\theta,\varphi)$$

$$|f\rangle \Rightarrow R_{n_f l_f}(r)\, Y_{l_f}^{m_f}(\theta,\varphi)$$

$$\langle f|z|i\rangle = \sqrt{\frac{4\pi}{3}} \int_0^\infty R^*_{n_f l_f}(r)\, R_{n_i l_i}(r)\, r^3 dr \,\cdot$$

$$z = r\cos\theta = r \cdot \sqrt{\frac{4\pi}{3}}\, Y_1^0$$

$$\cdot \int Y_{l_f}^{m_f *}(\theta,\varphi)\, Y_1^0(\theta)\, Y_{l_i}^{m_i}(\theta,\varphi)\, d\Omega$$

Recall Phys 652 $\Rightarrow$ addition of angular momenta + parity of Y_l^m

$$\boxed{\begin{aligned} l_f &= l_i \pm 1 \\ m_f &= m_i \end{aligned}}$$

$\leftarrow$ selection rules for z-polariz.

$\Delta m = m_f - m_i = \pm 1 \leftarrow$ for x, y-polariz.

<u>HW</u>: How is V_{DE} on p. 5 related to our "usual" $V = -e\vec{E}\cdot\vec{r}$ potential for interaction with electric fi[eld]

QM III
Phys 653

Lecture # 10

Interaction of an atom with an EM wave (cont)

Last time: $H = H_0 + \underbrace{\frac{e}{mc}\vec{P}\cdot\vec{A}(\vec{r},t)}_{①} + \underbrace{\frac{e}{mc}\vec{S}\cdot\vec{B}(\vec{r},t)}_{②} + \underbrace{\frac{e^2}{2mc^2}\vec{A}^2(}_{③}$

$V_{①} \gg V_{②} \gg V_{③}$

$\vec{A} = \left(A_0 e^{i(ky-\omega t)} + A_0^* e^{-i(ky-\omega t)}\right)\vec{e}_z$

$\vec{E} = E_0 \vec{e}_z \cos(ky-\omega t)$; $\frac{E_0}{B_0} = \frac{\omega}{k} = c$; $i\omega A_0 = \frac{E_0}{2}$

$\vec{B} = B_0 \vec{e}_x \cos(ky-\omega t)$; $ikA_0 = \frac{B_0}{2}$

$V_{①} = \frac{e}{mc}\vec{P}\cdot\vec{A}(\vec{r},t) = \underbrace{\frac{e}{mc}P_z\left(A_0 e^{iky}\right)}_{\hat{V}_0}e^{-i\omega t} + c.c$

$\hat{V}_0 = \underbrace{V_{0DE}}_{\text{electric dipole}} + \dots$

Transition rate $i \to f \Rightarrow$

$$P_{i\to f} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 |A_0|^2 \left|\langle f|e^{iky}P_z|i\rangle\right|^2,$$

$E_f = E_i + \hbar\omega$

Electric-dipole approx. :

$e^{iky} \approx 1 \Rightarrow \langle f|e^{iky}P_z|i\rangle \approx \langle f|P_z|i\rangle =$

$= im\omega_{fi}\langle f|z|i\rangle \Rightarrow$ selection rules
$\Delta l = \pm 1$
$\Delta m = 0$ (or ± 1 if x- or y-polar

↑
WS #10

Now take into account higher-order terms ⇒ (2)

$$e^{iky} \simeq 1 + \underbrace{iky}_{} + O(ky)^2$$

$$V_{0_{(1)}} - V_{0\,DE} \underset{\substack{\text{neglect}\\ \text{terms}\\ \sim (ky)^2}}{=} \frac{e}{mc} P_z \underbrace{A_0 \cdot (iky)}_{=\frac{B_0}{2}} = \frac{e}{mc}\frac{B_0}{2} P_z y =$$

$$= \frac{e}{mc}\frac{B_0}{2}\left[\frac{1}{2}(\underbrace{P_z y - z P_y}_{=L_x}) + \frac{1}{2}(P_z y + z P_y)\right] \qquad (11.1)$$

$$V_{0_{(2)}} = \frac{e}{mc}\vec{S}\cdot\vec{B} = \frac{e}{mc} S_x \frac{B_0}{2} \qquad (11.2)$$

only time-independent part (factor out $e^{\pm i\omega t}$)

$e^{iky} \approx 1$

$V_{(2)}(t) = \frac{e}{mc} S_x B_0 \underbrace{\cos\omega t}_{=\frac{1}{2}(e^{i\omega t} + e^{-i\omega t})}$

Combine (11.1) and (11.2) ⇒

$$V_0 = V_{0\,DE} + \underbrace{\frac{e}{mc}\frac{B_0}{2}\cdot\frac{1}{2}(L_x + 2S_x)}_{=V_{0\,DM}} + \underbrace{\frac{e}{mc}\frac{\overset{=\frac{E_0}{c}}{B_0}}{2}\frac{1}{2}(P_z y + z P_y)}_{=V_{0\,QE}}$$

$V_{0\,DM}$ ← magnetic dipole transitions

$V_{0\,QE}$ ← electric quadrupole transitions

magnetic dipole transitions ⟷ electric quadrupole transitions: the same order!

⇓

Selection rules?

⇓

$$\langle f | \hat{V}_{o_{DM}} | i \rangle \sim \langle f | L_x + 2S_x | i \rangle =$$

$$= \langle n_f \, l_f \, m_f \, m_{s_f} | \underbrace{L_x}_{\frac{L_+ + L_-}{2}} + 2 \underbrace{S_x}_{\frac{S_+ + S_-}{2}} | n_i \, l_i \, m_i \, m_{s_i} \rangle \neq 0$$ if

$m_f = m_i \pm 1$

$m_{s_f} = m_{s_i} \pm 1$

If $\vec{B} \parallel Oz \Rightarrow \langle f | L_z + 2S_z | i \rangle \neq 0$ if

$m_f = m_i$

$m_{s_f} = m_{s_f}$

Since $\hat{V}_{DM}$ doesn't act on l

$\Downarrow \quad \Delta l = l_f - l_i = 0$

So, selection rules for the magnetic dipole transition are $\Delta l = 0$; $\Delta M = \pm 1$ or 0

$\Delta M_s = \pm 1$ or 0

What about $\langle f | \hat{V}_{o_{QE}} | i \rangle$? $\Rightarrow$

$$\langle f | P_z y + z P_y | i \rangle = \langle f | \frac{im}{\hbar} [H_0, z] y + \frac{im}{\hbar} [H_0, y] z | i \rangle$$

$$= \langle f | \frac{im}{\hbar} [H_0, zy] | i \rangle \ominus \qquad P_{z,y} = \frac{im}{\hbar} [H_0, z_{,y}]$$

$$\ominus \; \frac{im}{\cancel{\hbar}} \omega_{fi} \cancel{\hbar} \langle f | zy | i \rangle$$

$\leftarrow$ component of quadrupole moment

$$yz \sim r^2 \left(A Y_2^1 + B Y_2^{-1}\right) \Rightarrow$$

$$\langle f | yz | i \rangle \sim \int Y_{l_f}^{m_f *} \, Y_2^{\pm 1} \, Y_{l_i}^{m_i} \, d\Omega \Rightarrow 0 \text{ unless}$$

also take into account parity of Y_l^m $\longrightarrow$ $\Delta l = 0, \pm 2$

$\Delta m = 0, \pm 1, \pm 2$

take into account all $\langle f | xy | i \rangle$, $\langle f | xz | i \rangle$, ...

Further expansion: electric octupole, magnetic quadrupole, ...

<u>Analysis</u>

- Because of selection rules V_{DM} and V_{QE} never compete with V_{DE}
- V_{DM} & V_{QE} can be separated by observing $\Delta l = \pm 2$ transitions $\Rightarrow$ e.g. 557.7 nm line of atomic oxygen

---

Back to electric dipole approximation and absorption, $\Rightarrow$

define an <u>absorption cross-section</u> σ_{abs} $\Rightarrow$

$$\sigma_{abs} = \frac{\text{Energy per unit time, absorbed by the atom}}{\text{Energy flux of the radiation field}} =$$

Sakurai p. 336

energy per area per unit time

5

$$= \frac{\hbar\omega \, P_{i\to f}}{cU} = \frac{\hbar\omega \left(\frac{2\pi}{\hbar}\right)\left(\frac{e}{mc}\right)^2 |A_0|^2 m^2 \omega_{fi}^2 |\langle f|z|i\rangle|^2}{\frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2}$$

$$cU = \frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2$$

energy density

energy absorbed by atom, $\underline{E_f = E_i + \hbar\omega}$

assume $\delta(E_f - E_i - \hbar\omega)$

$\omega_{fi} \approx \omega$

$$= 4\pi^2 \underbrace{\frac{e^2}{\hbar c}}_{=\alpha} \omega_{fi} |\langle f|z|i\rangle|^2 \delta(\omega_{fi} - \omega)$$

α ← fine-structure constant

Define <u>oscillator strength</u> $f_{fi} = \frac{2m\omega_{fi}}{\hbar}|\langle f|z|i\rangle|^2$

determines the strength of the transition

$$\sum_f f_{fi} = 1$$

all possible final states

Thomas-Reiche-Kuhn sum rule

Show! (HW)

Lecture # 11

Spontaneous emission of radiation

From last week;
transition rate for absorption $(\vec{A} \parallel Oz, \vec{k} \parallel Oy) \Rightarrow$

$$P_{i \to f} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 |A_0|^2 |\langle f | e^{iky} p_z | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

$$\Rightarrow \quad P_{i \to f} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 |A_0|^2 |\langle f | e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon}\cdot\vec{p} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

generalize to an arbitrary direction of $\vec{k}$ and light polarization $\vec{\epsilon}$

Recall:
$$V(t) = V_0 e^{-i\omega t} + V_0^* e^{i\omega t}$$
absorption emission

Transition rate for emission $\Rightarrow$

$$P_{i \to f} = \frac{2\pi}{\hbar}\left(\frac{e}{mc}\right)^2 |A_0|^2 |\langle f | e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}^*\cdot\vec{p} | i \rangle|^2 \delta(E_f - E_i + \hbar\omega)$$

So, the absorption process occurs when the atom receives a photon from the radiation, and the emission occurs when the radiation gains a photon from the decaying atom. Note that this is stimulated emission $\Rightarrow$

no emission if $\vec{A}=0$!! ⇒ use it for light amplification by stimulated emission of radiation (LASER) ⇒ if a large number of atoms are in the same excited state, and one photon is incident ⇒ cause chain reaction, as the atoms release photons of the same ω within a very short time

What happens if $\vec{A}=0$? Does it mean that the atoms will stay in the excited state forever? ⇒

nope! ⇒ <u>Spontaneous emission</u> ⇒ cannot be described by classical treatment of the EM field (as we did so far, in the case of absorption and stimulated emission) ⇒ need QM treatment of EM radiation

⇓

<u>Second quantization</u> ⇒ replace fields (such as $\vec{A}$, $\vec{E}$, $\vec{B}$) by operators expressed in terms of a^+, a ⇒ $\hat{A}_{\lambda,\vec{k}} = \sqrt{\frac{2\pi\hbar c^2}{\omega_k}}\, a_{\lambda,\vec{k}}$

$$H = \sum_{\vec{k}} \sum_{\lambda=1}^{2} \hbar\omega_k \left(a^+_{\lambda,\vec{k}} a_{\lambda,\vec{k}} + \frac{1}{2}\right) \Leftarrow \text{like in harmonic oscillator}$$

$\vec{k}$ ↑ wave number; λ ↑ polarization (2 components in the plane $\perp \vec{k}$)

$a^+_{\lambda,\vec{k}}$ → creates a photon of wave number $\vec{k}$ and polarization λ

$n_{\lambda,\vec{k}} = 0, 1, 2, \ldots$

↑ eigenvalues of $N_{\lambda,\vec{k}}$ ← number operator

$$\underbrace{|n_{\lambda,\vec{k}}\rangle}_{\text{state with}} = \frac{1}{\sqrt{n_{\lambda,\vec{k}}!}} \left(a^+_{\lambda,\vec{k}}\right)^{n_{\lambda,\vec{k}}} \underbrace{|0\rangle}_{\text{state with no photons ("vacuum state")}}$$

$n_{\lambda,\vec{k}}$ photons with wave vector $\vec{k}$ and polarization λ

"occupation number"

$$a_{\lambda,\vec{k}} |n_{\lambda,\vec{k}}\rangle = \sqrt{n_{\lambda,\vec{k}}}\, |n_{\lambda,\vec{k}} - 1\rangle$$

$$a^+_{\lambda,\vec{k}} |n_{\lambda,\vec{k}}\rangle = \sqrt{n_{\lambda,\vec{k}} + 1}\, |n_{\lambda,\vec{k}} + 1\rangle$$

Eigenstates of $H \Rightarrow |n_{\lambda_1\vec{k}_1}, n_{\lambda_2\vec{k}_2}, n_{\lambda_3\vec{k}_3}, \ldots\rangle$

$$E = \sum_{\vec{k}} \sum_{\lambda} \hbar\omega_k \left(n_{\lambda\vec{k}} + \frac{1}{2}\right)$$

↑ energy

EM field with $n_{\lambda_1\vec{k}_1}$ photons in the mode $(\lambda_1, \vec{k}_1)$ etc.

(assume EM in a box) volume

$$\vec{A}(\vec{r},t) = \sum_{\vec{k}} \sum_{\lambda} \sqrt{\frac{2\pi\hbar c^2}{\omega_k V}} \left[a_{\lambda,\vec{k}}\, e^{i(\vec{k}\cdot\vec{r} - \omega_k t)} \vec{\epsilon}_\lambda + a^+_{\lambda,\vec{k}}\, e^{-i(\vec{k}\cdot\vec{r} - \omega_k t)} \vec{\epsilon}^{\,*}_\lambda \right] \Rightarrow$$

$$V(t) = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{V}} \sum_{\vec{k}} \sum_{\lambda} \frac{1}{\sqrt{\omega_k}} \Big[a_{\lambda,\vec{k}}\, e^{i\vec{k}\cdot\vec{r}}\, \vec{\epsilon}_\lambda \cdot \vec{P} \cdot$$

$$\cdot\, e^{i\omega_k t} + a^{+}_{\lambda,\vec{k}}\, e^{-i\vec{k}\cdot\vec{r}}\, \vec{\epsilon}^{\,*}_\lambda \cdot \vec{P}\, e^{-i\omega_k t} \Big] =$$

$$= \sum_{\vec{k}} \sum_{\lambda} \Big(\underbrace{V_{0_{\lambda,\vec{k}}}\, e^{i\omega_k t}}_{\text{absorption (annihilation)}} + \underbrace{V_{0_{\lambda,\vec{k}}}\, e^{-i\omega_k t}}_{\text{(creation) emission}} \Big)$$

$\Downarrow$

as in the classical case, QM description has the structure of a <u>harmonic</u> perturbation

<u>Absorption</u> $\Rightarrow$ initial state $|\Phi_i\rangle = \underbrace{|\psi_i\rangle}_{\text{atom}} \underbrace{|n_{\lambda,\vec{k}}\rangle}_{\text{radiation}}$

final state $|\Phi_f\rangle = |\psi_f\rangle |n_{\lambda,k} - 1\rangle$

$$\langle \Phi_f | V_{0_{\lambda,\vec{k}}} | \Phi_i \rangle = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\, \sqrt{n_{\lambda,\vec{k}}}\, \langle \psi_f | e^{i\vec{k}\cdot\vec{r}} \cdot$$

$$\cdot\, \vec{\epsilon}_\lambda \cdot \vec{P} | \psi_i \rangle$$

$$a_{\lambda,\vec{k}} |n_{\lambda,\vec{k}}\rangle = \sqrt{n_{\lambda,\vec{k}}}\, |n_{\lambda,\vec{k}} - 1\rangle$$

$\Downarrow$

$$P_{i\to f} = \frac{4\pi^2 e^2}{m^2 \omega_k V}\, n_{\lambda,\vec{k}}\, |\langle \psi_f | e^{i\vec{k}\cdot\vec{r}}\, \vec{\epsilon}_\lambda \cdot \vec{P} | \psi_i \rangle|^2 \cdot$$

$$\cdot\, \delta(E_f - E_i - \hbar\omega_k)$$

$\nwarrow$ absorption of a photon of energy $\hbar\omega_k = \hbar c k$, wave number $\vec{k}$ and polaris. λ

Emission $\Rightarrow$ $|\varphi_f\rangle = |\psi_f\rangle |n_{\lambda,\vec{k}}+1\rangle$

$$\langle \varphi_f | V^{+}_{0\,\lambda,\vec{k}} | \varphi_i \rangle = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{\omega_k V}}\sqrt{n_{\lambda,\vec{k}}+1}\;\cdot$$

$$\cdot \langle \psi_f | e^{-i\vec{k}\cdot\vec{r}}\,\vec{\epsilon}^{\,*}_{\lambda}\cdot\vec{p}\,|\psi_i\rangle \quad\Rightarrow$$

$$P_{i\to f} = \frac{4\pi^2 e^2}{m^2 \omega_k V}\,(\underbrace{n_{\lambda,\vec{k}}}_{\text{stimulated}} + \underbrace{1}_{\text{spontaneous emission}})\,|\langle \psi_f | e^{-i\vec{k}\cdot\vec{r}}\,\vec{\epsilon}^{\,*}_{\lambda}\cdot\vec{p}\,|\psi_i\rangle|^2 \cdot \delta(E_f - E_i + \hbar\omega_k)$$

spontaneous emission $\downarrow$ is there even if $\vec{A}=0$ (i.e. $n_{\lambda,\vec{k}}=0$)

Consider spontaneous emission in the electric-dipole approx.

$\Downarrow$

$$n_{\lambda,\vec{k}}=0\;;\quad e^{-i\vec{k}\cdot\vec{r}} \simeq 1$$

$\Downarrow$ WS#10 $\quad \langle\psi_f|(-e\,\vec{r})|\psi_i\rangle$ "

$$\underbrace{P_{i\to f}}_{\text{probability of transition per unit time}} = \frac{4\pi^2 \omega_{fi}^2}{\omega_k V}\,|\vec{\epsilon}^{\,*}_{\lambda}\cdot \underbrace{\vec{d}_{fi}}_{\text{dipole moment matrix element}}|^2\,\delta(E_f - E_i + \hbar\omega_k)$$

probability of transition per unit time with spontaneous emission of a photon $\hbar\omega_k$

dipole moment matrix element

<u>Note</u>: spontaneous emission is typically <u>much</u> weaker (slower) than stimulated ($n_{\lambda,\vec{k}} \gg 1$) when radiation is present

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Now... The final states of the system is a product of a discrete atomic state and a continuum of photonic states $\Rightarrow$ need to integrate $P_{i\to f}$ with $\rho(E)\,dE$ to find a total transition rate.

Number of final photonic states within volume V, whose momenta are within the interval $[\vec{p}, \vec{p}+d\vec{p}]$, $\vec{p} = \hbar\vec{k}$ $\Rightarrow$

$$d^3 n = \underbrace{\frac{V}{(2\pi\hbar)^3}}_{\substack{\text{density of states} \\ \text{in } p\text{-space}}} d^3 p = \frac{V}{(2\pi\hbar)^3} \underbrace{p^2}_{\substack{\| \\ (\hbar \frac{\omega}{c})^2}} dp\, d\Omega = \frac{V\omega^2}{(2\pi c)^3} \cdot d\omega\, d\Omega$$

Transition rate corresponding to the emission of a photon in the solid angle $d\Omega$ $\Rightarrow$

$$dW^{em}_{i\to f} = \frac{V}{(2\pi c)^3}\, d\Omega \int \omega^2 P_{i\to f}\, d\omega =$$

$$= \frac{V}{(2\pi c)^3}\, d\Omega \cdot \frac{4\pi^2 \omega_{fi}^2}{\cancel{V}} \int \omega\, \delta(E_f - E_i + \hbar\omega)\, d\omega \cdot$$

$$\cdot \left|\vec{\epsilon}^{\,*}_\lambda \cdot \vec{d}_{fi}\right|^2 = \frac{\omega^3}{2\pi\hbar c^3} \left|\vec{\epsilon}^{\,*}_\lambda \cdot \vec{d}_{fi}\right|^2 d\Omega \qquad (12.1)$$

The transition rate (12.1) corresponds to a specific polarization. For any polarization $\Rightarrow$ average over pol.

arbitrary

$$\sum_{\lambda=1}^{2} |\vec{\epsilon}_\lambda^{\,*}\cdot\vec{d}_{fi}|^2 = |\vec{\epsilon}_1^{\,*}\cdot(d_{fi})_1|^2 + |\vec{\epsilon}_2^{\,*}(d_{fi})_2|^2 =$$

$$= |\vec{d}_{fi}|^2 - |(d_{fi})_3|^2 = |\vec{d}_{fi}|^2 - \frac{1}{3}|\vec{d}_{fi}|^2 =$$

$\parallel \vec{k}$

since all directions of $\vec{d}_{fi}$ are equivalent $\Rightarrow$

$$= \frac{2}{3}|\vec{d}_{fi}|^2 \Rightarrow$$

$$dW^{em}_{i\to f} = \frac{\omega^3}{3\pi\hbar c^3}|\vec{d}_{fi}|^2 d\Omega$$

Total transition rate associated with the emission of the photon $\Rightarrow \int d\Omega \Rightarrow 4\pi \Rightarrow$

$$W^{em}_{i\to f} = \frac{4}{3}\frac{\omega^3}{\hbar c^3}|\vec{d}_{fi}|^2 = \frac{4}{3}\frac{\omega^3 e^2}{\hbar c^3}|\langle\psi_f|\vec{r}|\psi_i\rangle|^2$$

$\omega = \dfrac{E_f - E_i}{\hbar}$; $\vec{d} = -e\vec{r}$ (for one-electron atoms)

Total power radiated

See E&M!

$$I_{i\to f} = \hbar\omega W^{em}_{i\to f} = \frac{4}{3}\frac{\omega^4 e^2}{c^3}|\langle\psi_f|\vec{r}|\psi_i\rangle|^2$$

The mean lifetime of an excited state $\Rightarrow$

$$\tau = \frac{1}{\sum_f W_{i\to f}} = \frac{1}{W}$$

Example A hydrogen atom is in 2p state. Find transition rate for $2p \to 1s$ transitions and the lifetime of the 2p state.

$$W_{2p\to 1s} = \frac{4}{3}\frac{e^2 \omega^3_{2p\to 1s}}{\hbar c^3} |\underbrace{\vec{r}_{fi}}_{\langle f|\vec{r}|i\rangle}|^2$$

$\langle f|\vec{r}|i\rangle$ $\Rightarrow$ need $\langle 21m| x, y, z |100\rangle$

$f = 21m$, $i = 100$

HW:

- obtain $|\vec{r}_{fi}|^2 = \text{const}\,(\delta_{m,1} + \delta_{m,-1} + \delta_{m,0})$
- if assume that all m-states equally contribute

$$\underbrace{W^{em}_{\substack{i\to f\\2p\ 1s}}}_{\Uparrow \text{ find it!}} = \frac{1}{3}\sum_{m=-1}^{1} W_{2pm\to 1s}$$

- Lifetime $\tau = \dfrac{1}{W_{2p\to 1s}}$

QM III
Phys 653

Lecture # 12

Lifetimes, line intensities, widths, shapes

Back to Lectures # 2-3 $\Rightarrow$ discrete states $\Rightarrow$

$$|\Psi(t)\rangle = \sum_n C_n(t)\, e^{-\frac{i}{\hbar}E_n t}|n\rangle$$

$$i\hbar \frac{dC_n(t)}{dt} = \lambda \sum_k V_{nk}(t)\, C_k(t)\, e^{i\omega_{nk}t}$$

$$P_{i\to f}(t) = |C_f(t)|^2$$

Two-level system $\Rightarrow$ $C_1(t)$, $C_2(t)$,

$C_1(0) = 1$, $C_2(0) = 0$ (Lecture #2)

As we've shown, under harmonic perturbation the system oscillates (in the resonance, i.e. $\omega = \omega_{21}$

$|C_1|^2 \sim \cos^2 \underbrace{\Omega}_{\frac{\gamma}{\hbar}} t$, $|C_2|^2 \sim \sin^2 \Omega t$

$\frac{\gamma}{\hbar} \leftarrow$ strength of perturbation

Can we think of an atom that can made a spontaneous transition from 2 to 1 as a two-level system? $\Rightarrow$ no, since the final state is actually a state of an atom together with that of a photon, which is continuous. These final states are

(2)

incoherent and cannot act cooperatively to build up the reverse transitions, so probability of finding the atom in state 2 decreases steadily with time. How do we describe it?

$$\mathcal{P}_2(t+dt) = \mathcal{P}_2(t)\underbrace{\left(1 - W_{21}^{em}\,dt\right)}$$

↑ probability of finding the atom in state 2 at t+dt

probability that no transition from 2 to 1 has taken place (due to spont. emission)

$$\mathcal{P}_2(t) = e^{-t/\tau}, \qquad \tau = \frac{1}{W_{21}^{em}} \rightarrow \text{lifetime}$$

⇓

$$C_2(t) = e^{-t/2\tau}$$

↑ assume C_2 is real

$$\Psi_2(\vec{r},t) = C_2(t)\,\Psi_2(\vec{r})\,e^{-\frac{i}{\hbar}E_2 t} =$$

$$= \Psi_2(\vec{r})\,e^{-\frac{i}{\hbar}\left(E_2 - \frac{i\hbar}{2\tau}\right)t} \leftarrow \text{a state with } \underline{\text{complex}} \text{ energy!!}$$

$$e^{-\frac{i}{\hbar}\left(E_2 - \frac{i\hbar}{2\tau}\right)t} = \frac{1}{(2\pi\hbar)^{1/2}}\int_{-\infty}^{+\infty} a(E')\,e^{-\frac{i}{\hbar}E't}\,dE'$$

↑ decompose into energy eigenstates

$$a(E) = \frac{1}{(2\pi\hbar)^{1/2}} \int_0^\infty e^{-\frac{i}{\hbar}\left(E_2 - \frac{i\hbar}{2\tau}\right)t}\, e^{\frac{i}{\hbar}E' t}\, dt =$$

↑ consider $\Psi_2(0) = 0$

$$= \frac{1}{(2\pi\hbar)^{1/2}} \frac{-i\hbar}{E_2 - E - \frac{i\hbar}{2\tau}}$$

Then, probability to find the system in state 2, but with definite energy E is $\sim |a(E)|^2 =$

$$= \frac{\hbar}{2\pi} \frac{1}{(E_2 - E)^2 + \frac{\hbar^2}{4\tau^2}}$$

Conservation of energy (assuming that state 1 does not decay).

$\Downarrow$

$$E = E_1 + \hbar\omega$$

$\Downarrow$

$$|a(E)|^2 = \frac{\hbar}{2\pi} \frac{1}{(\underbrace{E_2 - E_1}_{\hbar\omega_{21}} - \hbar\omega)^2 + \frac{\hbar^2}{4\tau^2}} = \leftarrow \text{Lorentzian distribution}$$

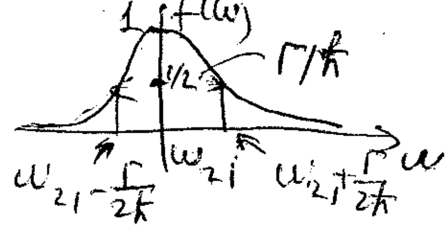
$$= \frac{1}{\hbar} \frac{1}{(\omega_{21} - \omega)^2 + \frac{\Gamma^2}{4\hbar^2}} \sim f(\omega) = \frac{\Gamma^2/4\hbar^2}{(\omega_{21} - \omega)^2 + \frac{\Gamma^2}{4\hbar^2}}$$

↑

$\Gamma = \frac{\hbar}{\tau}$

↑ natural width of the line

$\Downarrow$



Generally $\Rightarrow$ $\Delta E \sim \Gamma$ ← uncertainty in energy

$\Delta t \sim \tau$ ← in time

$$\Delta E \, \Delta t \gtrsim \hbar$$

If the final state 1 is not stable $\Rightarrow$

$$\Gamma = \hbar \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right)$$

lifetimes of states 1 & 2

If state 2 can decay to more than one state

$$W^{em}_{2\to1} \Rightarrow \sum_i W^{em}_{2\to i}$$

The natural width of atomic lines is very small $\Rightarrow$

(H) atom, 2p state $(E_{n=2} = -3.4\ eV) \Rightarrow \Gamma = 4 \cdot 10^{-7}\ eV$

$$\frac{\Gamma}{|E_{n=2}|} \sim 10^{-7} \ ! \qquad \tau = 1.6\ ns$$

Typically, observed spectral lines are much wider $\Rightarrow$

- pressure broadening $\Rightarrow$ a.k.a. collisional broadening

$$W^{em}_{i\to f} \Rightarrow W^{total}_{i\to f}$$ ← include $W_c = n v \sigma$,

where n is the number density of atoms, v is the relative velocity between pairs of atoms, σ is the collision cross-section.

· Mechanism: collision between atoms (especially relevant in gases) causes radiationless transitions. Since number of atoms participating in collisions (n) and their velocity (v) are functions of temperature and pressure of the gas $\Rightarrow$ measure spectral profiles and get this info (this is how we know these things about stellar atmospheres!!)

- Doppler broadening

wavelength of light emitted by a moving atom is shifted $\Rightarrow$ $\lambda = \lambda_0 \left(1 \pm \frac{v}{c}\right)$

going away from observer

approaching observer

emitted by a stationary atom

$$\omega = \omega_0 \left(1 \pm \frac{v}{c}\right)^{-1} \simeq \omega_0 \left(1 \mp \frac{v}{c}\right)$$

$$\omega = \frac{2\pi c}{\lambda}$$

⑥

atomic mass

$$\underbrace{dN}_{\uparrow} = N_0 \exp\left(-\frac{Mv^2}{2KT}\right)dv$$

Maxwell distribution

atoms

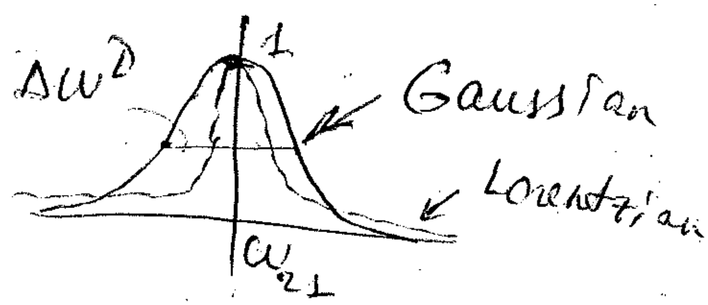
with velocities between v and $v+dv$

$$\underbrace{I(\omega)} = I(\omega_0)\exp\left[-\frac{Mc^2}{2KT}\left(\frac{\omega-\omega_0}{\omega_0}\right)^2\right]$$

ω_{21}

intensity of light emitted by atoms

Gaussian



Doppler width at half-max ⇒

$$\Delta\omega^D = \frac{2\omega_0}{c}\left[\frac{2KT}{M}\ln 2\right]^{1/2} \Rightarrow$$

↑ with temperature T and the frequency of the line ω_0

Typically observe a combination of Lorentzian and Gaussian ⇒ Voigt profile

homogeneous broadening

inhomogeneous broadening