Time dependent perturbation theory
special cases

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

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

$$V_{ni} = \langle n | V(t) | i \rangle$$

$$\rightarrow \quad c_n(t) = c_n^0(t) + \lambda c_n^1(t) + \lambda^2 c_n^2(t) + \ldots$$

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

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

let's instead use the propogator

$$|\alpha\, t_0; t\rangle_I = \mathcal{U}(t, t_0)\, |\alpha\, t_0; t_0\rangle_I$$

Schrödinger Picture: $i\hbar \frac{d\mathcal{U}_S}{dt} = H\mathcal{U}_S$

Interaction Picture: $i\hbar \frac{d}{dt} \mathcal{U}_I(t, t_0) = V_I(t)\, \mathcal{U}_I(t, t_0)$

then, initial condition is

$$\mathcal{U}_I(t_0\, t_0) = 1$$

$$\rightarrow \quad \mathcal{U}_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} V_I(t')\, \mathcal{U}_I(t', t_0)\, dt'$$

we haven't really solved it yet...

now we can continue to substitute

$$\cancel{\mathcal{U}_I(t\, t_0) = 1 - \frac{i}{\hbar}\left[V - \frac{i}{\hbar} \right.}$$

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

and so on...

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

$$\lambda^0 \qquad \lambda^1 \qquad \lambda^2 \qquad \dots$$

This series is called Dyson series.

Now we know the propogator. How do we apply it?

$$\mathcal{U}_I(t;t_0)\,|i, t_0, t_0\rangle_I = |i\ t_0\ t\rangle_I$$

$$= \sum_n c_n(t)|n\rangle$$

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

So $P_{i\to n} = |c_n|^2 = |\langle n|\mathcal{U}_I(t\,t_0)|i\rangle|^2$

if we discard higher order terms then we have

$$P_{i\to n} = \Big|\underbrace{\delta_{ni}}_{c_n^{(0)}} - \frac{i}{\hbar}\int_0^t V_{ni}(t')\,dt'\Big|^2$$

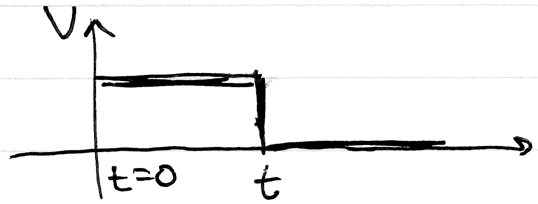
where $\quad V_I(t) = e^{\frac{i}{\hbar}H_0 t}\,V_s\,e^{-i/\hbar\, H_0 t}$

so that $\quad \langle n|V_I|i\rangle = \langle n|e^{\frac{i}{\hbar}H_0 t}\,V_s\,e^{-\frac{i}{\hbar}H t}|i\rangle$

$$= e^{i\omega_{ni}t}\,V_s$$

same result!

Now lets consider some examples

1: $V(t) =$ 

$$P_{i\to f}(t) = \frac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t'} V_{fi}(t')\,dt'\right|^2 \qquad i \neq f$$

$$\omega_{fi} = (E_f - E_i)/\hbar$$

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

$$\longrightarrow P_{i\to f} = \frac{1}{\hbar^2}|V_{fi}|^2\left|\int_0^t e^{i\omega_{fi}t'}\,dt'\right|^2$$

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

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

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

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

$$= \frac{|V_{fi}|^2}{\hbar^2}\left|t\,\mathrm{sinc}\left(\frac{\omega_{fi}t}{2}\right)\right|^2$$

Time-dep perturbation theory
Transitions between continuum states

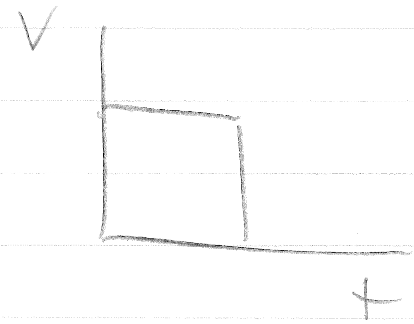
Recall: $H = H_0 + V(t)$

(first order) $$P_{i\to f}(t) = \frac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t'}\, V_{fi}(t')\,dt'\right|^2$$

$$\omega_{fi} = (E_f - E_i)/\hbar \;;$$

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

(a) $V(t) \neq$ function of time



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

$$P_{i\to f} = \frac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t}\left(e^{i\omega t} - e^{-i\omega t}\right)\right|^2 \frac{|V_{0fi}|^2}{4}$$

$$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

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

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

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

first term is resonant when

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

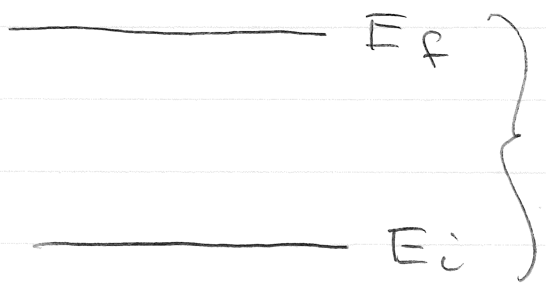
the second is resonant when

$$\omega = \omega_{fi}$$

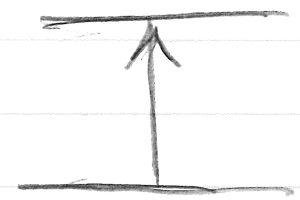
but these can not happen simultaneously
therefore, we need only consider
1 of the resonant terms.

Focusing on Resonant cases

$\omega = \omega_{fi}$

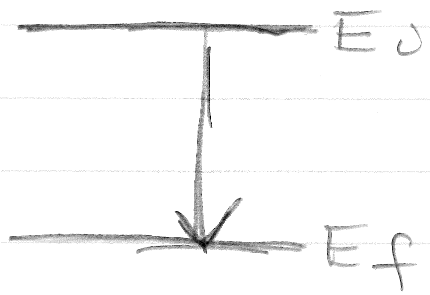


then, we have



resonant absorption

if $\omega = -\omega_{fi}$ then



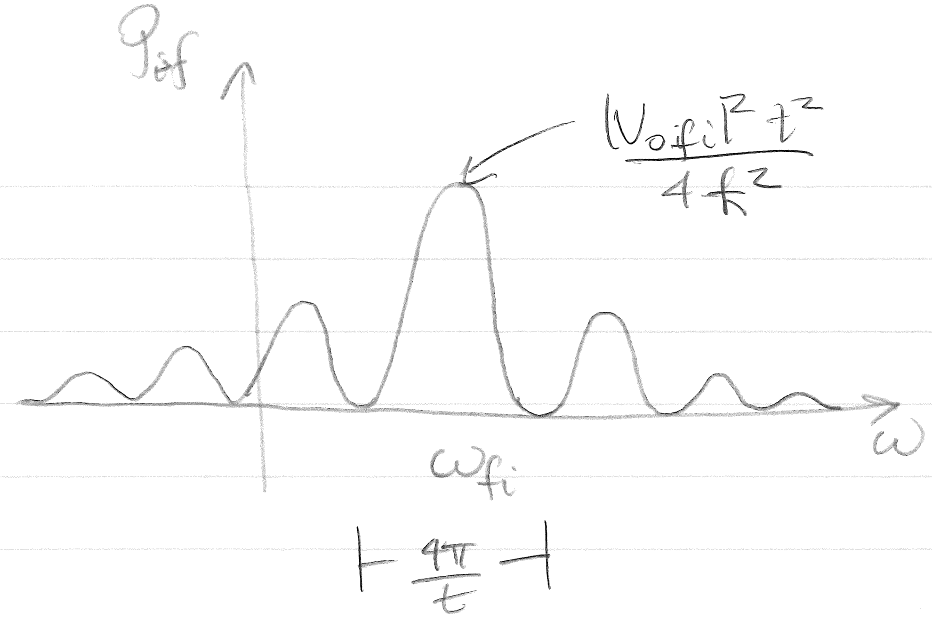
resonant emmision

Let's focus on resonant absorption

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

$$= \frac{|V_{0fi}|^2}{4\hbar^2} t^2 \,\mathrm{sinc}^2\left(\frac{\omega_{fi}-\omega}{2} t\right)$$

this is really close to the constant case.



so we have a band around E_f where the absorption ends.

Is this physical? We need to bound the amplitude so that it does not blow up, i.e. $t \ll \frac{\hbar}{|V_{0fi}|}$

We also must have a minimum bound to ensure we are dealing with a full sine wave, i.e.

$$t \gg \frac{2\pi}{\omega_{fi}}$$

$$\Longrightarrow \quad \frac{2\pi}{\omega_{fi}} \ll \frac{\hbar}{|V_{0fi}|}$$

$$\longrightarrow \quad \hbar\omega_{fi} \gg |V_{0fi}|$$

Continuum states
ex: ionization! discrete until
you free the electron.

$$H_0 \psi_n(\vec{r}) = E_n \psi_n(\vec{r}) \qquad H_0 \psi_\alpha(\vec{r}) = E_\alpha \psi_\alpha(\vec{r})$$

$n \rightarrow$ discrete $\qquad$ α - continuous

$$\psi_{\substack{n \\ \alpha}}(\vec{r},t) = \psi_{\substack{n \\ \alpha}}(\vec{r})\, \underbrace{e^{-\frac{i}{\hbar} E_{\substack{n \\ \alpha}} t}}_{\text{time dep phase.}}$$

orthogonality

$$\int \psi^*_{\substack{n' \\ \alpha' \\ \alpha'}}(\vec{r},t)\, \psi_{\substack{n \\ \alpha \\ n}}(\vec{r},t)\, dV = \begin{matrix} \delta_{n'n} \\ \delta(\alpha-\alpha') \\ 0 \end{matrix}$$

closure

$$\sum_n |\psi_n\rangle\langle\psi_n| + \int d\alpha\, |\psi_\alpha\rangle\langle\psi_\alpha| = 1$$

at $t=0 \Longrightarrow V(t)$ turns on

$$i\hbar \frac{\partial}{\partial t}\psi = [H_0 + V(t)]\psi$$

<u>wavefunction expansion</u>

$$\psi(\vec{r},t) = \sum_n \underbrace{c_n(t)}_{V(t)} \underbrace{e^{-\frac{i}{\hbar}E_n t}}_{H_0} \psi_n(\vec{r}) + \int d\alpha\, c_\alpha(t) e^{-\frac{i}{\hbar}E_\alpha t}\psi_\alpha(\vec{r})$$

$$\boxed{\sum_n |c_n(t)|^2 + \int d\alpha\, |c_\alpha(t)|^2 = 1}$$

substitute back into Schrödinger's Equ

$$i\hbar \frac{\partial}{\partial t}\left(\sum_n c_n(t) e^{-\frac{i}{\hbar}E_n t}\psi_n(\vec{r}) + \int d\alpha\, c_\alpha(t) e^{-\frac{i}{\hbar}E_\alpha t}\psi_\alpha(\vec{r})\right)$$

$$= \sum_n c_n(t) e^{-\frac{i}{\hbar}E_n t}$$

$\vdots$

do some algebra / calculus

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

4 $$i\hbar \frac{dC_{n'}}{dt} = \sum_n C_n(t) e^{i\omega_{n'n}t} V_{n'n}(t) + \int d\alpha\, C_\alpha(t) e^{i\omega_{n'\alpha}t} V_{n'\alpha}(t)$$

Now integrate against $e^{\frac{i}{\hbar}E_{\alpha'}t}\psi_{\alpha'}$

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

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

$\lambda^{(0)}$: $$i\hbar \frac{dC_{n'}^{(0)}}{dt} = 0 \quad ; \quad i\hbar \frac{dC_{\alpha'}^{(0)}}{dt} = 0$$

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

~~AAA~~ yikes.....

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

$$t=0 \implies |k\rangle \quad \begin{cases} c_{n'}^{(0)} = \delta_{n'k} \\ c_{\alpha'}^{(0)} = 0 \end{cases}$$