

Time dependent perturbation theory  $H = H_0 + U$

$H \psi_i = E_i \psi_i$  ← complete;  $\omega_i \equiv E_i / \hbar$

Assume 2 levels: a & b  $\Psi = c_a \psi_a e^{-i\omega_a t} + c_b \psi_b e^{-i\omega_b t}$

↑ depends on t  
 "transitions"  
 Note: since  $\hbar \omega$  we've had similar expressions but then  $c$ s were constant now  $c$  depends on time → transitions

$H \Psi = c_a E_a \psi_a e^{-i\omega_a t} + c_a V \psi_a e^{-i\omega_a t} + c_b E_b \psi_b e^{-i\omega_b t} + c_b V \psi_b e^{-i\omega_b t}$

$i\hbar \dot{\Psi} = i\hbar \dot{c}_a \psi_a e^{-i\omega_a t} + c_a E_a \psi_a e^{-i\omega_a t} + i\hbar \dot{c}_b \psi_b e^{-i\omega_b t} + c_b E_b \psi_b e^{-i\omega_b t}$

$c_a V \psi_a e^{-i\omega_a t} + c_b V \psi_b e^{-i\omega_b t} = i\hbar \left\{ \dot{c}_a \psi_a e^{-i\omega_a t} + \dot{c}_b \psi_b e^{-i\omega_b t} \right\}$

$\langle \psi_a | \Rightarrow c_a V_{aa} e^{-i\omega_a t} + c_b V_{ab} e^{-i\omega_b t} = i\hbar \dot{c}_a e^{-i\omega_a t}$

$\omega_0 \equiv \omega_b - \omega_a$

$c_a V_{aa} + c_b V_{ab} e^{-i\omega_0 t} = i\hbar \dot{c}_a$

$\langle \psi_b | \Rightarrow c_a V_{ba} e^{-i\omega_a t} + c_b V_{bb} e^{-i\omega_b t} = i\hbar \dot{c}_b e^{-i\omega_b t}$

$c_a V_{ba} e^{i\omega_0 t} + c_b V_{bb} = i\hbar \dot{c}_b$

assume  $V_{aa} = V_{bb} = 0$

→ strong assumption is most often the actual case

$\dot{c}_a = \frac{1}{i\hbar} c_b V_{ab} e^{-i\omega_0 t}$

$\dot{c}_b = \frac{1}{i\hbar} c_a V_{ba} e^{i\omega_0 t}$

$c_b = \frac{1}{i\hbar} \int_0^t V_{ba} e^{i\omega_0 t'} dt'$

Assume  $c_a = 1$   $c_b = 0$

iterate.  $\dot{c}_a = \frac{-1}{\hbar^2} \int_0^t V_{ba} e^{i\omega_0 t'} dt' V_{ab} e^{-i\omega_0 t}$   
 $c_a = 1 - \frac{1}{\hbar^2} \int_0^t \int_0^{t'} V_{ba} e^{i\omega_0 t''} dt'' V_{ab} e^{-i\omega_0 t} dt'$

Note: if had multiple states result for "b" stands result for "a" would involve same.

Sinusoidal perturbation (eg Light)  $V_{ab} = \tilde{V}_{ab} \cos(\omega t)$   
 note:  $\omega \sim 10^{15} \text{ Hz}$   
 does not depend on time

$$C_b = \frac{1}{i\hbar} \int_0^t \tilde{V}_{ba} \left( \frac{e^{i\omega t} + e^{-i\omega t}}{2} \right) e^{+i\omega_0 t} dt$$

$$= \frac{\tilde{V}_{ba}}{2i\hbar} \left\{ \int_0^t e^{i(\omega + \omega_0)t} + e^{i(\omega_0 - \omega)t} \right\} dt$$

small neglect

$$\frac{e^{i(\omega + \omega_0)t} - 1}{i(\omega + \omega_0)}$$

$$\frac{e^{i(\omega_0 - \omega)t} - 1}{i(\omega_0 - \omega)}$$

perhaps big if  $\omega_0 \approx \omega$

$$= \frac{\tilde{V}_{ba}}{i\hbar} \left\{ \frac{e^{i(\omega_0 - \omega)t} - 1}{2i(\omega_0 - \omega)} \right\} \rightarrow \left[ \frac{e^{i(\frac{\omega_0 - \omega}{2})t} - e^{-i(\frac{\omega_0 - \omega}{2})t}}{2} \right] e^{i(\frac{\omega_0 - \omega}{2})t}$$

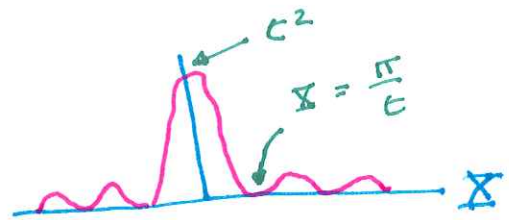
$$= \frac{\tilde{V}_{ba}}{2i\hbar} \frac{\sin\left[\frac{\omega_0 - \omega}{2}t\right]}{\frac{\omega_0 - \omega}{2}} e^{i\left(\frac{\omega_0 - \omega}{2}\right)t}$$

$$\bar{\Delta} = \frac{\omega_0 - \omega}{2}$$

$$|C_b|^2 = \frac{\tilde{V}_{ba}^2}{4\hbar^2} \frac{\sin^2[\bar{\Delta}t]}{\bar{\Delta}^2}$$

$$\frac{\sin^2[\bar{\Delta}t]}{\bar{\Delta}^2}$$

note  $\bar{\Delta} = 0 \leftrightarrow \omega_0 = \omega$



Note: for visible light & macroscopic times,  $\omega$  needs to be very close to  $\omega_0$  for  $|C_b|^2$  to be large re for transitions

Note: this result says  $|C_b|^2$  will oscillate but we've only done first order perturbation theory so we have not really shown that yet

The result  $|C_b|^2 \propto t^2$  for short times is unexpected  $\rightarrow$  transition rates where  $|C_b|^2 \propto t$  seem more normal. You'll see that under many circumstances  $|C_b|^2 \propto t$  (essentially) does happen