$H_0 \psi_a = E_a \psi_a \qquad H_0 \psi_b = E_b \psi_b$

$\langle \psi_a | \psi_b \rangle = 0$ complete set

Suppose $H = H_0 + H'(t)$

$$\Psi(t) = c_a(t)\psi_a e^{-iE_a t/\hbar} + c_b(t)\psi_b e^{-iE_b t/\hbar}$$

$$H\Psi = i\hbar \frac{d\Psi}{dt}$$

$$H\Psi = c_a(t)\cancel{\overbrace{H_0\psi_a}^{E_a\psi_a}} e^{-iE_a t/\hbar} + c_a(t) H'\psi_a e^{-iE_a t/\hbar} + \cancel{c_b(t) H_0 \psi_b e^{-iE_b t/\hbar}} + c_b H'\psi_b e^{-iE_b t/\hbar}$$

$$i\hbar \frac{d\Psi}{dt} = i\hbar\left[\dot{c}_a \psi_a e^{-iE_a t/\hbar} - \cancel{\frac{iE_a}{\hbar} c_a \psi_a e^{-iE_a t/\hbar}} + \dot{c}_b \psi_b e^{-iE_b t/\hbar} - \cancel{\frac{iE_b}{\hbar} c_b \psi_b e^{-iE_b t/\hbar}}\right]$$

$$\langle\psi_a| \quad c_a H'|\psi_a\rangle e^{-iE_a t/\hbar} + c_b H'\psi_b e^{-iE_b t/\hbar} = i\hbar \dot{c}_a \psi_a e^{-iE_a t/\hbar} + i\hbar \dot{c}_b \psi_b e^{-iE_b t/\hbar}$$

$$c_a \langle\psi_a|H'|\psi_a\rangle e^{-iE_a t/\hbar} + c_b \langle\psi_a|H'|\psi_b\rangle e^{-iE_b t/\hbar} = i\hbar \dot{c}_a e^{-iE_a t/\hbar}$$

$$H'_{ij} \equiv \langle \psi_i | H' | \psi_j \rangle \qquad i,j \in \{a,b\}$$

$$\dot{c}_a(t) = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab} e^{i(E_a - E_b)t/\hbar}\right]$$

$$\dot{c}_b(t) = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba} e^{i(E_b - E_a)t/\hbar}\right]$$

Often $H'_{aa} = H'_{bb} = 0$. $\qquad \omega_0 = \frac{E_b - E_a}{\hbar}$

$$\dot{c}_a(t) = -\frac{i}{\hbar} c_b H'_{ab} e^{-i\omega_0 t}$$

$$\dot{c}_b = -\frac{i}{\hbar} c_a H'_{ba} e^{+i\omega_0 t}$$

Suppose
Initial condition $c_a(t=0) = 1 \qquad c_b(t=0) = 0.$

To zeroth order $\quad c_{a0} = 1 \qquad c_{b0} = 0$

To first order,

$$\dot{c}_{a1} = -\frac{i}{\hbar} c_{b0} H'_{ab} e^{-i\omega_0 t}$$

$$\dot{c}_{b1} = -\frac{i}{\hbar} c_{a0} H'_{ba} e^{+i\omega_0 t}$$

$$\dot{c}_{a1} = 0 \rightarrow c_{a1} = 1$$

$$\dot{c}_{b1} = -\frac{i}{\hbar} H'_{ba} e^{+i\omega_0 t}$$

$$c_{b1} = -\frac{i}{\hbar}\int_0^t H'_{ba} e^{+i\omega_0 t'} dt'$$

2nd order

$$\dot{c}_{a2} = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t}\left(-\frac{i}{\hbar}\int_0^t H'_{ba} e^{+i\omega_0 t'} dt'\right)$$

$$c_{a2} = 1 - \frac{1}{\hbar^2}\int_0^t H'_{ab}(t') e^{-i\omega_0 t'}\left[\int_0^{t'} H'_{ba}(t'') e^{i\omega_0 t''} dt''\right] dt'$$

$$\dot{c}_{b2} = -\frac{i}{\hbar} H'_{ab} e^{+i\omega_0 t} c_{a1} \quad (c_{a1} = 1)$$

$\rightarrow c_{b2} = c_{b1}$

e.g. $\quad H' = V(\vec{r}) \cos \omega t$

$$H'_{ab} = V_{ab} \cos \omega t \qquad V_{ab} = \langle \psi_a | V | \psi_b \rangle$$

$$c_{b1}(t) = -\frac{i}{\hbar}\int_0^t V_{ba} \cos \omega t' e^{i\omega_0 t'} dt'$$

$$= -\frac{i}{\hbar} V_{ba}\left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega}\right]$$

if $\quad \omega$: frequency of perturbation

$\omega_0 = \frac{E_b - E_a}{\hbar}$

if ω : frequency of perturbation

$\omega_0 : \dfrac{E_b - E_a}{\hbar}$

if $\omega \approx \omega_0$

$$c_{b1} \approx -\frac{V_{ba}}{2\hbar}\frac{e^{i(\omega_0-\omega)t/2}}{\omega_0-\omega}\left[e^{i(\omega_0-\omega)t/2} - e^{-i(\omega_0-\omega)t/2}\right]$$

$$= -i\frac{V_{ba}}{\hbar}\frac{\sin[(\omega_0-\omega)t/2]}{\omega_0-\omega}e^{i(\omega_0-\omega)t/2}$$

$$\Psi(t) \approx 1\,\psi_a e^{-iE_at/\hbar} + \quad \psi_b e^{-iE_bt/\hbar}$$

$$P_{ba} = |\langle\psi_b|\Psi(t)\rangle|^2 = |c_{b1}|^2$$

$$P_{a\to b} = \frac{V_{ba}^2}{\hbar^2(\omega_0-\omega)^2}\sin^2\left[\frac{(\omega_0-\omega)t}{2}\right]$$