

Time dependent Perturbation Theory

Till now $\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$

but $V = V(r)$ only

So $\hat{H}\psi = E\psi$ and $\psi(r,t) = \psi(r)e^{-iEt/\hbar}$

Now let $\hat{H} = \hat{H}_0 + \hat{H}'(t)$ $\hat{H}' \ll \hat{H}_0$
 \downarrow
 $E' \ll E^0$

Start with just 2 states of \hat{H}_0

$\hat{H}_0 \psi_a = E_a \psi_a$ and $\hat{H}_0 \psi_b = E_b \psi_b$

$\langle \psi_i | \psi_j \rangle = \delta_{ij}$

$\psi(t=0) = c_a \psi_a + c_b \psi_b$

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

$|c_a|^2 + |c_b|^2 = 1$

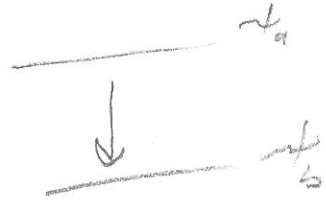
Now add $\hat{H}'(t)$

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

Want $c_a(t)$ and $c_b(t)$

Suppose $c_a(0) = 1$ and $c_b(0) = 0$ and later $c_a(t_1) = 0$ and $c_b(t_1) = 1$

State went from $\psi_a \rightarrow \psi_b$ Transition



Require $\hat{H}\psi = i\hbar \frac{\partial \psi}{\partial t}$ where $\hat{H} = H^0 + H'(t)$

$$\begin{aligned}
 \text{Now } & c_a [H^0 \psi_a] e^{-iE_a t/\hbar} + c_b [H^0 \psi_b] e^{-iE_b t/\hbar} \\
 & + c_a [H' \psi_a] e^{-iE_b t/\hbar} + c_b [H' \psi_b] e^{-iE_a t/\hbar} \\
 = & i\hbar \left[c_a \psi_a e^{-iE_a t/\hbar} + c_b \psi_b e^{-iE_b t/\hbar} \right. \\
 & \left. + i\hbar \left[c_a \psi_a \left(-\frac{E_a}{\hbar}\right) e^{-iE_a t/\hbar} + c_b \psi_b \left(-\frac{E_b}{\hbar}\right) e^{-iE_b t/\hbar} \right] \right]
 \end{aligned}$$

$$1 + 2 = 7 + 8$$

So

$$c_a [H' \psi_a] e^{-iE_a t/\hbar} + c_b [H' \psi_b] e^{-iE_b t/\hbar} = i\hbar \left[c_a \psi_a e^{-iE_a t/\hbar} + c_b \psi_b e^{-iE_b t/\hbar} \right]$$

Take IP with ψ_a

$$c_a \langle \psi_a | H | \psi_a \rangle e^{-iE_a t/\hbar} + c_b \langle \psi_a | H | \psi_b \rangle e^{-iE_b t/\hbar} = i\hbar \dot{c}_a e^{-iE_a t/\hbar}$$

Call $H'_{ij} = \langle \psi_i | H | \psi_j \rangle$ and multiply by $\frac{1}{i\hbar} e^{iE_a t/\hbar}$

Note $H'_{ij} = (H'_{ji})^*$

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

Similarly

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

Typically $H'_{aa} = H'_{bb} = 0$

NOT ALWAYS !!!

If so

$$c_a = -\frac{i}{\hbar} H'_{ab} e^{-i\omega_0 t}$$

$$c_b = -\frac{i}{\hbar} H'_{ba} e^{i\omega_0 t}$$

$$\omega_0 = \frac{E_b - E_a}{\hbar} \text{ where } E_b \geq E_a \text{ so } \omega_0 \geq 0$$

How to solve?

Successive Approximations

Suppose $c_a(0)=1$ and $c_b(0)=0$ No \hat{H}' No change

1: 0th order $\rightarrow c_a^{(0)}(T) = 1$ $c_b^{(0)}(T) = 0$ Starts in one state

2: 1st order \rightarrow use 0th order

$$\dot{c}_a^{(1)}(T) = -\frac{i}{\hbar} \hat{H}'_{ab} e^{-i\omega_0 T} c_b^{(0)} \quad \text{and} \quad \dot{c}_b^{(1)}(T) = -\frac{i}{\hbar} \hat{H}'_{ba} e^{i\omega_0 T} c_a^{(0)}$$

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

Now $\frac{d c_a^{(1)}}{dT} = 0$ or $c_a^{(1)}(T) = 1$

and $\frac{d c_b^{(1)}}{dT} = -\frac{i}{\hbar} \hat{H}'_{ba} e^{i\omega_0 T} \rightarrow c_b^{(1)}(T) = -\frac{i}{\hbar} \int_0^T \hat{H}'_{ba}(T') e^{i\omega_0 T'} dT'$

3: 2nd Order

$$c_a^{(2)}(T) = -\frac{i}{\hbar} \hat{H}'_{ab} e^{-i\omega_0 T} c_b^{(1)} \rightarrow \frac{d c_a^{(2)}}{dT} = -\frac{i}{\hbar} \hat{H}'_{ab}(T) e^{-i\omega_0 T} \left(-\frac{i}{\hbar} \int_0^T \hat{H}'_{ba}(T') e^{i\omega_0 T'} dT' \right)$$

$$c_a^{(2)}(T) = 1 - \frac{1}{\hbar^2} \int_0^T \hat{H}'_{ab}(T') e^{-i\omega_0 T'} \left[\int_0^{T'} \hat{H}'_{ba}(T'') e^{i\omega_0 T''} dT'' \right] dT'$$

and $c_b^{(2)}(T) = c_b^{(1)}(T)$ since $c_a^{(1)}(T) = 1$

$$\text{Ex.) } H'_{aa} \neq 0 \quad H'_{bb} \neq 0$$

use $\sigma \rightarrow 1$
 $1 \rightarrow 2$
 etc,

$$\Rightarrow \text{Otn } C_a^0(0) = 1 \quad C_b^0(0) = 0$$

$$\dot{C}_a = -\frac{i}{\hbar} [C_a H'_{aa} + C_b H'_{ab} e^{-i\omega_0 T}]$$

$$\dot{C}_b = \frac{-i}{\hbar} [C_b H'_{bb} + C_a H'_{ba} e^{i\omega_0 T}]$$

$$\dot{C}_a^{(1)} = -\frac{i}{\hbar} [H'_{aa}] \rightarrow C_a^{(1)}(T) = 1 - \frac{i}{\hbar} \int_0^T H'_{aa}(T') dT'$$

$$\dot{C}_b^{(1)} = \frac{-i}{\hbar} [H'_{ba}(T) e^{i\omega_0 T}] \rightarrow C_b^{(1)}(T) = -\frac{i}{\hbar} \int_0^T H'_{ba}(T') e^{i\omega_0 T'} dT'$$

$$|C_a^{(1)}(T)|^2 = \left| 1 - \frac{i}{\hbar} \int_0^T H'_{aa}(T') dT' \right|^2 \rightarrow 1 \text{ to 1st order}$$

$$|C_b^{(1)}(T)|^2 = \left[-\frac{i}{\hbar} \int_0^T H'_{ba}(T') e^{i\omega_0 T'} dT' \right] \left[\frac{i}{\hbar} \int_0^T H'_{ba}(T') e^{-i\omega_0 T'} dT' \right] = 0 \text{ to 1st order}$$