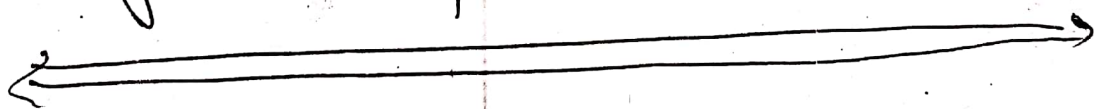


In principle one can obtain energy correction and wavefn correction to any order. However, the above the 2nd order calculation are not significantly effective, since the first and two orders are generally sufficiently accurate.

If the unperturbed energy levels are  $E_n^{(0)}$  and  $E_m^{(0)}$  are eq. (i.e. degenerate) the finite conditions of  $E_n$  and  $\psi_n$  will break down. So the degenerate energy levels require an approach that is different from the non-degenerate treatment.

### Degenerate Perturbation Theory:



Now we apply perturbation theory to determine the energy spectrum and the state of a system whose unperturbed Hamiltonian  $H_0$  is degenerate.

Let  $\psi_1^{(0)}$  and  $\psi_2^{(0)}$  be degenerate (9).

$$H_0 \psi_1^{(0)} = E^{(0)} \psi_1^{(0)}$$

$$H_0 \psi_2^{(0)} = E^{(0)} \psi_2^{(0)} \quad \text{with } \langle \psi_1 | \psi_2 \rangle = 0$$

Any linear combination of these states

$$\psi^{(0)} = a \psi_1^{(0)} + b \psi_2^{(0)}$$

is also an eigenstate of  $H_0$  with the same eigenvalue.

$$H_0 \psi^{(0)} = E^{(0)} \psi^{(0)}$$

when the system is perturbed, the Hamiltonian is expressed as

$$H = H_0 + \lambda H_1$$

obeying the Schrödinger equation.

$$H\psi = E\psi$$

with

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

$$\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots$$

With this expansion the Schrödinger equation above is written as.

$$H_0 \psi^{(0)} + \lambda (H_1 \psi^{(0)} + H_0 \psi^{(1)}) + \dots$$

$$= E^{(0)} \psi^{(0)} + \lambda (E^{(1)} \psi^{(0)} + E^{(0)} \psi^{(1)}) + \dots$$

Now take the first order perturbation:

$O(\lambda)$

$$H_0 \psi^{(1)} + H_1 \psi^{(0)} = E^{(0)} \psi^{(1)} + E^{(1)} \psi^{(0)}$$

Taking inner product with  $\psi_i^{(0)}$

$$\langle \psi_i^{(0)} | H_0 \psi^{(1)} \rangle = \langle \psi_i^{(0)} | H_1 \psi^{(0)} \rangle$$

$$= E^{(0)} \langle \psi_i^{(0)} | \psi^{(1)} \rangle + E^{(1)} \langle \psi_i^{(0)} | \psi^{(0)} \rangle$$

Since  $H_0$  is Hermitian, then

$$\langle H_0 \psi_i^{(0)} | \psi^{(1)} \rangle + \langle \psi_i^{(0)} | H_1 \psi^{(0)} \rangle$$

$$= 0 + E^{(1)} \langle \psi_i^{(0)} | \psi^{(0)} \rangle$$

$$0 + \langle \psi_i^{(0)} | H_1 \psi^{(0)} \rangle = E^{(1)} \langle \psi_i^{(0)} | \psi^{(0)} \rangle$$

or

$$\langle \psi_i^{(0)} | H_1 (a \psi_1^{(0)} + b \psi_2^{(0)}) \rangle$$

$$= E^{(1)} \langle \psi_i^{(0)} | (a \psi_1^{(0)} + b \psi_2^{(0)}) \rangle$$

$$a \langle \psi_1^{(0)} | H_1 | \psi_1^{(0)} \rangle + b \langle \psi_1^{(0)} | H_1 | \psi_2^{(0)} \rangle = a E^{(1)}$$

Can be written as

$$a (H_1)_{11} + b (H_1)_{12} = a E^{(1)} \quad (*)$$

Similarly,

$$a (H_1)_{21} + b (H_1)_{22} = b E^{(1)} \quad (**)$$

From equ. (\*)

$$a = \frac{-(H_1)_{12}}{(H_1)_{11} - E^{(1)}} b$$

$$a = \frac{(H_1)_{12}}{E^{(1)} - (H_1)_{11}} b$$

Put this value of "a" in (\*\*), we get

$$(H_1)_{12} (H_1)_{21} + [(H_1)_{22} - E^{(1)}] [E^{(1)} - (H_1)_{11}] = 0 \quad \text{--- (A)}$$

or, for  $E^{(1)}$ , we have

$$\begin{aligned} & (E^{(1)})^2 - E^{(1)} [(H_1)_{11} + (H_1)_{22}] \\ & + [(H_1)_{11} (H_1)_{22} - (H_1)_{12} (H_1)_{21}] = 0 \end{aligned}$$

By solving this quadratic eqn, we get two roots.

$$E_{\pm}^{(1)} = \frac{1}{2} \left[ (H_{11})_{11} + (H_{11})_{22} \pm \sqrt{((H_{11})_{11} - (H_{11})_{22})^2 + 4 |(H_{11})_{12}|^2} \right]$$

Since  $(H_{11})_{12}^* = (H_{11})_{21}$

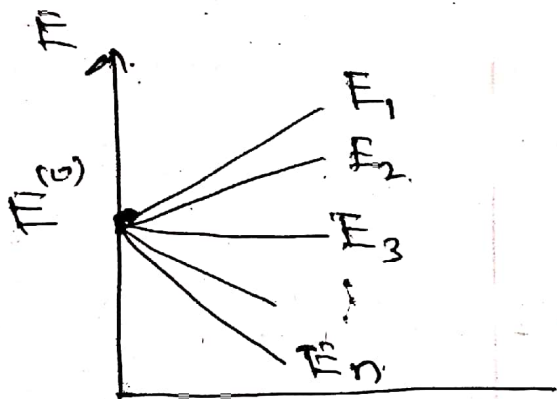
The two roots correspond to two energies. The states are no longer degenerate for two-fold degeneracy, eqn (A) can be expressed as

$$\begin{vmatrix} (H_{11})_{11} - E^{(1)} & (H_{11})_{12} \\ (H_{11})_{21} & (H_{11})_{22} - E^{(1)} \end{vmatrix} = 0$$

For n-fold degeneracy, one can have

$$\begin{vmatrix} (H_{11})_{11} - E^{(1)} & (H_{11})_{12} & \dots & (H_{11})_{1n} \\ (H_{11})_{21} & (H_{11})_{22} - E^{(1)} & \dots & (H_{11})_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ (H_{11})_{n1} & \dots & \dots & (H_{11})_{nn} - E^{(1)} \end{vmatrix} = 0$$

The  $n$ -fold degeneracy in  $H_0$  has been <sup>(11)</sup> removed, the  $n$ -fold degenerate level is separated into  $n$ -distinct levels. The separation of these distinct levels is proportional to the strength of the perturbation.



## Time Dependent Perturbation Theory: ①

So far we have discussed the time-independent Hamiltonian, Now we would like to discuss problems for which the Hamiltonian contains a part which has a time-dependence. This will lead to a kind of quantum dynamics which deals with the probability that a system undergoes a transition from one state to another.

Let us start with a free particle Schrodinger wave equation

$$i\hbar \frac{\partial}{\partial t} |\psi_0\rangle = H_0 |\psi_0\rangle$$

where  $|\psi_0\rangle$  is the state of the free particle and  $H_0$  is the free particle Hamiltonian.

In the presence of an interacting potential  $V(x,t)$ , the Hamiltonian is

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

where all time-dependence enters through the potential  $V(t)$ .  $V(t)$  characterizes the interaction of the system with external source.

of Perturbation.

Now the Schrodinger equation is

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = (H_0 + V(x,t)) |\psi(t)\rangle$$

The main task of time-dependent perturbation theory is that how does  $V(t)$  affect the system.

→ May be the system is initially in an unperturbed eigenstate  $|\psi_i\rangle$  of  $H_0$  what is the probability that the system will be found at a later time in an other unperturbed eigenstate  $|\psi_f\rangle$ .

The state  $|\psi(t)\rangle$  can be expanded as

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

called interaction representation.

with.

$$H_0 |\phi_n\rangle = E_n |\phi_n\rangle$$

where

$$\langle \phi_m | \phi_n \rangle = \delta_{mn}$$

$$\sum_n |\phi_n\rangle \langle \phi_n| = 1$$



The time-dependence of the coefficients  $a_n$  is a consequence of interaction  $V(x,t)$ . Now the Schrodinger equation is expressed as. (2)

$$i\hbar \frac{\partial}{\partial t} \left( \sum_n a_n(t) |\phi_n\rangle e^{-iE_n t/\hbar} \right) = (H_0 + V(t)) \sum_n a_n(t) |\phi_n\rangle e^{-iE_n t/\hbar}$$

$$i\hbar \sum_n \frac{\partial}{\partial t} a_n(t) |\phi_n\rangle e^{-iE_n t/\hbar} + i\hbar \sum_n a_n(t) |\phi_n\rangle \left( -\frac{E_n}{\hbar} \right) e^{-iE_n t/\hbar} + i\hbar \sum_n a_n(t) |\phi_n\rangle E_n e^{-iE_n t/\hbar}$$

$$= \sum_n a_n(t) \langle \phi_n | H_0 | \phi_n \rangle e^{-iE_n t/\hbar} + \sum_n V(t) a_n(t) |\phi_n\rangle e^{-iE_n t/\hbar}$$

$$i\hbar \sum_n \dot{a}_n(t) |\phi_n\rangle e^{-iE_n t/\hbar} + \sum_n a_n(t) E_n |\phi_n\rangle e^{-iE_n t/\hbar} - \sum_n a_n(t) E_n |\phi_n\rangle e^{-iE_n t/\hbar} + \sum_n V(t) a_n(t) |\phi_n\rangle e^{-iE_n t/\hbar}$$

$$= \sum_n \dot{a}_n(t) |\phi_n\rangle e^{-iE_n t/\hbar} + \sum_n V(t) a_n(t) |\phi_n\rangle e^{-iE_n t/\hbar}$$

or

$$i\hbar \sum_n \dot{a}_n(t) |\phi_n\rangle e^{-iE_n t/\hbar} = \sum_n V(t) a_n(t) |\phi_n\rangle e^{-iE_n t/\hbar}$$

Taking an inner Product with  $|\Phi_f\rangle$   
on both sides

$$i\hbar \sum_n \dot{a}_n(t) \langle \Phi_f | \Phi_n \rangle e^{-i E_n t / \hbar}$$

$$= \sum_n a_n(t) \langle \Phi_f | V(t) | \Phi_n \rangle e^{-i E_n t / \hbar}$$

$$\Rightarrow i\hbar \sum_n \dot{a}_n(t) \delta_{fn} e^{-i E_n t / \hbar}$$

$$= \sum_n a_n(t) V_{fn}(t) e^{-i E_n t / \hbar}$$

where

$$V_{fn}(t) = \langle \Phi_f | V(t) | \Phi_n \rangle \text{ is the}$$

matrix element of  $V(t)$

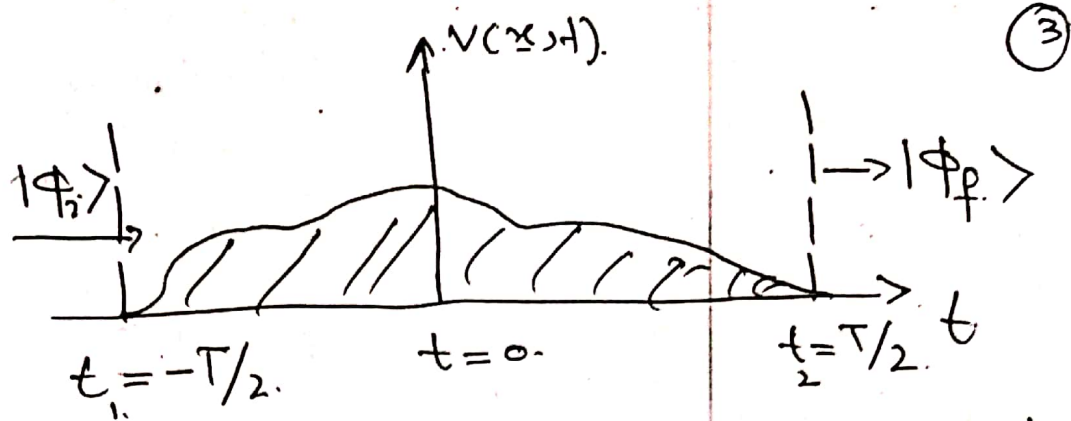
$\Rightarrow$  for  $f = n$ , above eqn will become

$$i\hbar \sum_n \dot{a}_n(t) e^{-i E_f t / \hbar} = \sum_n a_n(t) V_{fn}(t) e^{-i E_n t / \hbar}$$

Hence

$$\dot{a}_f = -\frac{i}{\hbar} \sum_n a_n(t) V_{fn}(t) e^{i(E_f - E_n)t / \hbar}$$

↳ ①



Before the action of  $V$ , the particle is in an eigenstate  $\phi_i$  of  $H_0$  i.e. at  $t_1 = -T/2$  we take

$$a_n(-T/2) = \delta_{ni}$$

i.e. for  $n = i$

$$a_i(-T/2) = 1$$

Hence Equ. 1 can be expressed as

$$a_f' = \frac{-i}{\hbar} V_{fi}(t) e^{i(E_f - E_i)t/\hbar} \quad \rightarrow \textcircled{2}$$

### Transition Probability

The transition probability corresponding to a transition from an initial unperturbed state  $|\phi_i\rangle$  to another unperturbed final state  $|\phi_f\rangle$  is obtained by integrating

of equ. (2)

$$\Rightarrow a_f(t) = \frac{-i}{\hbar} \int_{t_1}^{t_2} V_{fi}(t) e^{i(E_f - E_i)t/\hbar} dt$$

$$t_1 = -T/2, \quad t_2 = T/2$$

or

$$T_{fi} = a_f = \frac{-i}{\hbar} \int_{-T/2}^{T/2} V_{fi}(t) e^{i(E_f - E_i)t/\hbar} dt$$

$$T_{fi} = \frac{-i}{\hbar} \int_{-T/2}^{T/2} dt \langle \Phi_f | V(t) | \Phi_i \rangle e^{i(E_f - E_i)t/\hbar} \quad \rightarrow (3)$$

The quantity  $|T_{fi}|^2$  is the transition probability of a particle from an initial state  $|\Phi_i\rangle$  to a final state  $|\Phi_f\rangle$ .