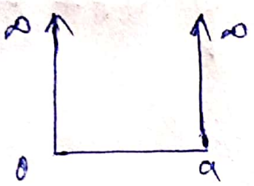
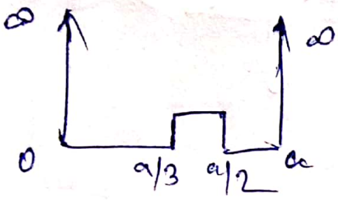
Perturbation theory

- **Perturbation** →

It is a small change or very small disturbance in Hamiltonian of the system.



→ assymetric unperturbed Potential well

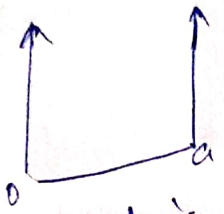


→ assymetric perturbed Potential well

In case of symmetric potential well we can find the solution of schrodinger equation & get the value of ψ_n & E_n. But in case of assymetric Potential well, we are not able to find the value of ψ_n & E_n by schrodinger equation. It can be obtained through approximation method or perturbation theory.

- **Perturbation theory** →

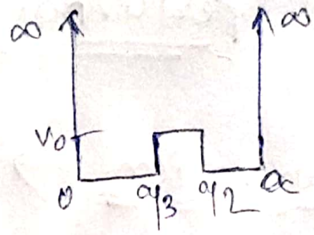
It is a tool or a systematic procedure for obtaining approximate solution to perturbed problems by using solution of unperturbed case.



assymetric unperturbed case

$$\psi_n = \sqrt{2/a}\,\sin\frac{n\pi x}{a}$$

$$\& \; E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$



assymetric ~~case~~ perturbed case

• here we get the value of ψ_{n_p} & E_{n_p} using value of ψ_n & E_n.

* Types of Perturbation theory →

$$H = H_0 + H'$$

H ↓ Perturbed Hamiltonian

H_0 ↓ unperturbed Hamiltonian

H' ↳ perturbed term

(1) Time Independent Perturbation theory

(2) Time Dependent Perturbation theory

→ (1) Time Independent PT

$$H' \neq H'(t)$$

exp (1) $H' = V_0$

$a/3 < x < a/2$

(2) $H' = g\cos kx$

(3) $H' = \delta(x-a)$

(2) Time Dependent Perturbation theory →

$$H' = H(t)$$

exp $H' = V_0 \cos\omega t$

$H' = V_0 \sin\omega t$

* Time Independent P.T are of 2 types →

(1) Non degenerate case

(2) Degenrate case

(1) Non degenerate time Independent Perturbation theor

→ If H_0 or unperturbed Hamiltonian have non degenrate energy eigenvalue, then it will be the case of Non deg time Independent P.T.

$H_0\psi_1 = E_1\psi_1$

$H_0\psi_2 = E_2\psi_2$

For diff eigenfunction, ψ, they have diff diff energy eigenvalue.

like, for ψ_1, E_1 be the energy eigenvalue, E_2 be the energy eigenvalue for ψ_2,

(2) Degenrate time Independent P.T →

If H_0 have degenrate energy eigenvalue

$H_0\psi_1 = E_1\psi_1$

$H_0\psi_2 = E_1\psi_2$

Notes →

(1) Perturbation term H' should be very small.

(2) By Perturbation theory we find approximate solution not exact solution.
Exact solution is obtained by solving schrodinger equation for perturbed Hamiltonian.

$$H = H_0 + H'$$

* Schematic of Perturbation theory
(Non deg. time Independent)

Hamiltonian of the system,

$$H = H_0 + H'$$

By P.T we get energy eigenvalue E_n for perturbed system.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \text{———} \quad (1)$$

$$|\psi_n\rangle = |\psi_n\rangle^{(0)} + |\psi_n\rangle^{(1)} + |\psi_n\rangle^{(2)} + \text{———} \quad (2)$$

where
E_n = corrected energy eigenvalue or energy eigenvalue for perturbed Hamiltonian for n^{th} state

$E_n^{(0)}$ = energy eigenvalue for unperturbed Hamiltonian for n^{th} state.

$E_n^{(1)} \rightarrow$ 1st order energy correction to energy eigenvalue for nth state

$E_n^{(2)} \rightarrow$ 2nd order energy correction to energy eigenvalue for nth state.

$|\psi_n\rangle$ = energy eigenfunction for perturbed Hamiltonian for nth state

$|\psi_n\rangle^{(0)}$ = energy eigenfunction for unperturbed Hamiltonian for nth state

$|\psi_n\rangle^{(1)}$ = 1st order correction to energy eigen-function for nth state

If we know the value of all correction term i.e. $E_n^{(1)}$, $E_n^{(2)}$ & $|\psi_n\rangle^{(1)}$ with the help of unperturbed term $E_n^{(0)}$ & $|\psi_n^{(0)}\rangle$ we can easily get the value of E_n & ψ_n using eq^n 1 & 2.

As, $E_n^{(0)} = \dfrac{n^2\pi^2\hbar^2}{2ma^2}$

& $|\psi_n\rangle^{(0)} = \sqrt{2/a}\,\sin\dfrac{n\pi x}{a}$

$\therefore\ E_n^{(1)} = \langle\psi_n^0|H'|\psi_n^0\rangle = \langle H'\rangle$

where $|\psi_n^0\rangle$ – Normalised energy function for nth state in unperturbed system.

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$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m | H' | \psi_n \rangle|^2}{E_n - E_m}$$

$$\& \quad |\psi_n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle \psi_m | H' | \psi_n \rangle}{E_n - E_m} |\psi_m\rangle$$

8.2. STATIONARY PERTURBATION THEORY (NON-DEGENERATE CASE) :

The stationary perturbation theory is concerned with finding the changes in the energy levels and eigen functions of a system when a small disturbance is applied. In such cases, the Hamiltonian can be broken up into two parts, one of which is large and represents a system for which the Schroedinger equation can be solved exactly, while other part is small and can be treated as perturbation term. If the potential energy is disturbed by the influence of additional forces, the energy levels are shifted and for a weak perturbation, the amount of shift can be estimated if the original unperturbed states are known.

Consider a physical system subjected to a perturbation which shifts the energy levels slightly : of course the arrangement remains ths same : Mathematically the effect of perturbation is to introduce additional terms in the Hamiltonian of the unperturbed system (or unchanged system). This additional term may by constant or it may be a function of both the space and momentum co-ordinates.

In other words, the Hamiltonian H in the Schroedinger equation can be written as the sum of two parts ; one of these parts H^0 corresponds to unperturbed system and other part H' corresponds to perturbation effect. Let us write Schroedinger wave equation

$$\hat{H}\,\psi = E\,\psi, \qquad \text{...(1)}$$

in which Hamiltonian $\hat{H}$ represents the operator

$$\hat{H} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla_i^2 + V. \qquad \text{...(2)}$$

Let E be the eigen value and ψ is eigen function of operator $\hat{H}$. $\hat{H}$ is the sum of two terms H^0 and H' already defined

$$H = H^0 + H' \quad ...(3)$$

where H' is small perturbation term.

Let ψ_k^0 and E_k^0 be a particular orthonormal eigen function and eigen value of unperturbed Hamiltonian H^0, *i.e.*,

$$H^0 \psi_k^0 = E_k^0 \psi_k^0$$

If we consider *non-degenerate system* that is the system for which there is one eigen function corresponding to each eigen value. In the stationary system, the Hamiltonian H does not depend upon time and it is possible to expand H in terms of some parameter λ yielding the expression

$$H = H^0 + \lambda H' + \lambda^2 H'' + \ldots \quad ...(4)$$

in which λ has been chosen in such a way that equation (1) for $\lambda = 0$ reduces to the form

$$H^0 \psi^0 - E^0 \psi^0 = 0 \quad ...(5)$$

It is to be remembered that there is one eigen function ψ and energy level E^0 corresponding to operator H^0. Equation (5) can be directly solved. This equation is said to be the *"wave equation of unperturbed system"* while the terms $\lambda H' + \lambda^2 H'' + \ldots$ are called the *perturbation terms.*

The unperturbed equation (5) has solutions

$$\psi_0^0, \psi_1^0, \psi_2^0, \ldots, \psi_k^0, \ldots$$

called the unperturbed eigen functions and corresponding eigen values are

$$E_0^0, E_1^0, E_2^0, \ldots, E_k^0, \ldots$$

The functions ψ_k^0 form a complete orthonormal set, *i.e.* they satisfy the condition

$$\int \psi_i^{0*} \psi_j^0 \, d\tau = \delta_{ij} \quad ...(6)$$

where δ_{ij} is Kronecker delta symbol defined as

$$\delta_{ij} = 0 \text{ for } i \neq j$$
$$= 1 \text{ for } i = j$$

Now let us consider the effect of perturbation. The application of perturbation does not cause large changes : hence the energy values and wave-functions for the perturbed system will be near to those for the unperturbed system. We can expand the energy E and the wave-function ψ for the perturbed system in terms of λ, so

$$\psi_k = \psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + , \quad ...(7)$$

$$E_k = E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots \quad ...(8)$$

If the perturbation is small, then terms of the series (7) and (8) will become repidly smaller *i.e.*, the series will be convergent.

Now substituting (6), (7) and (8) in equation (1), we get

$$= (H^0 + \lambda H' + \lambda^2 H'' + \ldots)(\psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots) = (E_k^0 + \lambda E_k' + \lambda^2 E_k'' + \ldots)(\psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k'' + \ldots)$$

On collecting the coefficients of like powers of λ.

$$(H_0\,\psi_k^0 - E_k^0\,\psi_k^0) + (H^0\,\psi_k' + H'\,\psi_k^0 - E_k^0\,\psi_k' - E_k'\,\psi_k^0)\,\lambda + (H^0\,\psi_k'' + H'\,\psi_k' + H''\,\psi_k^0 - E_k^0\,\psi_k'' - E_k'\,\psi_k' - E_k''\,\psi_k^0)\,\lambda^2 + \ldots = 0.$$

If this series is properly convergent *i.e.*, equal to zero for all possible values of λ, then coefficients of various powers of λ must vanish separately. These equations will have successively higher orders of the perturbation. The coeficient of λ^0 gives

$$(H^0 - E_k^0)\,\psi_k^0 = 0 \qquad \ldots(10a)$$

The coefficient of λ gives the equation.

$$(H^0\,\psi_k' + H'\,\psi_k^0 - E_k^0\,\psi_k' - E_k'\,\psi_k^0) = 0$$

or

$$(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0 \qquad \ldots(10b)$$

The coefficient of λ^2 gives the equation

$$(H^0\,\psi_k'' + H'\,\psi_k' + \psi_k' + H''\,\psi_k^0 - E_k^0\,\psi_k'' - E_k'\,\psi_k' - E_k''\,\psi_k^0) = 0$$

$$(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' + (H'' - E_k'')\,\psi_k^0 = 0 \qquad \ldots(10c)$$

Similarly, the coefficient of λ^3 yield

$$(H^0 - E_k^0)\,\psi_k''' + (H' - E_k')\,\psi_k'' + (H'' - E_k'')\,\psi_k' + (H''' - E_k''')\,\psi_k^0 = 0 \qquad \ldots(10d)$$

But if we limit the total Hamiltonian H upto $\lambda\,H'$, *i.e.*, if we put $H = H^0 + \lambda\,H'$, then equations (10) will be modified as

$$\left.\begin{aligned}
&(H^0 - E_k^0)\,\psi_k^0 = 0 && \ldots(a)\\
&(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0 && \ldots(b)\\
&(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k' - E_k''\,\psi_k^0 = 0 && \ldots(c)\\
&(H^0 - E_k^0)\,\psi_k'' + (H' - E_k')\,\psi_k'' - E_k''\,\psi_k' - E_k'''\,\psi_k^0 = 0 && \ldots(d)
\end{aligned}\right] \qquad \ldots(11)$$

First order perturbation : Equation (11 b) is

$$(H^0 - E_k^0)\,\psi_k' + (H' - E_k')\,\psi_k^0 = 0$$

To solve this equation we use *expansion theorem.* As perturbation is very small, the deviations form unperturbed state are small, therefore the first order perturbation correction function ψ_k' can be expanded in terms of unperturbed functions $\psi_1^0, \psi_2^0, \ldots, \psi_l^0, \ldots$, since ψ_l^0 form a normalized orthonormal set. Hence we write

$$\psi_k' = \sum_{l=0}^{\infty} a_l\,\psi_l^0. \qquad \ldots(12)$$

Substituting ψ_k' from (12) in (11 b), we get

$$(H^0 - E_k^0)\sum_l a_l\,\psi_l^0 + (H' - E_k')\,\psi_k^0 = 0$$

i.e.

$$\sum_l a_l\,H^0\,\psi_l^0 - E_k^0\sum_l a_l\,\psi_l^0 + (H' - E_k')\,\psi_k^0 = 0.$$

Using $H^0\,\psi_l^0 = E_l^0\,\psi_l^0$, we get

$$\sum_l a_l E_l^0 \psi_l^0 - E_k^0 \sum_l a_l \psi_l^0 + (H' - E_k') \psi_k^0 = 0.$$

$$\sum_l a_l (E_l^0 - E_k^0) \psi_k^0 = (E_k' - H') \psi_k^0 \qquad ...(13)$$

Multiplying above equation by ψ_m^{0*} and integrating over configuration space, we get

$$\sum_i a_l (E_l^0 - E_k^0) \int \psi_m^{0*} \psi_l^0 \, d\tau = \int \psi_m^{0*} (E_k' - H') \psi_k^0 \, d\tau$$

Using the *condition of orthonormalisation* of ψ_0's,

i.e.
$$\int \psi_i^{0*} \psi_j^0 \, d\tau = \delta_{ij} = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}$$

we get
$$\sum_i a_l (E_l^0 - E_k^0) \delta_{ml} = \int \psi_m^{0*} E_k' \psi_k^0 \, d\tau - \int \psi_m^{0*} H' \psi_k^0 \, d\tau$$

$$= E_k' \delta_{mk} - \int \psi_m^{0*} H' \psi_k^0 \, d\tau$$

Using the notations

$$\int \psi_m^{0*} H' \psi_k^0 \, d\tau = <m \mid H' \mid k>.$$

we get

$$\sum_i a_l (E_l^0 - E_k^0) \delta_{ml} = E_k' \delta_{mk} - <m \mid H' \mid k>. \qquad ...(14)$$

Evaluation of first order energy E_k' : Setting $m = k$ in eqn. (14), we observe that

$$\sum_i a_l (E_l^0 - E_k^0) \delta_{kl} = 0 \text{ always.}$$

Since for $l = k$, $E_l^0 - E_k^0 = 0$ and for $l \neq k$, $\delta_{kl} = 0$ so that, we get

$$0 = E_k' - <km \mid H' \mid k>,$$

or
$$E_k' = <k \mid H' \mid k> = \int \Psi_k^{0*} H' \Psi_k^0 \, d\tau. \qquad ...(15)$$

This expression gives first order perturbation energy correction. Accordingly the *"first order perturbation energy correction for a non-degenerate system is just the expectation value of first order perturbed hamiltonian (H ') over the unperturbed state of the system."*

Evaluation of first order correction to wave function :

Equation (14) may be expressed as

$$a_m (E_m^0 - E_k^0) = E_k' \delta_{mk} - <m \mid H' \mid k> \qquad ...(16)$$

$$\text{Since } \delta_{ml} \begin{cases} = 0 & \text{for } l \neq m \\ = 1 & \text{for } l = m \end{cases}$$

For $m \neq k$, equation (16) gives

$$a_m (E_m^0 - E_k^0) = - <m \mid H' \mid k>$$

or
$$a_m = - \frac{<m \mid H' \mid k>}{E_m^0 - E_k^0} = \frac{<m \mid H' \mid k>}{E_k^0 - E_m^0}$$

Setting
$$m = l,\ a_l = \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0}. \quad \text{...(17)}$$

If we retain only first order corection terms, then
$$\left.\begin{aligned} E_k &= E_k^0 + \lambda E_k' & \text{...}(a) \\ \psi_k &= \psi_k^0 + \lambda \psi_k' & \text{...}(b) \end{aligned}\right\} \quad \text{...(18)}$$

$\therefore$ Keeping in view equations (12) and (17), we get from (18b),
$$\psi_k = \psi_k^0 + \lambda \sum_l{}' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 + \lambda a_k \psi_k^0 \quad \text{...(19)}$$

where prime (or dash) on summation indicates that the term $l = m$ has been omitted from the summation (or it reminds that $l \neq k$).

The value of constant a_k may be evaluatd by requiring that ψ_k is normalised, *i.e.*
$$\int \psi_k^* \psi_k \, d\tau = 1 \quad \text{..(20)}$$

Substituting ψ_k from (19) and retaining only first order terms in λ : we get
$$\int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda a_k \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda a_k^* \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda \sum_l{}' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \delta_{lk}$$
$$+ \lambda \sum_l{}' \frac{[<l \mid H' \mid k>]^*}{E_k^0 - E_l^0} \delta_{lk} = 1$$

or
$$\lambda a_k + \lambda a_k^* = 0 \quad i.e.\ a_k + a_k^* = 0 \quad \text{...(21)}$$

This equation indicates that the real part of a_k is zero and still it leaves an arbitrary choice for the imaginary part.

Let us take $a_k = i\gamma$.

The wave function ψ_k can then be expressed as
$$\psi_k = \psi_k^0 + \lambda i \gamma \psi_k^0 + \lambda \sum_l{}' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0$$
$$= \psi_k^0 (1 + i\lambda\gamma) + \lambda \sum_l{}' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 \quad \text{...(22)}$$

The term containing γ merely gives a phase shift in the unperturbed function ψ_k^0 and for normalisation, this shift can be put equal to zero, so that equation (22) gives
$$\psi_k = \psi_k^0 + \lambda \sum_l \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0. \quad \text{...(23)}$$

The arbitrary λ can be put equal to 1 and it may be included in symbols, *i.e.* $\lambda H' \to H'$; then eigen values and eigen functions of the system upto first order perturbation correction terms are expressible as
$$\left.\begin{aligned} E_n \quad E_k &= E_k^0 + <k \mid H' \mid k> & \text{...}(a) \\ \text{and} \quad \psi_n \quad \psi_k &= \psi_k^0 + \sum_l{}' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 & \text{...}(b) \end{aligned}\right\} \quad \text{...(24)}$$

Second Order Perturbation : The second order perturbation equation (11 c) is
$$(H^0 - E_k^0)\, \psi_k'' + (H' - E_k')\, \psi_k' - E_k''\, \psi_k^0 = 0 \quad \text{...(11c)}$$

Expanding second order wave functions ψ_k'' as a linear combination of unperturbed orthonormal wave functions ψ_m^0 by expansion theorem, *i.e.*

$$\psi_k'' = \sum_m b_m \psi_m^0 \qquad \ldots(25)$$

Substituting $\psi_k' = \sum_l' \dfrac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0$; $\psi_k'' = \sum_m b_m \psi_m^0$

and $E_k' = <k \mid H' \mid k>$ in (11c); we get

$$(H^0 - E_k^0) \sum_m b_m \psi_m^0 + (H' - <k \mid H' \mid k>) \sum_l' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 - E_k'' \psi_k^0 = 0$$

or $$\sum_m b_m H^0 \psi_m^0 - E_k^0 \sum_m b_m \psi_m^0 + (H' - <k \mid H' \mid k>) \sum_l' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 - E_k'' \psi_k^0 = 0$$

Using unperturbed Schroedinger equation

$H^0 \psi_m^0 = E_m^0 \psi_m^0$, we get

$$\sum_m b_m E_m^0 \psi_m^0 - E_k^0 \sum_m b_m \psi_m^0 + (H' - <k \mid H' \mid k>) \sum_l' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 - E_k'' \psi_k^0 = 0$$

or $$\sum_m b_m (E_m^0 - E_k^0) \psi_m^0 + (H' - <k \mid H' \mid k>) \sum' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 - E_k'' \psi_k^0 = 0$$

Multiplying by ψ_n^0 and integrating over all space, we get

$$\sum_m b_m (E_m^0 - E_k^0) \int \psi_n^{0*} \psi_m^0 \, d\tau + \int \psi_n^{0*} (H' - <k \mid H' \mid k>) \sum' \frac{<l \mid H' \mid k>}{E_k^0 - E_l^0} \psi_l^0 \, d\tau - E_k'' \int \psi_n^{0*} \psi_k^0 \, d\tau = 0$$

Using orthonormal property of unperturbed wave functions ψ^0's, we get

$$\sum_m b_m (E_m^0 - E_k^0) \delta_{nm} + \sum_l' \frac{<l \mid H' \mid k><n \mid H' \mid l>}{E_k^0 - E_l^0} - \sum_l' \frac{<k \mid H' \mid k><l \mid H' \mid k>}{E_k^0 - E_l^0} \delta_{nl} - E_k'' \delta_{nk} = 0 \qquad \ldots(26)$$

$E^{(2)}$

Evaluation of second order energy correction :

Setting $n = k$ in (26), we get

$$\sum_m b_m (E_m^0 - E_k^0) \delta_{km} + \sum_l' \frac{<l \mid H' \mid k><k \mid H' \mid l>}{E_k^0 - E_l^0} - \sum_l' \frac{<k \mid H' \mid k><l \mid H' \mid k>}{E_k^0 - E_l^0} \delta_{kl} - E_k'' \delta_{kk} = 0 \qquad \ldots(27)$$

As $\delta_{kk} = 1$ and $\sum_m b_m (E_m^0 - E_k^0) \delta_{km} = 0$ for all values of m, equation (27) gives

$$E_k'' = \sum_l' \frac{<l \mid H' \mid k><k \mid H' \mid l>}{E_k^0 - E_l^0} - \sum_l' \frac{<k \mid H' \mid k><l \mid H' \mid k>}{E_k^0 - E_l^0} \delta_{kl} \qquad \ldots(28)$$

Considering the second term in equation (28), we note that this term is zero since $\delta_{kl} = 0$ for all values of l except for $l = k$ and this term is not included in the summation. Then equation (28) gives

$$E_k'' = \sum_l{}' \frac{<l \mid H' \mid k><k \mid H' \mid l>}{E_k^0 - E_l^0}$$

If we assume that H' is *Hermitian operator*, we may write

$$E_k'' = \sum_l{}' \frac{|<k \mid H' \mid l>|^2}{E_k^0 - E_l^0} \qquad \text{...(29)}$$

This equation gives second order energy correction term E_k''. The prime on summation reminds the omissioni of the term $l = k$ in the summation.

(2) 19m7 **Evaluation of second order correction to wave function :**

For $m \neq n$, equation (26) gives

$$b_n (E_n^0 - E_k^0) + \sum_l{}' \frac{<l \mid H' \mid k><n \mid H' \mid l>}{E_k^0 - E_l^0} - \sum_l{}' \frac{<l\, k \mid H' \mid k><l \mid H' \mid k>}{E_k^0 - E_l^0}\delta_{nl} = 0$$

or
$$b_n (E_n^0 - E_k^0) + \sum_l{}' \frac{<l \mid H' \mid k><n \mid H' \mid l>}{E_k^0 - E_l^0} - \frac{<l\, k \mid H' \mid k><n \mid H' \mid k>}{E_k^0 - E_n^0} = 0$$

This gives

$$b_n = \sum_l{}' \frac{<l \mid H' \mid k><n \mid H' \mid l>}{(E_k^0 - E_l^0)(E_k^0 - E_n^0)^2} - \frac{<l\, k \mid H' \mid k><n \mid H' \mid k>}{(E_k^0 - E_n^0)^2}$$

Setting $n = m$, we get

$$b_m = \sum_l{}' \frac{<l \mid H' \mid k><m \mid H' \mid l>}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} - \frac{<l\, k \mid H' \mid k><m \mid H' \mid k>}{(E_k^0 - E_m^0)^2} \qquad \text{...(30)}$$

This equation determines all coefficinets b_m's but not b_k. The coeffimient b_k is determined by the normalization condition for ψ_k retaining only terms upto second order in λ.

$$\psi_k = \psi_k^0 + \lambda\psi_k' + \lambda^2\psi_k'' = \psi_k^0 + \lambda\psi_k' + \lambda^2 \Sigma\, b_m \psi_m^0$$
$$= \psi_k^0 + \lambda\psi_k' + \lambda^2 b_k \psi_k^0$$
$$+ \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{<l \mid H' \mid k><k \mid H' \mid l>}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} - \frac{<k \mid H' \mid k><m \mid H' \mid k>}{(E_k^0 - E_m^0)^2} \right\} \psi_m^0 \qquad \text{...(31)}$$

The nornalization condition for ψ_k gives

$$\int \psi_k^* \psi_k \, d\tau = 1$$

Substituting ψ_k from (31); we get

$$\int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda \int \psi_k^{0*} \psi_k' \, d\tau + \lambda^2 b_k \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{<l \mid H' \mid k><k \mid H' \mid l>}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} \right.$$
$$\left. - \frac{<k \mid H' \mid k><m \mid H' \mid k>}{(E_k^0 - E_m^0)^2} \right\} \int \psi_k^{0*} \psi_m^0 \, d\tau + \lambda \int \psi_k^{0*} \psi_k^0 \, d\tau + \lambda^2 b_k^* \int \psi_k^{0*} \psi_k^0 \, d\tau$$
$$+ \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{<l \mid H' \mid k>^* <k \mid H' \mid l>^*}{(E_k^0 - E_l^0)(E_k^0 - E_m^0)} - \frac{<k \mid H' \mid k>^* <m \mid H' \mid k>^*}{(E_k^0 - E_m^0)^2} \right\} \int \psi_m^{0*} \psi_m^0 \, d\tau$$
$$+ \lambda^2 \int \psi_k'^* \psi_k' = 1$$

$$d\tau + 0 + \lambda^2 b_k + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{<l\,|\,H'\,|\,k><k\,|\,H'\,|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|\,H'\,|\,k><m\,|\,H'\,|\,k>}{(E_k^0\ E_m^0)^2} \right\} \delta_{km}$$

$$+ 0 + \lambda^2 b_k^* + \lambda^2 \sum_m{}' \left\{ \sum_l{}' \frac{<l\,|\,H'\,|\,k>^* <k\,|\,H'\,|\,l>^*}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|\,H'\,|\,k>^* <m\,|\,H'\,|\,k>^*}{(E_k^0 - E_m^0)^2} \right\} \delta_{mk}$$

$$+ \lambda^2 \sum_l{}' \sum_m{}' \frac{<l\,|\,H'\,|\,k>^* <m\,|\,H'\,|\,k>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} \int \psi_l^{0*}\, \psi_m^*\, d\tau = 1$$

[using ψ_k' from 24 (b)]

or
$$\lambda^2 b_k + \lambda^2 b_k^* + \lambda^2 \sum_l{}' \sum_m{}' \frac{<l\,|\,H'\,|\,k>^* <m\,|\,H'\,|\,k>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} \delta_{lm} = 0$$

or
$$\lambda^2 \left[b_k + b_k^* + \sum_l{}' \frac{<l\,|\,H'\,|\,k>^* <l\,|\,H'\,|\,k>}{(E_k^0 - E_l^0)\,(E_k^0 - E_l^0)} \right] = 0$$

As $\lambda^2 \neq 0$, therefore, we have

or
$$b_k + b_k^* = - \sum_l{}' \frac{|<l\,|\,H'\,|\,k>|^2}{(E_k^0 - E_l^0)^2} \qquad \text{...(32)}$$

The real part of b_k is fixed by this equation but the imaginary part is arbitray. The choice of imaginary part simply affects the phase of the unperturbed wave function and it does not affect the energy of the system. Hence the imaginary part of b_k may be equal to zero. Thus, we have

$$b_k = - \sum_l{}' \frac{|<l\,|\,H'\,|\,k>|^2}{2(E_k^0 - E_l^0)^2} \qquad \text{...(33)}$$

Then
$$\psi_k'' = \sum_m b_m \psi_m^0 = b_k \psi_k^0 + \sum_m{}' b_m \psi_m^0$$

$$= - \sum_l{}' \frac{|<l\,|\,H'\,|\,k>|^2}{2(E_k^0 - E_l^0)^2} \psi_k^0 + \sum_m{}' \left\{ \sum_l{}' \frac{<l\,|\,H'\,|\,k><k\,|\,H'\,|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|\,H'\,|\,k><m\,|\,H'\,|\,k>}{(E_k^0 - E_m^0)^2} \right\} \psi_m^0 \qquad \text{...(34)}$$

Thus the complete eigen values and eigen function corrected upto second order perturbation terms are given by

En
$$E_k = E_k^0 + \lambda E_k' + \lambda^2 E_k''$$

$$= E_k^0 + \lambda <k\,|\,H'\,|\,k>\ \lambda^2 \sum_l{}' \frac{|<k\,|\,H'\,|\,l>|^2}{E_k^0 - E_l^0} \qquad \text{...(35)}$$

and
$$\psi_k = \psi_k^0 + \lambda \psi_k' + \lambda^2 \psi_k''$$

ψn
$$= \psi_k^0 + \lambda \sum_l{}' \frac{<l\,|\,H'\,|\,k>}{E_k^0 - E_l^0} \psi_l^0 + \lambda^2 \left[- \sum_l{}' \frac{|<l\,|\,H'\,|\,k>|^2}{2(E_k^0 - E_l^0)^2} \psi_k^0 \right.$$

$$\left. + \sum_m{}' \left\{ \sum_l{}' \frac{<l\,|\,H'\,|\,k><k\,|\,H'\,|\,l>}{(E_k^0 - E_l^0)\,(E_k^0 - E_m^0)} - \frac{<k\,|\,H'\,|\,k><m\,|\,H'\,|\,k>}{(E_k^0 - E_m^0)^2} \right\} \psi_m^0 \right] \qquad \text{...(36)}$$