* TIME INDEPENDENT PERTURBATION THEORY.

Non-degenerate Perturbation theory.

The time independent Schrodinger equation for some potential say for one-dimensional infinite square well.

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad \ldots (1)$$

obtaining a complete set of orthonormal eigen-functions ψ_n^0,

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad \ldots (2)$$

and the corresponding eigenvalues E_n^0.

→ The new eigenfunctions and eigenvalues after perturbing the potential slightly will be.

$$H\psi_n = E_n \psi_n \quad \ldots (3)$$

PERTURBATION THEORY is a systematic procedure for obtaining approximate solutions to the perturbed problem, by building on the known exact solutions to the unperturbed case.

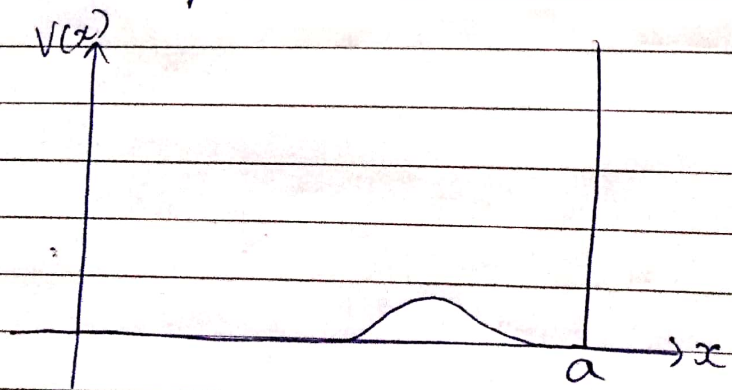

Fig: Infinite square well with small perturbation.

Writing the new Hamiltonian, as the sum of 2 terms::

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

$H' \rightarrow$ perturbation
$\lambda \rightarrow$ small number.
$H \rightarrow$ True Hamiltonian.

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \quad (5)$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (6)$$

$E_n^1 \rightarrow$ first order correction to the n^{th} eigenvalue.
$\psi_n^1 \rightarrow$ " " " " " " eigenfunction

Substituting equation (5) and (6) in (3)

$$(H^0 + \lambda H')[\lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots]$$

The lowest order would be $H^0 \psi_n^0 = E_n^0 \psi_n^0$
first order $H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$ (7)
second order $H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^0 + E_n^1 \psi_n^1 + E_n^2 \psi_n^2$ — (8)

* First order Theory.
Taking inner product of (7) with ψ_n^0

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle$$

H^0 is Hermitian and $\langle \psi_n^0 | \psi_n^0 \rangle = 1$ so
$$\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle} \quad (9)$$

This is the first order perturbation theory. It says that the first order correction to the energy is the ~~expectation~~ expectation value of the perturbation in the unperturbed state.

The first order correction to the wave function can be given by rewriting eq^n (7)

$$(H^0 - E_n^0)\psi_n' = -(H' - E_n')\psi_n^0 \quad \dots \quad (10)$$

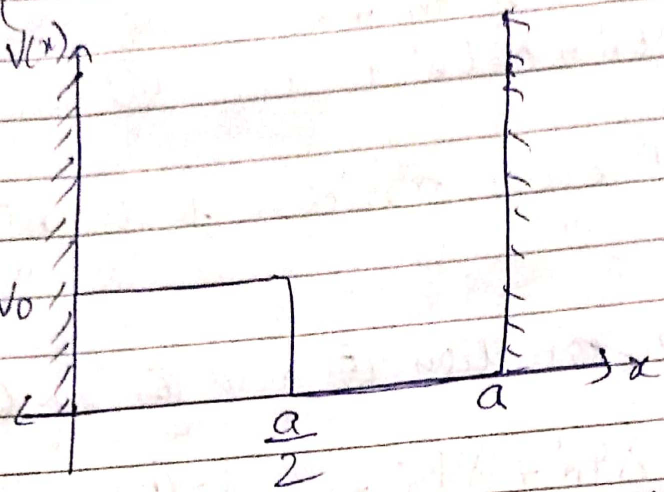

Fig: constant perturbation over half the well

The right side of equation (10) amounts to an inhomogenous differential equation for ψ_n'.

$$\therefore \psi_n' = \sum_{n \neq m} c_m^{(n)} \psi_m^0 \quad \dots \quad (11)$$

Substituting equation (11) in (10) and ψ_m^0 satisfies the unperturbed Schrodinger equation, we get

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n')\psi_n^0.$$

Taking inner product with ψ_l^0:

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n' \langle \psi_l^0 | \psi_n^0 \rangle.$$

If $l = n$, the left side is zero and we recover equation 9

if $l \neq n$

$$\therefore c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \quad \dots \quad (12)$$

$$\psi_n^1 = \sum_{m\neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0 \quad \ldots (13)$$

→ There is no coefficient with $m=n$ as long as the unperturbed energy spectrum is non-degenerate.

→ If 2 different unperturbed states share the same energy then degenerate perturbation theory is needed.

* Second Order Energies:

Taking inner product of (8) with ψ_n^0

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^2 \rangle$$

Again $H^0 \rightarrow$ Hermiticity

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle$$

Also $\langle \psi_n^0 | \psi_n^0 \rangle = 1$.

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle \quad \ldots (14)$$

But

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m\neq n} C_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0$$

So

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m\neq n} C_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle$$

$$= \sum_{m\neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}.$$

Finally, $$\boxed{E_n^2 = \sum_{m\neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}} \quad \ldots (15)$$

This is the fundamental result of second-order perturbation theory.

* Degenerate Perturbation Theory

→ If the unperturbed states are degenerate then ordinary perturbation theory fails. There has to be some other way to handle the problem.

Two-Fold Degeneracy

Suppose

$$\left.\begin{array}{l} H^0\psi_a^0 = E^0\psi_a^0 \\ H^0\psi_b^0 = E^0\psi_b^0 \\ \langle\psi_a^0|\psi_b^0\rangle = 0 \end{array}\right\} \quad \cdots (16)$$

with ψ_a^0 and ψ_b^0 both normalised. Any linear combination of these states

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0 \quad \cdots (17)$$

is still an eigenstate of H^0 with the same eigenvalue E^0.

$$H^0\psi^0 = E^0\psi^0 \quad \cdots (18)$$

Solving the Schrodinger equation $H\psi = E\psi \cdots (19)$ with $H = H^0 + \lambda H'$ and

$$E = E^0 + \lambda E' + \lambda^2 E^2 + \cdots, \quad \psi = \psi^0 + \lambda\psi^1 + \lambda^2\psi^2 + \cdots (20)$$

Substituting the above equation in (19),

$$H^0\psi^0 + \lambda(H'\psi^0 + H^0\psi') + \cdots = E^0\psi^0 + \lambda(E'\psi^0 + E^0\psi') + \cdots$$

But $H^0\psi^0 = E^0\psi^0$. The first terms cancel at order λ^1, we have

$$H^0\psi' + H'\psi^0 = E^0\psi' + E'\psi^0 \quad \cdots (21)$$

Taking inner product with ψ_a^0 and the substituting in equation (17) and using the orthonormality condition, we have

$$\alpha\langle\psi_a^0|H'|\psi_a^0\rangle + \beta\langle\psi_a^0|H'|\psi_b^0\rangle = \alpha E'.$$

or rewritten compactly as

$$\alpha W_{aa} + \beta W_{ab} = \alpha E' \quad \cdots (22)$$

where $W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle \quad (i,j = a, b) \quad \cdots (23)$

III'ly the inner product with ψ_b^0 yields

$$\alpha W_{ba} + \beta W_{bb} = \beta E' \quad \cdots (24)$$

W_{ij} are the matrix elements of H' w.r.t the unperturbed wave functions ψ_a^0 & ψ_b^0.

Multiplying eq^n (24) by W_{ab} and using eq^n (22) to eliminate βW_{ab}, we find

$$\alpha \left[W_{ab} W_{ba} - (E' - W_{aa})(E' - W_{bb}) \right] = 0 \quad \cdots (25)$$

If α is not zero, (25) leads to

$$(E')^2 - E'(W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0 \quad \cdots (26)$$

$W_{ab} = W_{ba}$ gives

$$\boxed{E'_{\pm} = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right] \quad \cdots (27)}$$

This is the result of degenerate perturbation theory;

→ For $\alpha = 0$, $\beta = 1$ giving $E' = W_{bb}$.

* Theorem: Let A be a hermitian operator that commutes with H^0 and H'. If ψ_a^0 & ψ_b^0 are also eigenfunctions of A, with distinct eigenvalues.

$$A\psi_a^0 = \mu \psi_a^0, \quad A\psi_b^0 = \nu \psi_b^0, \quad \mu \neq \nu \text{. then } W_{ab} = 0$$

and ψ_a^0 & ψ_b^0 are the "good" states to use in perturbation theory.

Proof: By assumption $[A, H'] = 0$ so.

$$\langle \psi_a^0 | [A, H'] \psi_b^0 \rangle = 0.$$

$$= \langle \psi_a^0 | A H' \psi_b^0 \rangle - \langle \psi_a^0 | H' A \psi_b^0 \rangle$$

$$= (\mu - \nu) \langle \psi_a^0 | H' \psi_b^0 \rangle = (\mu - \nu) W_{ab}$$

$\mu \neq \nu$ so $W_{ab} = 0$.