CH # 2 (P1)

Perturbation Theory.

It is the approximation method which is applied to the complicated Problems. In complicated problems the Hamiltonian operates on the system. This Hamiltonian is some of many parts and of which is very large as compared to the other parts. Basically the behaviour of the system depends upon the large part but variation due to perturbation is due to small parts.

Approximation due to Perturbation depends upon the nature of the system and perturbation applied on the system. For example. in Hydrogen atom, and in Harmonic oscillator we apply Perturbation due to electromagnetic waves. The sudden variation in potential also cause the Perturbation. The megnetic field in light waves is basically the source of Perturbation.

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Time independent Perturbation Theory:

To explain this theory we use schroundinger equation which is $\hat{H}\psi = E\psi$ ——(1)

When system is not subjected to perturbation due to magnetic field than schroundingers equation is

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \quad \text{——(2)}$$

When system is Perturbed by magnetic field than Hamiltonian changes due to variation in the Potential. the Hamiltonian becomes. Now we may again write the schroundinger equation for Perturbed states.

$$(\hat{H}^{(0)} + \lambda\hat{V})\psi_n = E_n\psi_n \quad \text{--- (2)}$$

where λV is the additional amount of energy due to Perturbation. Here we may take $\lambda = 1$.

After Perturbation Eign function and Eign values of energy changes from 0^{th} order to higher orders we have

$E_n^{(0)}, E_n^{(1)}, E_n^{(2)} \ldots\ldots$

Similarly $\psi_n^{(0)}, \psi_n^{(1)}, \psi_n^{(2)} \ldots\ldots$

The Eign function of the system for perturbed and unperturbed states satisfies the orthonormal condition. For example the orthonormal condition is shown by the following integral for 0^{th} order function.

$$\int \psi_i^{(0)} \psi_j^{(0)} \, dJ = \delta_{ij}$$

$\delta_{ij} = 1$ when $i = j$ (normalization) ∵ $\delta_{ij} \rightarrow$ kronoincer delta: for max perturbation)

$\delta_{ij} = 0$ when $i \neq j$ (orthognal condition for min perturbation

Now we again apply schroundingers equation in the form of expansion.

$$(H^{(0)}+\lambda V)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda\psi_n^{(2)}+\dots) = (E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+\dots)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}\dots)$$

$$(H^{(0)}+\lambda V)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\dots) = (E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}\dots)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\dots)$$

By xing the factors

$$(H\psi_n^{(0)}+H^{(0)}\lambda\psi_n^{(1)}+H^{(0)}\lambda^2\psi_n^{(2)}\dots)+(\lambda V\psi_n^{(0)}+\lambda^2 V\psi_n^{(1)}+\lambda^3 V\psi_n^{(2)}+\dots) = E_n^{(0)}\psi_n^{(0)}+E_n^{(0)}\lambda\psi_n^{(1)}+E_n^{(0)}\lambda^2\psi_n^{(2)}+\dots)(\lambda E_n^{(1)}\psi_n^{(0)}+\lambda^2 E_n^{(1)}\psi_n^{(1)}+\lambda^3 E_n^{(1)}\psi_n^{(2)}+\dots)(\lambda^2 E_n^{(2)}\psi_n^{(0)}+\lambda^3 E_n^{(2)}\psi_n^{(1)}+\lambda^4 E_n^{(2)}\psi_n^{(2)}\dots)$$

Neglect higher power becouse perturbation is very small and rearrange the equation according to the powers of λ.

$$(E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+\dots)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\dots)$$

$$(H^{(0)}\psi_n^{(0)}+\lambda(H^{(0)}\psi_n^{(1)}+V\psi_n^{(0)})+\lambda^2(H^{(0)}\psi_n^{(2)}+V\psi_n^{(1)})$$

$$= E_n^{(0)}\psi_n^{(0)}+\lambda(E_n^{(1)}\psi_n^{(0)}+E_n^{(0)}\psi_n^{(1)})+\lambda^2(E_n^{(0)}\psi_n^{(2)}+E_n^{(1)}\psi_n^{(1)}+E_n^{(2)}\psi_n^{(0)}) \quad \text{— (9)}$$

By equating the cofficients of equal powers of λ at both sides

$$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad \text{— (9a)}$$

Assumptions:

(1) Energy is associated with $H^{(0)}$ is very large as compared to λV.

(2) It is possible to expand Eign energies and Eign functions of corresponding Hamiltonion after perturbation in the form of series. For example energy E_n is represented by the following expression:

$$E_n = E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+\lambda^3 E_n^{(3)}+\dots \quad (4)$$

similarly. The Eign function ψ_n is given by

$$\psi_n = \psi_n^{(0)}+\lambda\psi_n^{(1)}+\lambda^2\psi_n^{(2)}+\lambda^3\psi_n^{(3)}\dots \quad (5)$$

where $E_n^{(1)}$, $E_n^{(2)}$ and $E_n^{(3)}$ are 1st, 2nd and 3rd orders of energy. Similarly $\psi_n^{(1)}$, $\psi_n^{(2)}$ and $\psi_n^{(3)}$ are 1st, 2nd and 3rd order Eign function.

The Eign function $\psi_n^{(1)}$ and $\psi_n^{(2)}$ depend upon the cofficients, so they are expressed in terms of expension depending upon the cofficients.

$$\psi_n^{(1)} = \sum_m C_{nm}^{(1)}\psi_m^{(0)} \quad \text{— (6)}$$

$$\psi_n^{(2)} = \sum_m C_{nm}^{(2)}\psi_m^{(0)} \quad \text{— (7)}$$

where ~~$\psi_{nm}^{(2)}$ and~~ $C_{nm}^{(1)}$ and $C_{nm}^{(2)}$ are cofficients.

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$$H^{(0)}\psi_n^{(1)} + V\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)} \quad \text{— (9}$$

$$H^{(0)}\psi_n^{(2)} + V\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} \quad \text{— 9}$$

These equations are 0^{th} order, Ist order and 2nd order equations.

★ Calculation of Ist order Energy $E_n^{(1)}$

we have the 0^{th} order state shown by the following equation:

$$H^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad \text{— (1)}$$

The Ist order perturbation is shown by the following equation.

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

Now rearrange this eq.

$$(H^{(0)} - E_n^{(0)})\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} - V\psi_n^{(0)} \quad \text{— (3)}$$

Now xing this eq on both sides by $\psi_n^{*(0)}$ and integrate w.r.t all coordinates

$$\int \psi_n^{*(0)}(H^{(0)} - E_n^{(0)})\psi_n^{(1)}\, d\tau = \int \psi_n^{*(0)} E_n^{(1)}\psi_n^{(0)}\, d\tau - \int \psi_n^{*(0)} V\psi_n^{(0)}\, d\tau \quad \text{— (4)}$$

take the Ist term of R.H.S and Solve it

$$\int \psi_n^{(0)*} E_n^{(1)}\psi_n^{(0)}\, d\tau$$

Take out $E_n^{(1)}$ out side the integral and apply the normalization condition then integral becomes equal to 1.

$$\int \psi_n^{*(0)} E_n^{(1)}\psi_n^{(0)}\, d\tau = E_n^{(1)}\int \psi_n^{*(0)}\psi_n^{(0)}\, d\tau$$
$$= E_n^{(1)}$$

Put it in eq (4) $\quad \because \int \psi_n^{*(0)}\psi_n^{(0)}\, d\tau = 1$

$$\int \psi_n^{*(0)}(H^{(0)} - E_n^{(0)})\psi_n^{(1)}\, d\tau = E_n^{(1)} - \int \psi_n^{*(0)} V\psi_n^{(0)}\, d\tau \quad \text{— (4a)}$$

$$= \int \psi_n^{*(0)} V\psi_n^{(0)}\, d\tau = V_{nn}$$

Substitute in the form of the symbol. V_{nn}

$$\int \psi_n^{*(0)} V\psi_n^{(0)}\, d\tau = V_{nn} \quad \because V_{nn} \text{ is degenerated form}$$

Put in eq (4)

$$\int \psi_n^{*(0)}(H^{(0)} - E_n^{(0)})\psi_n^{(1)}\, d\tau = E_n^{(1)} - V_{nn} \quad \text{— (4b)}$$

Now take the L.H.S of eq (4b) and solve it.

$$= \int \psi_n^{*(0)}(H^{(0)} - E_n^{(0)})\psi_n^{(1)}\, d\tau$$

As the $H^{(0)}$ can not operat on $\psi_n^{(1)}$ it can only operate on the $\psi_n^{(0)}$ So we take Ist term of the integral and substitute in the form of energy.

$$\psi_n^{*(0)} H^{(0)} = H^{(0)}\psi_n^{*(0)} = E_n^{*(0)}\psi_n^{*(0)}$$

Now mult this equation by $\psi_m^{*(0)}$ on both sides and integrate w.r.t all coordinates

$$\int \psi_m^{*(0)} (H^{(0)} - E_n^{(0)}) \psi_n^{(1)} d\tau = \int \psi_m^{(0)*} E_n^{(1)} \psi_n^{(0)} d\tau - \int \psi_m^{(0)*} V \psi_n^{(0)} d\tau \quad \text{— (6)}$$

take the 1st term of R.H.S and solve it.

$$\Rightarrow \int \psi_m^{(0)*} E_n^{(1)} \psi_n^{(0)} d\tau$$

take out energy of the integral

$$= E_n^{(1)} \int \psi_m^{(0)*} \psi_n^{(0)} d\tau$$

take the condition of orthogonality $m \neq n$

we take condition $m \neq n$ so we apply the condition of orthogonality. so our integral becomes zero.

$$\int \psi_m^{(0)*} \psi_n^{(0)} d\tau = 0$$

so our 1st term is zero. Now substitute this equality in eq (6)

$$\int \psi_m^{*(0)} (H^{(0)} - E_n^{(0)}) \psi_n^{(1)} d\tau = 0 - \int \psi_m^{(0)*} V \psi_n^{(0)} d\tau \quad \text{— (6a)}$$

Now take the 2nd term of R.H.S and substitute in the form of symbol.

ie $\int \psi_m^{(0)*} V \psi_n^{(0)} d\tau = V_{mn}$

putting in eq (6a).

$$= \psi_n^{*(0)} E_n^{*(0)}$$

substitute this value in the integral.

$$= \int \psi_n^{*(0)} (E_n^{*(0)} - E_n^{*(0)}) \psi_n^{(1)} d\tau$$

As we have $\because E_n^{*(0)} = E_n^{(0)}$ $\because$ energy can not be imaginary.

substitute in the relation.

$$\int \psi_n^{*(0)} (E_n^{(0)} - E_n^{(0)}) \psi_n^{(1)} d\tau = 0$$

substitute this value in eq (4b).

$$0 = E_n^{(1)} - V_{nn}$$

(4c) — $\boxed{E_n^{(1)} = V_{nn}}$

$$E_n^{(1)} = \int \psi_n^{*(0)} V \psi_n^{(0)} d\tau$$

So we have calculated the 1st order perturbation energy.

Calculation of 1st order correction to wave function:

Write the 1st order equation and rearrange it.

$$H^{(0)} \psi_n^{(1)} + V \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \psi_n^{(1)}$$

Now re-arrange it

$$(H^{(0)} - E_n^{(0)}) \psi_n^{(1)} = E_n^{(1)} \psi_n^{(0)} - V \psi_n^{(0)} \quad \text{— (5)}$$