## Approximate method:-

Preturbation theory expresses the solution to one problem in terms of Another problem solved previously.

Schrodinger Equation

$$\hat{H}\psi = E\psi$$

For some particular system

Hamiltonian operator for a Helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} \quad \text{— (1)}$$

This equation can be written as

$$\hat{H} = \hat{H}_H(1) + \hat{H}_H(2) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} \quad \text{— (2)}$$

where

$$\hat{H}_H(j) = -\frac{\hbar^2}{2m}\nabla_j^2 - \frac{2e^2}{4\pi\epsilon_0}\frac{1}{r_j} \qquad j = 1 \text{ and } 2 \quad \text{— (3)}$$

$\hat{H}_H(j)$ is Hamiltonian for a single ~~operator~~ electron around a helium nucleus.

Thus $\hat{H}_H(j) = -\frac{\hbar^2}{2m}\nabla_j^2 - \frac{2e^2}{4\pi\epsilon_0}\frac{1}{r_j}$ $\quad j = 1$ and $2$

become

$$\hat{H}_H(j)\psi_H(r_j, \theta_j, \phi_j) = E_j\,\psi_H(r_j, \theta_j, \phi_j) \quad j = 1 \text{ and } 2 \quad \text{— (4)}$$

where $\psi_H(r_j, \theta_j, \phi_j)$ is hydrogen like wave function with $Z = 2$ and $E_j$ are given by

$$E_j = -\frac{Z^2 \mu e^4}{8 \epsilon_0^2 h^2 n_j^2} \qquad j = 1 \text{ and } 2 \quad — (5)$$

with $Z = 2$

In the absence of interelectronic repulsion term $\frac{e^2}{4\pi\epsilon_0 r_{12}}$ in equation (2), the Hamiltonian operator for a Helium atom would be seperable and helium atomic wave functions would be products of Hydrogen-like atomic wave functions.

According to the Taylor expansion of a general potential about the equilibrium nuclear separation.

Let us consider an anharmonic oscillator given by equation

$$U(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4 \quad — (6)$$

The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4 \quad — (7)$$

If $\gamma = b = 0$, the equation is Hamiltonian operator for a harmonic oscillator.

Eq. (1) and (7) gives us basic idea of perturbation.

The Hamiltonian consists of two parts, one for which schrodinger equation can be solved exactly and an additional term ~~gives~~ prevents the same exact solution

Hence, the first term is called unpertubed and the additional term is called perturbation.

The unpertubed Hamiltonian by $\hat{H}^{(0)}$ and the perturbation by $\hat{H}^{(1)}$ and write

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \quad \text{—— (8)}$$

Associated with $\hat{H}^{(0)}$ is a Schrodinger equation and hence we get equation

$$\hat{H}^{(0)} \psi^{(0)} = E^{(0)} \psi^{(0)} \quad \text{—— (9)}$$

where $\psi^{(0)}$ and $E^{(0)}$ are called eigenfunctions and eigenvalues of $\hat{H}^{(0)}$.

equation (9) specifies the unperturbed system. In the case of Helium atom

$$\hat{H}^{(0)} = \hat{H}_H(1) + \hat{H}_H(2)$$

$$\psi^{(0)} = \psi_H(r_1, \theta_1, \phi_1)\, \psi_H(r_2, \phi_2, \theta_2) \quad \text{—— (10)}$$

and
$$E^{(0)} = -\frac{4\mu e^4}{8\epsilon_0^2 h^2 n_1^2} - \frac{4\cdot\mu e^4}{8\epsilon_0^2 h^2 n^2}$$

and
$$\hat{H}^{(1)} = \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

In case of an anharmonic oscillator we have

$$\hat{H}^{(0)} = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$\psi^{(0)} = \frac{(\alpha/\pi)^{1/4}}{(2^n n!)^{1/2}} e^{-\alpha x^2/2} H_n(\alpha^{1/2}x) \quad \text{—— (11)}$$

$$E^{(0)} = \left(n + \frac{1}{2}\right) h\nu$$

and $$\hat{H}^{(1)} = \frac{\gamma}{6}x^3 + \frac{b}{24}x^4$$

If the perturbation terms are not large, the pertubed terms are ~~not~~ close to the unpertubed problem.

If the anharmonicity terms $\gamma x^3/6$ and $bx^4/24$ are small. The unpertubed system is only pertubed only when they are small and not altered drastically by additional term.