Lecture 6

Approximation methods

1. **Time-Independent Perturbation Theory**
2. **Variation method**

The exact solution is S.E is possible only for the Hydrogen Like atom, when many electron exist , the situation become mole complicated de to e-e interaction(repulsion) so there is a need for Approximation

Time Independent Perturbation Theory

Introduction

One often finds in QM that the Hamiltonian for a particular problem can be written as:

$$H = H^{(0)} + H^{(1)}$$

$H^{(0)}$ is an exactly solvable Hamiltonian; i.e. $H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$

$H^{(1)}$ is a smaller term which keeps the Schrödinger Equation from being solvable exactly.

One example is the Anharmonic Oscillator:

$$H = \underbrace{\boxed{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2}}_{\substack{H^{(0)} \\ \text{Exactly Solvable}}} + \underbrace{\boxed{\gamma x^3 + \delta x^4 + \ldots}}_{\substack{H^{(1)} \\ \text{Correction Term}}}$$

$$H = H^{(0)} + H^{(1)} \qquad \text{where} \qquad H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

In this case, one may use a method called “Perturbation Theory” to perform one or more of a series of increasingly higher order corrections to both the Energies and Wavefunctions.

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots + E^{(n)}$$

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots + \psi^{(n)}$$

Some textbooks** outline the method for higher order corrections. However, we will restrict the treatment here to first order perturbation corrections

We will use the notation: $E = E^{(0)} + \Delta E$ and $\psi = \psi^{(0)} + \Delta\psi$

e.g. *Quantum Chemistry* (7th. Ed.), by I. N. Levine, Chap. 9

First Order Perturbation Theory

$H = H^{(0)} + H^{(1)}$ where $H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$

Assume: $E = E^{(0)} + \Delta E$ and $\psi = \psi^{(0)} + \Delta\psi$

$$H\psi = E\psi$$

$$\left(H^{(0)} + H^{(1)}\right)\left(\psi^{(0)} + \Delta\psi\right) = \left(E^{(0)} + \Delta E\right)\left(\psi^{(0)} + \Delta\psi\right)$$

$$H^{(0)}\psi^{(0)} + H^{(1)}\psi^{(0)} + H^{(0)}\Delta\psi + H^{(1)}\Delta\psi$$
$$= E^{(0)}\psi^{(0)} + \Delta E\psi^{(0)} + E^{(0)}\Delta\psi + \Delta E\Delta\psi$$

$$\cancel{H^{(0)}\psi^{(0)}} + H^{(1)}\psi^{(0)} + H^{(0)}\Delta\psi + \cancel{H^{(1)}\Delta\psi} = \cancel{E^{(0)}\psi^{(0)}} + \Delta E\psi^{(0)} + E^{(0)}\Delta\psi + \cancel{\Delta E\Delta\psi}$$

One can eliminate the two terms involving the product of two small corrections.

One can eliminate two additional terms because: $H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$

$$H^{(1)}\psi^{(0)} + H^{(0)}\Delta\psi = \Delta E\psi^{(0)} + E^{(0)}\Delta\psi$$

Multiply all terms by $\psi^{(0)*}$ and integrate:

$$\int \psi^{(0)*} H^{(1)}\psi^{(0)} d\tau + \int \psi^{(0)*} H^{(0)}\Delta\psi \, d\tau = \int \psi^{(0)*} \Delta E\psi^{(0)} d\tau + \int \psi^{(0)*} E^{(0)}\Delta\psi \, d\tau$$

$H^{(0)}$ is Hermitian. Therefore:

$$\int \psi^{(0)*} H^{(0)}\Delta\psi \, d\tau = \int \Delta\psi \left(H^{(0)}\psi^{(0)}\right)^* d\tau = \int \Delta\psi \left(E^{(0)}\psi^{(0)}\right)^* d\tau = E^{(0)}\int \psi^{(0)*} \Delta\psi \, d\tau$$

Plug in to get:

$$\int \psi^{(0)*} H^{(1)}\psi^{(0)} d\tau + \cancel{E^{(0)}\int \psi^{(0)*} \Delta\psi \, d\tau} = \int \psi^{(0)*} \Delta E\psi^{(0)} d\tau + \cancel{\int \psi^{(0)*} E^{(0)}\Delta\psi \, d\tau}$$

Therefore: $\int \psi^{(0)*} H^{(1)}\psi^{(0)} d\tau = \Delta E \int \psi^{(0)*} \psi^{(0)} d\tau = \Delta E$

$\boxed{\Delta E = \int \psi^{(0)*} H^{(1)}\psi^{(0)} d\tau}$ is the first order perturbation theory correction to the energy.

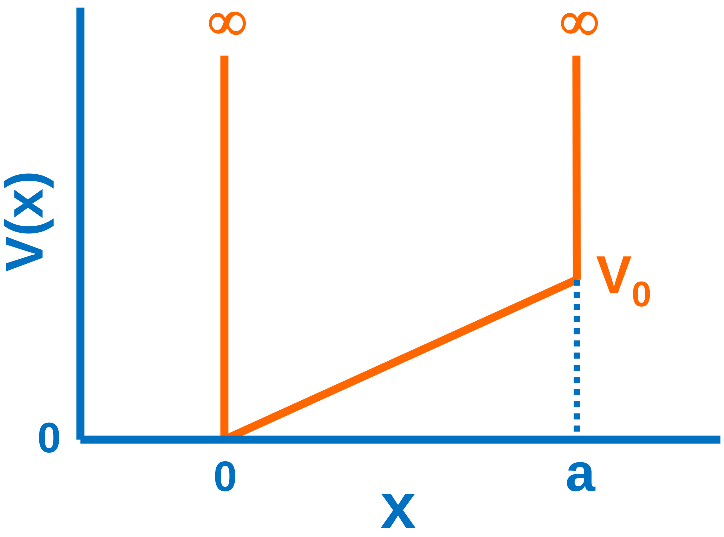
Applications of First Order Perturbation Theory

PIB with slanted floor

Consider a particle in a box with the potential:

$$V(x) \to \infty \quad x < 0\,,\ x > a$$

$$V(x) = \frac{V_0}{a}x \quad 0 \le x \le a$$



For this problem:

$$H^{(0)} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + 0$$

$$E_n^{(0)} = \frac{n^2h^2}{8ma^2}$$

$$\psi_n^{(0)} = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

The perturbing potential is: $H^{(1)} = \dfrac{V_0}{a}x$

Integral Info

$$\int x\sin^2(\alpha x)dx = \frac{x^2}{4} - \frac{x\sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

$$\sin(2\alpha a) = \sin\left(2\frac{n\pi}{a}a\right) = 0$$

$$\cos(2\alpha a) = \cos\left(2\frac{n\pi}{a}a\right) = 1$$

We will calculate the first order correction to the n^th energy level.
In this particular case, the correction to all energy levels is the same.

$$\Delta E = \int \psi^{(0)} * H^{(1)}\psi^{(0)} d\tau = \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)\cdot\left(\frac{V_0}{a}x\right)\cdot\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)dx$$

$$= \frac{2}{a}\frac{V_0}{a}\int_0^a x\cdot\sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{2V_0}{a^2}\int_0^a x\cdot\sin^2(\alpha x)dx \qquad \alpha = \frac{n\pi}{a}$$

$$= \frac{2V_0}{a^2}\left[\left(\frac{a^2}{4} - \frac{a\sin(2\alpha a)}{4\alpha} - \frac{\cos(2\alpha a)}{8\alpha^2}\right) - \left(0 - 0 - \frac{\cos(0)}{8\alpha^2}\right)\right]$$

$$= \frac{2V_0}{a^2}\left[\left(\frac{a^2}{4} - \frac{1}{8\alpha^2}\right) - \left(-\frac{1}{8\alpha^2}\right)\right] \longrightarrow \boxed{\Delta E = \frac{V_0}{2}}$$

Independent of n

Anharmonic Oscillator

Consider an anharmonic oscillator with the potential energy of the form:

$$V(x) = \frac{1}{2}kx^2 + \gamma x^3 + \delta x^4$$

We'll calculate the first order perturbation theory correction to the ground state energy.

For this problem:

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

$$E_0^{(0)} = \frac{1}{2}\hbar\omega$$

$$\psi_0^{(0)} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\omega = \sqrt{\frac{k}{\mu}} \qquad \alpha = \frac{\sqrt{k\mu}}{\hbar}$$

The perturbing potential is:

$$H^{(1)} = \gamma x^3 + \delta x^4$$

$$\Delta E = \int \psi_0^{(0)*} H^{(1)} \psi_0^{(0)} d\tau$$

$$= \int_{-\infty}^{\infty} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \cdot \left(\gamma x^3 + \delta x^4\right) \cdot \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \left(\gamma x^3 + \delta x^4\right) e^{-\alpha x^2} dx$$

$$\Delta E = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \left(\gamma x^3 + \delta x^4\right) e^{-\alpha x^2} dx = \gamma \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} dx + \delta \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx$$

$$= 0 + 2\delta \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{0}^{\infty} x^4 e^{-\alpha x^2} dx = 2\delta \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{3}{8\alpha^2}\right) \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$\int_0^{\infty} x^4 e^{-\beta x^2} dx = \frac{3}{8\beta^2}\sqrt{\frac{\pi}{\beta}}$$

$$\Delta E = \frac{3\delta}{4\alpha^2} = \frac{3\delta}{4\left(\frac{\sqrt{k\mu}}{\hbar}\right)^2} = \frac{3\hbar^2\delta}{4k\mu}$$

Note: There is no First order Perturbation Theory correction due to the cubic term in the Hamiltonian.

However, there IS a correction due to the cubic term when Second order Perturbation Theory is applied.

Brief Introduction to Second Order Perturbation Theory

As noted above, one also can obtain additional corrections to the energy using higher orders of Perturbation Theory; i.e.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots$$

$E_n^{(0)}$ is the energy of the nth level for the unperturbed Hamiltonian

$E_n^{(1)}$ is the first order correction to the energy, which we have called ΔE

$E_n^{(2)}$ is the second order correction to the energy, etc.

The second order correction to the energy of the nth level is given by:

$$E_n^{(2)} = \sum_{k=1}^{\infty} \frac{\left|\left\langle \psi_k^{(0)} \middle| H^{(1)} \middle| \psi_n^{(0)} \right\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}} \quad for\ k \neq n$$

where $\left\langle \psi_k^{(0)} \middle| H^{(1)} \middle| \psi_n^{(0)} \right\rangle = \int \psi_k^{(0)*} H^{(1)} \psi_n^{(0)} d\tau$

If the correction is to the ground state (for which we'll assume n=1), then:

$$E_1^{(2)} = \sum_{k=2}^{\infty} \frac{\left|\left\langle \psi_k^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_k^{(0)}}$$

$$E_1^{(2)} = \frac{\left|\left\langle \psi_2^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{\left|\left\langle \psi_3^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_3^{(0)}} + \frac{\left|\left\langle \psi_4^{(0)} \middle| H^{(1)} \middle| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_4^{(0)}} + \cdots$$

Note that the second order Perturbation Theory correction is actually an infinite sum of terms.

However, the successive terms contribute less and less to the overall correction as the energy, $E_k^{(0)}$, increases.