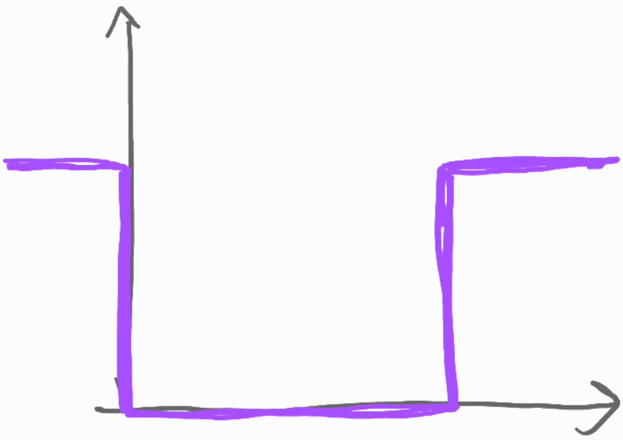
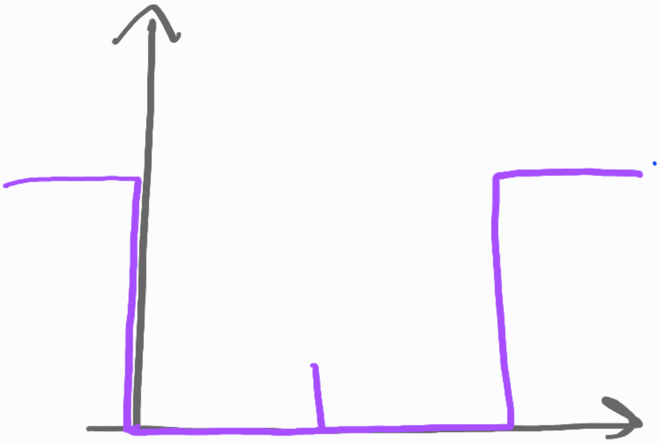
Non-Degenerate Perturbation Theory



unperturbed system



perturbed system

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

$$i\hbar \frac{d}{dt} |\psi_{new}\rangle = \hat{H}_{new} |\psi_{new}\rangle$$

where $\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$

$$\hat{H}_{new} = \hat{H}_0 + \alpha\,\delta\left(\frac{a}{2}\right)$$

$$i\hbar \frac{d}{dt} |\psi_0\rangle = \hat{H} |\psi_0\rangle$$

$$\Downarrow$$

$$\hat{H}_0 + \lambda\,\alpha\,\delta\left(\frac{a}{2}\right)$$

$$|\psi_{new}^{n}\rangle = |\psi_0^{n}\rangle + \lambda |\psi_1^{(n)}\rangle + \ldots + \lambda^2 |\psi_2^{(n)}\rangle \ldots + \lambda^3 |\psi_3^{n}\rangle \ldots$$

1st order Approximation

$$\boxed{E_{new}^{n} \simeq E_0^{n} + \lambda E_1^{n}}$$

$$E_1^{n} = \frac{\langle \psi_0^{n} | \hat{V}_{new} | \psi_0^{n}\rangle}{\langle \psi_0^{n} | \psi_0^{n}\rangle} + \ldots$$

$$|\psi_{new}^{n}\rangle \approx |\psi_0^{n}\rangle + \lambda |\psi_1^{n}\rangle$$

Derivation of Perturbation Theory

$$H_0 \phi_n = E_n^{(0)} \phi_n \Rightarrow \text{the unperturbed problem}$$

$$(H_0 + \lambda H_I)\, \psi_n = E_n \psi_n$$

$$\psi_n = \left\{ \phi_n + \sum_{k\neq n} c_{nk}(\lambda)\, \phi_k \right\} \quad \text{where} \quad c_{nk}(\lambda = 0) = 0$$

$$\boxed{0 \leq \lambda \leq 1}$$

$$c_{nk}(\lambda) = \lambda c_{nk}^{(1)} + \lambda^2 \underset{\text{1st order correction}}{c_{nk}^{(2)}} + \lambda^3 \underset{\text{2nd order correction}}{c_{nk}^{(3)}} + \dots$$

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

$$\psi_n \cong \underset{= \phi_n}{\psi_n^{(0)}} + \psi_n^{(1)} + \psi_n^{(2)} + \dots$$

$$\psi_n^{(1)} = \sum_{k\neq n} \lambda c_{nk}^{(1)} \phi_k \rightarrow \text{eigenfunctions}$$

$$\psi_n^{(2)} = \sum_{k\neq n} \lambda^2 c_{nk}^{(2)} \phi_k \quad \dots$$

$$(H_0 + \lambda H_I) \left\{ \overset{\psi_n^0}{\phi_n} + \overset{\psi_n^1}{\sum_{k\neq n} \lambda c_{nk}^{(1)} \phi_k} + \overset{\psi_n^2}{\sum_{k\neq n} \lambda^2 c_{nk}^{(2)} \phi_k} + \overset{\dots}{\dots} \right\}$$

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

$$H_0 \psi_n^0 + \lambda\left(\underbrace{H_0 \psi_n^{(1)} + H_I \psi_n^{(0)}}\right) + \lambda^2\left(\underbrace{H_0 \psi_n^{(2)} + H_I \psi_n^{(1)}}\right) + \dots$$

$$= E_n^0 \psi_n^0 + \lambda\left(\underbrace{E_n^{(0)} \psi_n^{(1)} + E_n^1 \psi_n^0}\right) + \lambda^2\left(\underbrace{E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0}\right) + \dots$$

Zeroth Order (λ^0) $\quad H_0 \psi_n^0 = E_n^0 \psi_n^0$

First Order (λ^1) $\quad H_0 \psi_n^1 + H_I \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

Second Order (λ^2) $\quad H_0 \psi_n^2 + H_I \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$

Expand it

$$\lambda \Big[H_0 \underbrace{\sum_{k \neq n} c_{nk}^{(1)} \phi_k}_{\psi_n^{(1)}} + H_I \underbrace{\phi_n}_{\psi_n^0} \Big] = \lambda \Big(E_n^0 \sum_{k \neq n} c_{nk}^{(1)} \phi_k + E_n^1 \phi_n \Big)$$

$$\lambda \Big[\sum_{k \neq n} c_{nk}^{(1)} E_k^{(0)} \phi_k + H_I \phi_n \Big] = \lambda \Big(\sum_{k \neq n} c_{nk}^{(1)} E_n^{(0)} \phi_k + E_n^{(1)} \phi_n \Big)$$

$$\lambda \Big[\sum_{k \neq n} c_{nk}^{(1)} (E_k^0 - E_n^0) \phi_k + H_I \phi_n \Big] = \lambda E_n^{(1)} \phi_n$$

Take the projection of ϕ_i^*

$$\Big[\sum_{k \neq n} \lambda c_{nk}^{(1)} (E_k^{(0)} - E_n^{(0)}) \underbrace{\langle \phi_i | \phi_k \rangle}_{0} + \langle \phi_i | \lambda H_I | \phi_n \rangle \Big] = \lambda E_n^{(1)} \underbrace{\langle \phi_i | \phi_n \rangle}_{1}$$

since $n \neq k$

For $i = n$

$$\langle \phi_n | \lambda H_I | \phi_n \rangle = \lambda E_n^{(1)}$$

$$\boxed{\langle \lambda H_I \rangle = \lambda E_n^{(1)}}$$

$$\boxed{E_n = E_n^{(0)} + \lambda E_n^{(1)} = E_n^{(0)} + \langle \phi_n | \lambda H_I | \phi_n \rangle}$$

For $i = k$ & $k \neq n$

$$\left[\sum_{k \neq n} \lambda c_{nk}^{(1)} \left(E_k^{(0)} - E_n^{(0)} \right) \underbrace{\langle \phi_i | \phi_k \rangle}_{1} + \langle \phi_i | \lambda H_I | \phi_n \rangle \right] = \lambda E_n^{(1)} \underbrace{\langle \phi_i | \phi_n \rangle}_{0}$$

$$\lambda c_{ni}^{(1)} \left(E_i^{(0)} - E_n^{(0)} \right) + \langle \phi_i | \lambda H_I | \phi_n \rangle = 0$$

$$\boxed{\lambda c_{ni}^{(1)} = \frac{\langle \phi_i | \lambda H_I | \phi_n \rangle}{\left(E_n^{(0)} - E_i^{(0)} \right)}} \qquad (*)$$

$$\psi_n^{(1)} = \sum_{i \neq n} \lambda c_{ni}^{(1)} \phi_i = \sum_{i \neq n} \frac{\langle \phi_i | \lambda H_I | \phi_n \rangle}{\left(E_n^{(0)} - E_i^{(0)} \right)} \phi_i$$

The full-wave fn. corrected upto the 1st order in perturbation

$$\psi_n \cong \phi_n + \sum_{i \neq n} \frac{\langle \phi_i | \lambda H_I | \phi_n \rangle}{\left(E_n^{(0)} - E_i^{(0)} \right)} \phi_i$$

Second Order (λ^2)

$$H_0 \Psi_n^2 + H_I \Psi_n^1 = E_n^0 \Psi_n^2 + E_n^1 \Psi_n^1 + E_n^2 \Psi_n^0$$

$$\lambda^2 \left[H_0 \sum_{k \neq n} c_{nk}^{(2)} \phi_k + H_I \sum_{k \neq n} c_{nk}^{(1)} \phi_k \right]$$

$$= \lambda^2 \left[E_n^0 \sum_{k \neq n} c_{nk}^2 \phi_k + E_n^1 \sum_{k \neq n} c_{nk}^1 \phi_k + E_n^0 \phi_n \right]$$

$$\lambda^2 \left[\sum_{k \neq n} c_{nk}^2 E_k^0 \langle \phi_i | \phi_k \rangle + \sum_{k \neq n} c_{nk} \langle \phi_i | H_I | \phi_k \rangle \right]$$

$$= \lambda^2 \left[\sum_{k \neq n} c_{nk}^{(2)} E_n^0 \langle \phi_i | \phi_k \rangle + \sum_{k = n} c_{nk}^{(1)} E_n^{(1)} \langle \phi_i | \phi_k \rangle + E_n^{(2)} \langle \phi_i | \phi_n \rangle \right]$$

For $i = n$ & $(n \neq k)$

$$\langle \phi_i | \phi_k \rangle = \langle \phi_n | \phi_k \rangle = 0$$

$$\lambda^2 E_n^{(2)} = \sum_{k \neq n} \lambda c_{nk}^{(1)} \langle \phi_n | \lambda H_I | \phi_k \rangle$$

From *

$$\lambda^2 E_n^{(2)} = \sum_{k \neq n} \frac{\langle \phi_k | \lambda H_I | \phi_n \rangle \langle \phi_n | \lambda H_I | \phi_k \rangle}{(E_n^0 - E_k^0)}$$

$$\boxed{\lambda^2 E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \phi_n | \lambda H_I | \phi_k \rangle|^2}{(E_n^0 - E_k^0)}}$$

$$\hat{E}_n \cong E_n^{0} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}$$

$$\boxed{\hat{E}_n \cong \hat{E}_n^{(0)} + \langle \phi_n | \lambda H_I | \phi_n \rangle + \sum_{k \neq n} \frac{|\langle \phi_n | \lambda H_I | \phi_n \rangle|^2}{(E_n^{(0)} - E_k^{(0)})}}$$