Non-degeneret perturbation theory

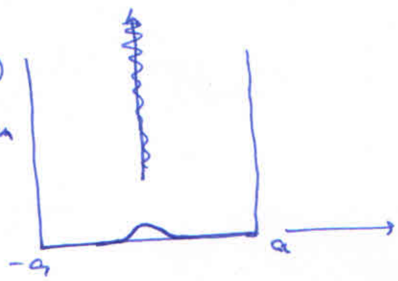
$$\hat{H}_0|\psi_{n0}\rangle = E_{n0}|\psi_{n0}\rangle \quad \Big\}\ \text{unperturbed Hamiltonian } \hat{H}_0$$
$$\langle\psi_{n0}|\psi_{m0}\rangle = \delta_{mn}$$

Potential $V(x) = V_0(x) + v(x)$
$v(x) \ll V_0(x)$

Perturbed Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_p$, we are looking for solutions

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \qquad \boxed{\hat{H}_p \ll H_0}$$

→ unperturbed Hamiltonian



we write $\hat{H} = \hat{H}_0 + \lambda\hat{H}_p$ → perturbation

and the possible solution as $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$??

$$|\psi_n\rangle = |\psi_{n0}\rangle + \lambda|\psi_{n1}\rangle + \lambda^2|\psi_{n2}\rangle + \cdots \quad \left[\Rightarrow \int_{-\infty}^{\infty}|\psi_{n0}(x)|^2dx \gg \int_{-\infty}^{\infty}|\psi_{n1}(x)|^2dx \gg \int_{-\infty}^{\infty}|\psi_{n2}(x)|^2dx \cdots\right]$$
$$E_n = E_{n0} + \lambda E_{n1} + \lambda^2 E_{n2} + \cdots \quad \left[\Rightarrow E_{n0} \gg E_{n1} \gg E_{n2} \cdots\right]$$

Now $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

$$\Rightarrow (\hat{H}_0 + \lambda\hat{H}_p)\left[|\psi_{n0}\rangle + \lambda|\psi_{n1}\rangle + \lambda^2|\psi_{n2}\rangle + \cdots\right] = \left[E_{n0} + \lambda E_{n1} + \lambda^2 E_{n2} + \cdots\right]\left[|\psi_{n0}\rangle + \lambda|\psi_{n1}\rangle + \lambda^2|\psi_{n2}\rangle + \cdots\right]$$

like powers of λ on each side should be the same.

$$\hat{H}_0|\psi_{n0}\rangle + \lambda\left[\hat{H}_0|\psi_{n1}\rangle + \hat{H}_p|\psi_{n0}\rangle\right] + \lambda^2\left[\hat{H}_0|\psi_{n2}\rangle + \hat{H}_1|\psi_{n1}\rangle\right] + \cdots$$
$$= E_{n0}|\psi_{n0}\rangle + \lambda\left[E_{n0}|\psi_{n1}\rangle + E_{n1}|\psi_{n0}\rangle\right] + \lambda^2\left[E_{n0}|\psi_{n2}\rangle + E_{n1}|\psi_{n1}\rangle + E_{n2}|\psi_{n0}\rangle\right] + \cdots$$

$$\Rightarrow \hat{H}_0|\psi_{n0}\rangle = E_{n0}|\psi_{n0}\rangle \quad \text{——— (1)}$$
$$\hat{H}_0|\psi_{n1}\rangle + \hat{H}_p|\psi_{n0}\rangle = E_{n0}|\psi_{n1}\rangle + E_{n1}|\psi_{n0}\rangle \quad \text{——— (2)}$$
$$\hat{H}_0|\psi_{n2}\rangle + \hat{H}_p|\psi_{n1}\rangle = E_{n0}|\psi_{n2}\rangle + E_{n1}|\psi_{n1}\rangle + E_{n2}|\psi_{n0}\rangle \quad \text{——— (3)}$$

Equation (1) is the schrödiger equation for the unperturbed Hamiltonian

First order corrections :

Eq (2) $\Rightarrow$
$$\hat{H}_0|\psi_{n1}\rangle + \hat{H}_p|\psi_{n0}\rangle = E_{n0}|\psi_{n1}\rangle + E_{n1}|\psi_{n0}\rangle$$

take the inner product with $|\psi_{n0}\rangle$, we get

$$\langle\psi_{n0}|\hat{H}_0|\psi_{n1}\rangle + \langle\psi_{n0}|\hat{H}_p|\psi_{n0}\rangle = E_{n0}\langle\psi_{n0}|\psi_{n1}\rangle + E_{n1}\overbrace{\langle\psi_{n0}|\psi_{n0}\rangle}^{=1}$$

$$\left[\hat{H}_0|\psi_{n0}\rangle = E_{n0}|\psi_{n0}\rangle \Rightarrow \langle\psi_{n0}|\hat{H}_0^{\dagger} = \langle\psi_{n0}|E_{n0}^{*} \Rightarrow \langle\psi_{n0}|\hat{H}_0 = \langle\psi_{n0}|E_{n0}\right]$$

$$\Rightarrow E_{n0}\langle\psi_{n0}|\psi_{n1}\rangle + \langle\psi_{n0}|\hat{H}_p|\psi_{n0}\rangle = E_{n0}\langle\psi_{n0}|\psi_{n1}\rangle + E_{n1}$$

$$\Rightarrow \boxed{E_{n1} = \langle\psi_{n0}|\hat{H}_p|\psi_{n0}\rangle}$$

→ first order correction to the energy is equal to the expectation value of the perturbation Hamiltonian in the unperturbed state.

What is the first order correction to the wave-function:

$$\text{Eq}^{n}(2) \Rightarrow \quad \hat{H}_0|\psi_{n1}\rangle + \hat{H}_p|\psi_{n0}\rangle = E_{n0}|\psi_{n1}\rangle + E_{n1}|\psi_{n0}\rangle$$

$$\text{or,} \quad (\hat{H}_0 - E_{n0})|\psi_{n1}\rangle = -(\hat{H}_p - E_{n1})|\psi_{n0}\rangle$$

Since $|\psi_{n0}\rangle$ forms a complete set $\sum_n |\psi_{n0}\rangle\langle\psi_{n0}| = I$, we can write $|\psi_{n1}\rangle$ in terms of $|\psi_{n0}\rangle$, that is,

$$|\psi_{n1}\rangle = \sum_m c_m |\psi_{m0}\rangle$$

$$\Rightarrow \sum_m (\hat{H}_0 - E_{n0}) c_m |\psi_{m0}\rangle = -(\hat{H}_p - E_{n1})|\psi_{n0}\rangle$$

$$\text{or,} \quad \sum_m (E_{m0} - E_{n0}) c_m |\psi_{m0}\rangle = -(\hat{H}_p - E_{n1})|\psi_{n0}\rangle$$

Take the inner product with $|\psi_{l0}\rangle$

$$\sum_m (E_{m0} - E_{n0}) c_m \langle\psi_{l0}|\psi_{m0}\rangle = -\langle\psi_{l0}|\hat{H}_p|\psi_{n0}\rangle + E_{n1}\langle\psi_{l0}|\psi_{n0}\rangle$$

If $l = n$

$$\sum_m (E_{m0} - E_{n0}) c_m \langle\psi_{n0}|\psi_{m0}\rangle = -\langle\psi_{n0}|\hat{H}_p|\psi_{n0}\rangle + E_{n1}\overbrace{\langle\psi_{n0}|\psi_{n0}\rangle}^{=1}$$

$$\text{or,} \quad \sum_m (E_{m0} - E_{n0}) c_m \delta_{nm} = -\langle\psi_{n0}|\hat{H}_p|\psi_{n0}\rangle + E_{n1}$$

$$\text{or,} \quad \sum_m (E_{m0} - E_{n0}) c_m \delta_{nm} = 0$$

$$\text{or,} \quad \sum_{m \neq n} (E_{m0} - E_{n0}) c_m \delta_{mn} + (E_{n0} - E_{n0}) c_n = 0$$

$$\text{or,} \quad 0 = 0$$

If $l \neq n$

$$\sum_m (E_{m0} - E_{n0}) c_m \langle\psi_{l0}|\psi_{m0}\rangle = -\langle\psi_{l0}|\hat{H}_p|\psi_{n0}\rangle + E_{n1}\overbrace{\langle\psi_{l0}|\psi_{n0}\rangle}^{=0}$$

$$\text{or,} \quad \sum_{m \neq n} (E_{m0} - E_{n0}) c_m \underbrace{\langle\psi_{l0}|\psi_{m0}\rangle}_{\delta_{lm}} + \cancel{(E_{n0} - E_{n0})} c_n \langle\psi_{l0}|\psi_{n0}\rangle = -\langle\psi_{l0}|\hat{H}_p|\psi_{n0}\rangle$$

$$\text{or} \quad (E_{l0} - E_{n0}) c_l = -\langle\psi_{l0}|\hat{H}_p|\psi_{n0}\rangle$$

$$\Rightarrow \boxed{c_l = \frac{\langle\psi_{l0}|\hat{H}_p|\psi_{n0}\rangle}{(E_{n0} - E_{l0})}}$$

$$\text{or,} \quad \boxed{c_m = \frac{\langle\psi_{m0}|\hat{H}_p|\psi_{n0}\rangle}{(E_{n0} - E_{m0})}} \quad m \neq n$$

What is c_n ?

what is C_m (when $m=n$)

we have $\quad |\psi_n\rangle = |\psi_{n0}\rangle + \lambda|\psi_{n1}\rangle \quad$ (with $\lambda = 1$)

- $|\psi_n\rangle$ is a solution to the Schrödinger equation $\hat{H}|\psi\rangle_n = E_n|\psi_n\rangle$
  Thus $|\psi_n\rangle$ is defined only to within a constant. We choose the ~~constant such that~~ amplitude of this constant such that
  $\langle\psi_n|\psi_n\rangle = 1$ and we choose the phase of this constant
  such that $\langle\psi_{n0}|\psi_n\rangle$ is real

with this take the inner product of the above equation with $\langle\psi_{n0}|$.
This gives

$$\langle\psi_{n0}|\psi_n\rangle = \overset{\simeq 0}{\langle\psi_{n0}|\psi_{m}\rangle} + \lambda\langle\psi_{n0}|\psi_{n1}\rangle$$

since left side is real and λ on the right side is
real, we have $\langle\psi_{n0}|\psi_{n1}\rangle$ as real.

Now, take the inner product of the above equation with itself. We get.

$$\langle\psi_n|\psi_n\rangle = \langle\psi_{n0}|\psi_{n0}\rangle + \lambda\langle\psi_{n0}|\psi_{n1}\rangle + \lambda\langle\psi_{n1}|\psi_{n0}\rangle + \lambda^2\langle\psi_{n1}|\psi_{n1}\rangle$$

$$\text{or,}\quad 1 = 1 + \lambda\left[\langle\psi_{n0}|\psi_{n1}\rangle + \langle\psi_{n1}|\psi_{n0}\rangle\right] + 0$$

$$\Rightarrow \langle\psi_{n0}|\psi_{n1}\rangle = 0 \quad \Rightarrow \quad \langle\psi_{n0}|\Big\{\sum_m C_m|\psi_{m0}\rangle\Big\} = 0$$

$$\text{or,}\quad \sum_m C_m\langle\psi_{n0}|\psi_{m0}\rangle = 0$$

$$\text{or,}\quad \sum_m C_m\delta_{mn} = 0 \quad \Rightarrow \quad \boxed{C_n = 0}$$

$$\therefore \boxed{|\psi_{n1}\rangle = \sum_{m\neq n} C_m|\psi_{m0}\rangle = \sum_{m\neq n}\frac{\langle\psi_{m0}|\hat{H}_p|\psi_{n0}\rangle}{E_{n0}-E_{m0}}}$$

$\longrightarrow$ This is the first-order correction to the wave-function

Second-order correction (in energy)

$$(3) \Rightarrow \hat{H}_0|\psi_{n2}\rangle + \hat{H}_p|\psi_{n1}\rangle = E_{n0}|\psi_{n2}\rangle + E_{n1}|\psi_{n1}\rangle + E_{n2}|\psi_{n0}\rangle$$

take the inner product with $|\psi_{n0}\rangle$

$$\langle\psi_{n0}|\hat{H}_0|\psi_{n2}\rangle + \langle\psi_{n0}|\hat{H}_p|\psi_{n1}\rangle = E_{n0}\langle\psi_{n0}|\psi_{n2}\rangle + E_{n1}\langle\psi_{n0}|\psi_{n1}\rangle + E_{n2}\overset{=1}{\langle\psi_{n0}|\psi_{n0}\rangle}$$

$$\text{or,}\quad \cancel{E_{n0}\langle\psi_{n0}|\psi_{n2}\rangle} + \langle\psi_{n0}|\hat{H}_p|\psi_{n1}\rangle = \cancel{E_{n0}\langle\psi_{n0}|\psi_{n2}\rangle} + E_{n1}\langle\psi_{n0}|\psi_{n1}\rangle + E_{n2}$$

But $\langle\psi_{n0}|\psi_{n1}\rangle = \langle\psi_{n0}|\sum_{n\neq n} C_m|\psi_{m0}\rangle = 0$

therefore,

$$E_{n2} = \langle\psi_{n0}|\hat{H}_p|\psi_{n1}\rangle = \langle\psi_{n0}|\hat{H}_p|\sum_{m\neq n} C_m|\psi_{m0}\rangle$$

$$= \sum_{m\neq n} C_m\langle\psi_{n0}|\hat{H}_p|\psi_{m0}\rangle = \sum_{m\neq n}\frac{\langle\psi_{m0}|\hat{H}_p|\psi_{n0}\rangle}{E_{n0}-E_{m0}}\cdot\langle\psi_{n0}|\hat{H}_p|\psi_{m0}\rangle$$

$$\therefore \boxed{E_{n2} = \sum_{m\neq n}\frac{|\langle\psi_{m0}|\hat{H}_p|\psi_{n0}\rangle|^2}{E_{n0}-E_{m0}}}$$

$\longrightarrow$ One can go on calculating like this up to n^{th} order.