Second order Energy corrections

$$H^0|\psi_n^2\rangle + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

Take IP with $\langle\psi_n^0|$

$$\underbrace{\langle\psi_n^0|H^0|\psi_n^2\rangle}_{1} + \underbrace{\langle\psi_n^0|H'|\psi_n^1\rangle}_{2} = \underbrace{\langle\psi_n^0|E_n^0|\psi_n^2\rangle}_{3} + \underbrace{\langle\psi_n^0|E_n^1|\psi_n^1\rangle}_{4} + \underbrace{\langle\psi_n^0|E_n^2|\psi_n^0\rangle}_{5}$$

But $\langle\psi_n^0|H^0|\psi_n^2\rangle = \langle H^0\psi_n^0|\psi_n^2\rangle = \langle E_n^0\psi_n^0|\psi_n^2\rangle$

So $1 = 3$

or $\langle\psi_n^0|H'|\psi_n^1\rangle = \langle\psi_n^0|E_n^1|\psi_n^1\rangle + \langle\psi_n^0|E_n^2|\psi_n^0\rangle$

but $\langle\psi_n^0|E_n^2|\psi_n^0\rangle = E_n^2\langle\psi_n^0|\psi_n^0\rangle = E_n^2$

or $E_n^2 = \langle\psi_n^0|H'|\psi_n^1\rangle - \langle\psi_n^0|E_n^1|\psi_n^1\rangle$

but $\langle\psi_n^0|E_n^1|\psi_n^1\rangle = E_n^1\langle\psi_n^0|\psi_n^1\rangle = E_n^1\sum_{m\neq n} C_m^{(n)}\langle\psi_n^0|\psi_m^0\rangle = 0$

So $E_n^2 = \langle\psi_n^0|H'|\psi_n^1\rangle$

but $$\psi_n^1 = \sum_{m\neq n}\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle$$

↑ ket can be moved

↖ # $C_m^{(n)}$

$$\psi_n^1 = \sum_{m\neq n}|\psi_m^0\rangle\frac{\langle\psi_m^0|H'|\psi_n^0\rangle}{E_n^0 - E_m^0}$$ So

$$E_n^2 = \sum_{m \neq n} \frac{\langle \psi_n^0 | H' | \psi_m^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}$$

$$\boxed{\text{Or} \quad E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n - E_m}}$$

Procedure $\rightarrow$ Calculate $\dfrac{\left(\int \psi_m^0 H' \psi_n^0 \, dx\right)^2}{E_n - E_m}$ For all $m \neq n$

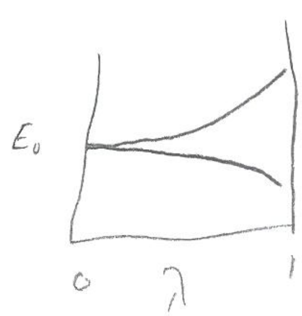
E_n^2 is the Sum For $H' = \alpha \delta(x - \frac{a}{2})$ in ISW $\langle \psi_m^0 | H' | \psi_n^0 \rangle = \frac{2\alpha}{a} \sin(\frac{m\pi}{2}) \sin(\frac{n\pi}{2})$

<u>Degenerate Perturbation theory</u>

What if $H^0 \psi_a^0 = E^0 \psi_a^0$ and $H^0 \psi_b^0 = E^0 \psi_b^0$ 2 ψ's Same Energy?

$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0 \rightarrow$ Same $H^0 \psi^0 = E^0 \psi^0$ note $\langle \psi_a | \psi_b \rangle = 0$

$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$ but what ψ^0? $\alpha = ?$ $\beta = ?$



H' Splits

Evidently 2 states are $\alpha \psi_a^0 + \beta \psi_b^0 \rightarrow$ upper energy $\delta \psi_a^0 - \gamma \psi_b^0 \rightarrow$ lower energy

go back to $\hat{H}\psi = E\psi$ with $\hat{H} = \hat{H}_0 + \lambda H'$, $E = E^0 + \lambda E' + \lambda^2 E^2 + \dots$

$\psi = \psi^0 + \lambda \psi' + \lambda^2 \psi^2, \dots$

gives $\underset{1}{H^0\psi^0} + \lambda(\underset{2}{H'\psi_0 + H^0\psi'}) + \dots = \underset{3}{E^0\psi^0} + \lambda(\underset{4}{E'\psi^0 + E^0\psi'}) + \dots$

$1 = 3$ so $H'\psi_0 + H^0\psi' = E'\psi^0 + E^0\psi'$

1) Take IP with $\langle \psi_a^0 |$

$\underset{1}{\langle \psi_a^0 | H' | \psi_0 \rangle} + \underset{2}{\langle \psi_a^0 | H^0 | \psi' \rangle} = \underset{3}{\langle \psi_a^0 | E' | \psi^0 \rangle} + \underset{4}{\langle \psi_a^0 | E^0 \psi' \rangle}$

$2 = 4$ $\langle \psi_a^0 | H' | \psi_0 \rangle = \langle \psi_a^0 | E' | \psi^0 \rangle$

or $\langle \psi_a^0 | H' | \psi_0 \rangle = E' \langle \psi_a^0 | \psi^0 \rangle$

or $\langle \psi_a^0 | H' | \psi_0 \rangle = E' \left[\underbrace{\langle \psi_a^0 | \alpha \psi_a^0 \rangle}_{\alpha} + \underbrace{\langle \psi_a^0 | \beta | \psi_b^0 \rangle}_{0} \right]$

$$\boxed{\langle \psi_a^0 | H' | \psi_0 \rangle = \alpha E'}$$

Expanding $\langle \psi_a^0 | H' | \alpha \psi_a^0 \rangle + \langle \psi_a^0 | H' | \beta \psi_B^0 \rangle = \alpha E'$

or $\boxed{\alpha W_{aa} + \beta W_{ab} = \alpha E'}$

where $W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$ $i = a$ $j = b$

Starting at 1) and taking IP with $\langle \psi_b^0|$

$$\boxed{\alpha W_{ba} + \beta W_{bb} = \beta E'} \rightarrow \alpha \langle \psi_b^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_b^0 | H' | \psi_b^0 \rangle$$

$$\begin{pmatrix} \alpha W_{aa} & \beta W_{ab} \\ \alpha W_{ba} & \beta W_{bb} \end{pmatrix} = \begin{pmatrix} \alpha E' \\ \beta E' \end{pmatrix}$$ How to Solve?

$$(\alpha W_{ba} + \beta W_{bb}) W_{ab} = W_{ab} \beta E' \qquad \beta W_{ab} = \alpha E' - \alpha W_{aa}$$

$$\alpha W_{ba} W_{ab} + \beta W_{ab} (W_{BB}) - \beta W_{ab} E' = 0$$

$$\alpha W_{ba} W_{ab} + \beta W_{ab} [W_{BB} - E'] = 0$$

$$\alpha W_{ba} W_{ab} + \alpha (E' - W_{aa})(W_{bb} - E') = 0$$

$$\alpha [W_{ba} W_{ab} + (E' - W_{aa})(W_{bb} - E')] = 0$$

For $\alpha \neq 0$ $(E')^2 - E'(W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0$

$$\boxed{\text{or} \quad E'_{\pm} = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 - 4|W_{ab}|^2}\right]}$$

if $\alpha = 0$ $\beta = 1$ and $W_{ab} = 0$

if $\beta = 0$ $\alpha = 1$ and $W_{ba} = 0$

So $E_\pm = \frac{1}{2}\left[W_{aa} + W_{bb} \pm (W_{aa} - W_{bb})\right]$

$$= \underset{\alpha=1}{W_{aa}},\ \underset{\beta=1}{W_{bb}}$$

Silly Way to do it

For n Fold degeneracy make $n \times n$ matrix

$\psi_0 = \alpha\psi_a^0 + \beta\psi_b^0 \rightarrow$ $\begin{array}{l}\alpha W_{aa} + \beta W_{ab} = \alpha E' \\ \alpha W_{ba} + \beta W_{bb} = \beta E'\end{array} \longrightarrow \begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} + & W_{bb} \end{pmatrix}\begin{pmatrix}\alpha \\ \beta\end{pmatrix} = E\begin{pmatrix}\alpha \\ \beta\end{pmatrix}$

$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle \quad i,j = a,b$

Solve eigen value equation $(W_{aa} - \lambda)(W_{bb} - \lambda) - W_{ab}W_{ba}$

done

Ex. 3D Cube

$V(x,y,z) = 0$ inside $[a,a,a]$

∞ else

$$\psi^0_{n_x,n_y,n_z} = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

$$E^0_{n_x,n_y,n_z} = \underbrace{\frac{\pi^2\hbar^2}{2ma^2}}_{k}(n_x^2+n_y^2+n_z^2)$$

$$E_0^0 \to \psi_{111} = 3k$$

1st State E_1^0 3 Fold degenerate $\underset{\psi_a}{\psi_{112}}, \underset{\psi_b}{\psi_{121}}, \underset{\psi_c}{\psi_{211}} \to 6k$

Let $H' = \begin{cases} V_0 & x \in [0, a/2] \quad y \in [0, a/2] \\ 0 & \text{else} \end{cases}$

$$E_0^1 = \langle \psi_{111} | H' | \psi_{111} \rangle = \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi x}{a}\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi y}{a}\right) \int_0^{a} \sin^2\left(\frac{\pi z}{a}\right) dz$$

$$E_0^1 = \frac{1}{4} V_0$$

Want $\begin{pmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{pmatrix}$ $W_{aa} = W_{bb} = W_{cc} = \frac{V_0}{4}$

calculate rest $\to$ Show example

$k = \left(\frac{8}{3\pi}\right)^2$

$$W = \frac{V_0}{4} \left\| \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & k \\ 0 & k & 1 \end{pmatrix} \right\| \to (1-\lambda)\left[(1-\lambda)^2 - k^2\right]$$

$$\to (1-\lambda)^3 - (1-\lambda)k^2 = 0 \qquad \lambda = 1,\ 1-k,\ 1+k$$

$$(1-\lambda)^2 = k^2$$

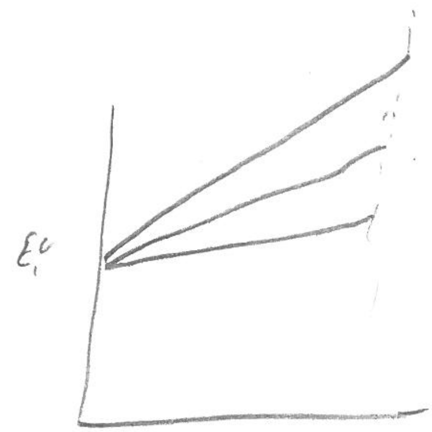
$$1-\lambda = \pm k$$

$$1 \mp k = \lambda$$

So $E_1 = E_1^0 + \frac{V_0}{4}, \quad E_1^0 + (1+k)\frac{V_0}{4}, \quad E_1^0 + (1-k)\frac{V_0}{4}$

and $\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0 + \gamma\psi_c^0$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & k \\ 0 & k & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \omega\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$



$$\psi_0 = \begin{cases} \psi_a \\ (\psi_b + \psi_c)/\sqrt{2} \\ (\psi_b - \psi_c)/\sqrt{2} \end{cases}$$