Non-degenerate perturbation theory

$\hat{H}^{(0)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ $\qquad \hat{H} = \hat{H}_0^{(0)} + \hat{H}'$

$V_{nm} = \langle \psi_n^{(0)} | \hat{H}' | \psi_m^{(0)} \rangle$

Order	Energy	Wave function
1	$E_n^{(1)} = V_{nn}$	$\psi_n^{(1)} = \sum_{m \neq n} \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$
2	$E_n^{(2)} = \sum_{m \neq n} \frac{\lvert V_{mn} \rvert^2}{E_n^{(0)} - E_m^{(0)}}$	...

Let's look at a two-level system:

$E_1^{(0)}, \psi_1^{(0)}$
$E_2^{(0)}, \psi_2^{(0)}$

$H_{nm}^{(0)} = \langle \psi_m | \hat{H}^{(0)} \psi_n^{(0)} \rangle = E_n \delta_{mn}$

$\hat{H}^{(0)} = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix}$ diagonal in the eigenbasis

Similarly, $\hat{H}' = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$

If $\hat{H}'$ is diagonal: $V_{12} = V_{21} = 0$ $\qquad \hat{H}' = \begin{pmatrix} V_{11} & 0 \\ 0 & V_{22} \end{pmatrix}$

Then: $E_{1,2}^{(1)} = V_{11}$ or V_{22} $\qquad \psi_n^{(1)} = 0$

Wavefunctions do not change in the first order!

If $\hat{H}'$ is diagonal $\leftrightarrow$ $\psi_{1,2}$ are its eigenfunctions!

$\hat{H}' \psi_1 = V_{11} \psi_1$

$\hat{H}' \psi_2 = V_{22} \psi_2$

So in general if $\{\psi_n^{(0)}\}$ are the eigenfunctions of both $\hat{H}^{(0)}$ and $\hat{H}'$, then only energy states are shifted

$E_n = E_n^{(0)} + V_{nn}^{(0)}$

But what if $V_{11} = V_{22} = 0$ $\quad V_{12} = V_{21}^*$

$$\hat{H}' = \begin{pmatrix} 0 & V_{12} \\ V_{21} & 0 \end{pmatrix}$$ Stark

First-order correction to the wave function

$$c_{12} = \frac{V_{12}}{E_1^{(0)} - E_2^{(0)}} \qquad \psi_1 = \psi_1^{(0)} + \frac{V_{21}}{E_1^{(0)} - E_2^{(0)}} \psi_2^{(0)}$$

$$E_{1,2}^{(2)} = |V_{21}|^2 / (E_{1,2}^{(0)} - E_{2,1}^{(0)})$$ quadratic correction

With an off-diagonal perturbation the states get mixed.

But let's solve the two-level system exactly:

$$\hat{H} = \begin{pmatrix} E_1^{(0)} & V_{12} \\ V_{21} & E_2^{(0)} \end{pmatrix} \qquad \hat{H}\psi_n = E_n\psi_n \Rightarrow (\hat{H} - E_n)\psi_n = 0$$

$$\det \begin{vmatrix} E_1^{(0)} - E_n & V_{12} \\ V_{21} & E_2^{(0)} - E_n \end{vmatrix} = 0$$

$$E_{1,2} = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \sqrt{\frac{(E_1^{(0)} - E_2^{(0)})^2}{4} + |V_{12}|^2}$$

as $|E_1^{(0)} - E_2^{(0)}| \gg V_{1,2}$ (perturbation limit)

$$\sqrt{\frac{(E_1^{(0)} - E_2^{(0)})^2}{4} + |V_{12}|^2} \approx \frac{E_1^{(0)} - E_2^{(0)}}{2} \sqrt{1 + \frac{4|V_{12}|^2}{(E_1^{(0)} - E_2^{(0)})^2}} \approx$$

$$\approx \frac{(E_1^{(0)} - E_2^{(0)})}{2} \left(1 \pm \frac{1}{2} \frac{4|V_{12}|^2}{(E_1^{(0)} - E_2^{(0)})^2} \cdots\right) \approx$$

$$E_1 \approx E_1^{(0)} + \frac{|V_{12}|^2}{E_1^{(0)} - E_2^{(0)}} = (\text{if } E_2^{(0)} > E_1^{(0)}) = E_1^{(0)} - \frac{|V_{12}|^2}{E_2^{(0)} - E_1^{(0)}}$$

$$E_2 \approx E_2^{(0)} - \frac{|V_{12}|^2}{E_1^{(0)} - E_2^{(0)}} = \cdots = E_2^{(0)} + \frac{|V_{12}|^2}{E_2^{(0)} - E_1^{(0)}}$$

$E_2^{(0)}$ —— $+ \hat{H}' \Rightarrow$ ═══ ↑ two states

$E_1^{(0)}$ —— ═══ ↓ push apart, $\Delta E = \frac{|V_{12}|^2}{E_2^{(0)} - E_1^{(0)}}$

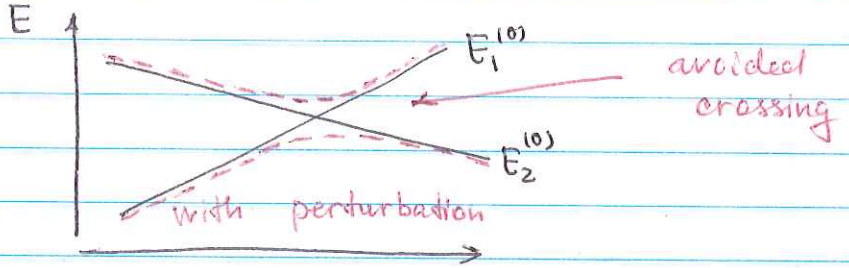
But what if $E_1^{(0)} = E_2^{(0)} = E^{(0)} \Rightarrow E_1^{(0)} - E_2^{(0)} = 0$

$$E_{1,2} = E_i^{(0)} \pm |V_{12}|$$

E_0 — $|\psi_1\rangle$, $|\psi_2\rangle$ — $+\hat{H}'$ $\Rightarrow$ $\uparrow |V_{12}|$, $\downarrow |V_{12}|$

linear shift

Perturbation makes level "repel" each other



So how can we obtain this result using the perturbation theory?

Let's consider a degenerate two-level system: $E^{(0)}$, $\{\psi_1^{(0)}, \psi_2^{(0)}\}$
(For simplicity let's say $E^{(0)} = E_0$)
Note that <u>any</u> normalized superposition of $\psi_1^{(0)}$ and $\psi_2^{(0)}$ is also an eigenfunction of $\hat{H}^{(0)}$! So in case of a degenerate system we are free to choose the exact two state we can use.
So we will use them such that the perturbation Hamiltonian is diagonal in this basis; then calculating the level shifts is easy!

$$\hat{V} = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \longrightarrow \begin{matrix} \tilde{\psi}_1^{(0)} = \alpha_1 \psi_1^{(0)} + \beta_1 \psi_2^{(0)} \\ \tilde{\psi}_2^{(0)} = \alpha_2 \psi_2^{(0)} + \beta_2 \psi_2^{(0)} \end{matrix}$$

$\psi_1^{(0)}, \psi_2^{(0)}$

$$\hat{V} = \begin{pmatrix} \tilde{V}_{11} & 0 \\ 0 & \tilde{V}_{22} \end{pmatrix}$$

shift for $\tilde{\psi}_1^{(0)}$
shift for $\tilde{\psi}_2^{(0)}$

So The general steps to calculate the energy ~~state~~ level corrections for degenerate case

1. Identify the subset of degenerate eigenstates of $\hat{H}^{(0)}$: $\psi_1^{(0)}, \ldots \psi_N^{(0)}$ for N-degenerate state

2. Find the N linear combinations of the original states that are also eigenvalues of $\hat{H}'$: $\tilde{\psi} = c_1\psi_1^{(0)} + c_2\psi_2^{(0)} + \ldots c_N\psi_N^{(0)}$

$\hat{H}'\tilde{\psi} = \lambda\tilde{\psi}$ → eigenvalues give the diagonal matrix elements, and eigenfunctions – the new basis $\tilde{\psi}_1^{(0)} \ldots \tilde{\psi}_n^{(0)}$. These functions are simultaneously the eigenfunctions of both $\hat{H}_0$ and $\hat{H}'$

$$\hat{H}_0\tilde{\psi}_i^{(0)} = E_0\tilde{\psi}_i^{(0)}$$

$$\hat{H}_0 = \begin{pmatrix} E_0 & & 0 \\ & E_0 & \\ 0 & & E_0 \end{pmatrix}$$

$$\hat{V} = \begin{pmatrix} V_{11} & & \\ & V_{22} & \\ & & V_{NN} \end{pmatrix}$$

Thus, each new state $\tilde{\psi}_i$ is shifted by V_{ii}

Let's come back to the original two-level system with

$$\hat{V} = \begin{pmatrix} 0 & V_{12} \\ V_{21} & 0 \end{pmatrix} \qquad \psi_1^{(0)}, \psi_2^{(0)} \text{ – original states}$$

(I'll skip (0) for now)

$$\tilde{\psi} = \alpha\psi_1 + \beta\psi_2$$

$$\hat{V}\tilde{\psi} = \lambda\tilde{\psi} \qquad \begin{pmatrix} -\lambda & V_{12} \\ V_{12} & -\lambda \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

$$\det \begin{vmatrix} -\lambda & V_{12} \\ V_{12} & -\lambda \end{vmatrix} = 0 \qquad \lambda_{1,2} = \pm |V_{12}|$$

For simplicity, let's assume that V_{12} is real and positive

$\lambda_1 = V_{12}$: $\begin{pmatrix} -V_{12} & V_{12} \\ V_{12} & -V_{12} \end{pmatrix}\begin{pmatrix} \alpha_1 \\ \beta_1 \end{pmatrix} = 0$ $\quad \alpha_1 = \beta_1$

$$\tilde{\psi}_1 = \frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{2}}\psi_2$$

$\lambda_2 = -V_{12}$ $\begin{pmatrix} +V_{12} & V_{12} \\ V_{12} & V_{12} \end{pmatrix}\begin{pmatrix} \alpha_2 \\ \beta_2 \end{pmatrix} = 0$ $\quad \alpha_2 = -\beta_2$

$$\tilde{\psi}_2 = \frac{1}{\sqrt{2}}\psi_1 - \frac{1}{\sqrt{2}}\psi_2$$

State $\tilde{\psi}_1 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$ is shifted up $E^{(1)} = V_{12}$

State $\tilde{\psi}_2 = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$ — " — down $E^{(2)} = -V_{12}$

Sometimes we can find the right basis using physics, rather than math! If we can identify a hermitian operator, that commute both with $\hat{H}^{(0)}$ and $\hat{H}'$, then $\hat{H}'$ will be diagonal in the basis of the eigenfunctions of $\hat{A}$: