P423, Lecture 5 : Perturbation theory (nondegenerate, degenerate)

(Griffiths 6.1 and 6.2)

Most realistic problems can not be solved exactly. We always have to resort to approximation methods:

1) Perturbation theory : Allows the calculation of energy eigenvalues and eigenstates when the problem differs from an exactly solvable problem by a small amount.

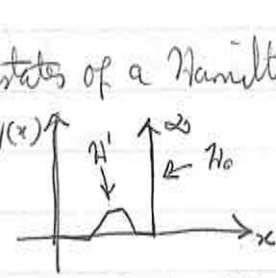
2) Variational Principle : Allows the calculation of the ground state wavefunction and its energy if we have a qualitative idea of the answer.

3) WKB or semiclassical method : Allows the solution of problems when they are in the semi-classical limit.

Perturbation theory : Non-degenerate case

We want to find the eigenenergies and eigenstates of a Hamiltonian like

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{H}'$$



where we know the exact eigenenergies and eigenstates of $\mathcal{H}_0$:

$$\mathcal{H}_0 \underbrace{|n^0\rangle}_{\text{"unperturbed eigenstates"}} = \underbrace{E_n^0}_{\text{"unperturbed energies"}} |n^0\rangle$$

We assume for now that the E_n^0 are all different (non-degenerate).
$\mathcal{H}'$ is called a "small perturbation"; we also introduce λ that we can think of

as a "small parameter" but later we will take $\lambda \to 1$ and this will give us a correction to the energies.

We want to find: $(H_0 + \lambda H')\,|n\rangle = E_n |n\rangle$

So we propose the expansion

$$|n\rangle = |n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \lambda^3 |n^3\rangle + \dots$$

(Can assume $\langle n^0 | n^i \rangle = 0$ for $i \geq 1$, because any $|n^0\rangle$ component in $|n^i\rangle$ can be combined with 1st term).

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \lambda^3 E_n^3 + \dots$$

Plug this into $H|n\rangle = E_n |n\rangle$:

$$(H_0 + \lambda H')\left(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \lambda^3 |n^3\rangle + \dots\right) =$$

$$= \left(E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \lambda^3 E_n^3 + \dots\right)\left(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + \dots\right)$$

Collect terms in powers of λ:

$$\cancel{H_0 |n^0\rangle} + \lambda\left(H_0 |n^1\rangle + H' |n^0\rangle\right) + \lambda^2\left(H_0 |n^2\rangle + H' |n^1\rangle\right) + \dots$$

$$= \cancel{E_n^0 |n^0\rangle} + \lambda\left(E_n^0 |n^1\rangle + E_n^1 |n^0\rangle\right) + \lambda^2\left(E_n^0 |n^2\rangle + E_n^1 |n^1\rangle + E_n^2 |n^0\rangle\right) + \dots$$

Hence we get to 1st order:

$$H_0 |n^1\rangle + H' |n^0\rangle = E_n^0 |n^1\rangle + E_n^1 |n^0\rangle \qquad (1)$$

And to 2nd order:

$$H_0 |n^2\rangle + H' |n_1\rangle = E_n^0 |n^2\rangle + E_n^1 |n^1\rangle + E_n^2 |n^0\rangle \qquad (2)$$

We can now take $\lambda \to 1$; we only needed λ to keep track of the orders.

Take the inner product with $\langle n^0|$ in the Eq (1):

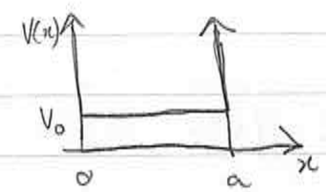
$$\underbrace{\langle n^0|H_0|n^1\rangle}_{= E_n^0 \cancel{\langle n^0|n^1\rangle}} + \langle n^0|H^1|n^0\rangle = \cancel{E_n^0 \langle n^0|n^1\rangle} + E_n^1 \underbrace{\langle n^0|n^0\rangle}_{=1}$$

$$\Rightarrow \boxed{E_n^1 = \langle n^0|H^1|n^0\rangle}$$ First order correction to the energy.

Example:

H_0 is infinite square well, $\langle x|n^0\rangle = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi}{a}x\right)$ $(n = 1, 2, 3, \dots)$

(a) $H^1 = V_0$



$$\Rightarrow E_n^1 = \langle n^0|H^1|n^0\rangle = V_0 \langle n^0|n^0\rangle = V_0 \longrightarrow E_n = E_n^0 + V_0 \quad (\text{exact!})$$

(b) $H^1 = \begin{cases} V_0 & \text{for } 0 < x < a/2 \\ 0 & \text{for } x \geq a/2 \end{cases}$

$$E_n^1 = \langle n^0|H^1|n^0\rangle = \int_0^{a/2} dx\, \psi_n^{0*}(x)\, V_0\, \psi_n^0(x) = V_0 \frac{2}{a}\int_0^{a/2} dx\, \underbrace{\sin^2\left(\frac{n\pi}{a}x\right)}_{=\frac{1}{2}\left[1 - \cos\left(\frac{2n\pi}{a}x\right)\right]}$$

$$= \frac{\cancel{2}V_0}{a}\,\frac{1}{\cancel{2}}\left[x - \frac{a}{2n\pi}\sin\left(\frac{2n\pi}{a}x\right)\right]_0^{a/2} = \frac{V_0}{a}\,\frac{a}{2} = \frac{V_0}{2}$$

$$\Rightarrow E_n \simeq E_n^0 + \frac{V_0}{2} + \underbrace{\cdots}_{\text{higher order corrections.}}$$

1st order correction to eigenstate:

Rewrite Eq (1): $$(\mathcal{H}_0 - E_n^0)\underbrace{|n^1\rangle}_{\text{unknown fnc}} = -\underbrace{(\mathcal{H}' - E_n^1)|n^0\rangle}_{\text{Known fnc}}$$

This gives rise to a differential eqn for $|n^1\rangle$ that can be solved.

Let's write an expansion for $|n^1\rangle$: $$|n^1\rangle = \sum_{m\neq n} c_m^{(n)} |m^0\rangle$$

(Note: From def. of $|n^1\rangle$, $|n^0\rangle$ is not included).

Plug into Eq (1):

$$(\mathcal{H}_0 - E_n^0) \sum_{m\neq n} c_m^{(n)} |m^0\rangle = -(\mathcal{H}' - E_n^1)|n^0\rangle$$

$$\sum_{m\neq n} (E_m^0 - E_n^0)\, c_m^{(n)} |m^0\rangle = -(\mathcal{H}' - E_n^1)|n^0\rangle$$

Dot with $\langle m^0|$:

$$(E_m^0 - E_n^0)\, c_m^{(n)} = -\langle m^0|(\mathcal{H}' - E_n^1)|n^0\rangle = -\langle m^0|\mathcal{H}'|n^0\rangle + E_n^1 \underbrace{\langle m^0|n^0\rangle}_{=0}$$

$$\Rightarrow \quad c_m^{(n)} = -\frac{\langle m^0|\mathcal{H}'|n^0\rangle}{(E_m^0 - E_n^0)} \quad \text{and}$$

$$\boxed{|n^1\rangle = -\sum_{m\neq n} |m^0\rangle \frac{\langle m^0|\mathcal{H}'|n^0\rangle}{(E_m^0 - E_n^0)}}$$

Note: If one of the $E_m^0 = E_n^0$ we would get ∞! Only works in non-degenerate case.

Using this we can find the E_n^2, 2nd order correction to energy:

Dot Eq(2) with $\langle n^0|$:

$$\underbrace{\langle n^0|H_0|n^2\rangle}_{=E_n^0\langle n^0|n^2\rangle = 0} + \langle n^0|H'|n^1\rangle = E_n^0 \cancelto{0}{\langle n^0|n^2\rangle} + E_n^1 \cancelto{0}{\langle n^0|n^1\rangle} + E_n^2 \underbrace{\langle n^0|n^0\rangle}_{=1}$$

$$\Rightarrow \quad E_n^2 = \langle n^0|H'|n^1\rangle = \langle n^0|H'\left(-\sum_{m\neq n} |m^0\rangle \frac{\langle m^0|H'|n^0\rangle}{(E_m^0 - E_n^0)}\right)$$

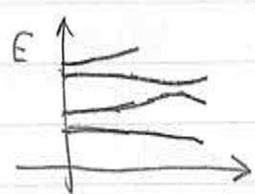
$$= -\sum_{m\neq n} \frac{\langle n^0|H'|m^0\rangle\langle m^0|H'|n^0\rangle}{(E_m^0 - E_n^0)}$$

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

Remarks: (i) For ground state, 2nd order shift is always negative (For all H'!)

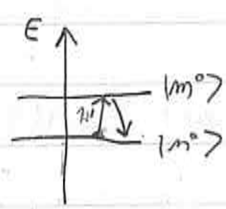
(ii) If matrix elements of H' are comparable, neighboring levels always make a larger contribution to energy shift.

(iii) Levels tend to repel each other



Physical interpretation of

$$|n\rangle \approx |n^0\rangle + |n^1\rangle = |n^0\rangle - \sum_{m\neq n} |m^0\rangle \frac{\langle m^0|H'|n^0\rangle}{(E_m^0 - E_n^0)}$$



"Virtual transition" from $|n^0\rangle$ to $|m^0\rangle$ with probability $\left|\frac{\langle m^0|H'|n^0\rangle}{(E_m^0 - E_n^0)}\right|^2$. More formal picture later with time dependent pert theory.

Degenerate perturbation theory

Consider a degenerate subspace $\{|n^0_a\rangle, |n^0_b\rangle, |n^0_c\rangle, \dots\}$ such that $\mathcal{H}_0|n^0_i\rangle = E_0|n^0_i\rangle$.
We showed that perturbation theory is an expansion in powers of $\lambda \dfrac{\langle m^0|\mathcal{H}'|n^0\rangle}{(E^0_m - E^0_n)}$.

Hence the only way to avoid getting $\frac{1}{0}$'s is to force

$\langle m^0|\mathcal{H}'|n^0\rangle$ to be zero. In otherwords, we need to find a new basis

$$\{|n^0_i\rangle\} \to \{|n^0_\alpha\rangle\} \quad \text{where}$$

$$\langle n^0_\alpha|\mathcal{H}'|n^0_\beta\rangle = H'_\alpha\, \delta_{\alpha\beta}$$

This is achieved by diagonalizing $\mathcal{H}'$ in the degenerate subspace.

Example: Two level system

$$\begin{aligned}\mathcal{H}_0|0\rangle &= E_0|0\rangle\\ \mathcal{H}_0|1\rangle &= E_0|1\rangle\end{aligned} \Rightarrow [\mathcal{H}_0] = \begin{pmatrix}\langle 0|\mathcal{H}_0|0\rangle & \langle 0|\mathcal{H}_0|1\rangle\\ \langle 1|\mathcal{H}_0|0\rangle & \langle 1|\mathcal{H}_0|1\rangle\end{pmatrix} = \begin{pmatrix}E_0 & 0\\ 0 & E_0\end{pmatrix}$$

Assume $$\begin{aligned}\mathcal{H}'|0\rangle &= V|1\rangle\\ \mathcal{H}'|1\rangle &= V^*|0\rangle\end{aligned} \Rightarrow [\mathcal{H}'] = \begin{pmatrix}0 & V^*\\ V & 0\end{pmatrix}$$

Diagonalize $\mathcal{H}'$: $\quad \det[\mathcal{H}' - \lambda\mathbb{1}] = \begin{vmatrix}-\lambda & V^*\\ V & -\lambda\end{vmatrix} = \lambda^2 - |V|^2 = 0 \Rightarrow \lambda_\pm = \pm|V|$

Energies: $E_\pm = E_0 \pm |V|$.

Eigenstates:

$$\begin{pmatrix}0 & V^*\\ V & 0\end{pmatrix}\begin{pmatrix}\alpha_\pm\\ \beta_\pm\end{pmatrix} = E_\pm\begin{pmatrix}\alpha_\pm\\ \beta_\pm\end{pmatrix} \Rightarrow \begin{cases}V^*\beta_\pm = E_\pm\alpha_\pm\\ V\alpha_\pm = E_\pm\beta_\pm\end{cases} \Rightarrow \frac{\beta_\pm}{\alpha_\pm} = \frac{E_\pm}{V^*} = \frac{\pm\sqrt{VV^*}}{V^*} = \pm\sqrt{\frac{V}{V^*}}.$$

Assume $V = V_0 e^{i\theta} \Rightarrow \begin{pmatrix}\alpha_+\\ \beta_+\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ e^{i\theta}\end{pmatrix}, \quad \begin{pmatrix}\alpha_-\\ \beta_-\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ -e^{i\theta}\end{pmatrix}$

Eigenstates: $|\pm\rangle = \frac{1}{\sqrt{2}}\left(|0\rangle \pm e^{i\theta}|1\rangle\right)$

Check:

$$\mathcal{H}|\pm\rangle = (H_0 + \mathcal{H}')|\pm\rangle = E_0|\pm\rangle + \frac{1}{\sqrt{2}}\mathcal{H}'\left(|0\rangle \pm e^{i\theta}|1\rangle\right)$$

$$= E_0|\pm\rangle + \frac{1}{\sqrt{2}}\left(V|1\rangle \pm e^{i\theta}\underbrace{V^*}_{=V_0 e^{-i\theta}}|0\rangle\right)$$

$$= E_0|\pm\rangle + \frac{1}{\sqrt{2}}\underbrace{\left(V_0 e^{i\theta}|1\rangle \pm V_0|0\rangle\right)}_{=\pm V_0\left(|0\rangle \pm e^{i\theta}|1\rangle\right)}$$

$$\mathcal{H}|\pm\rangle = (E_0 \pm V_0)|\pm\rangle$$

Useful trick: We can guess the basis where $\mathcal{H}'$ is diagonal if we know a Hermitian operator $\hat{A}$ that satisfies the following properties:

(i) $[\hat{A}, \hat{H}_0] = [\hat{A}, \hat{\mathcal{H}}'] = 0$;

(ii) We know a basis $\{|a_i\rangle\}$ of the degenerate subspace $H_0|a_i\rangle = E_0|a_i\rangle$

that is diagonal for $\hat{A}$, $\hat{A}|a_i\rangle = a_i|a_i\rangle$ for a_i nondegenerate.

$\Rightarrow$ In that case $|a_i\rangle$ is the "good basis", i.e., the basis that diagonalizes $(H_0 + \mathcal{H}')$ in the degenerate subspace.

Proof: $\langle a_i|[\hat{A}, \hat{\mathcal{H}}']|a_{i'}\rangle = \langle a_i|(\hat{A}\hat{\mathcal{H}}' - \hat{\mathcal{H}}'\hat{A})|a_{i'}\rangle =$

$$0 = \underbrace{(a_i - a_{i'})}_{\neq 0 \text{ for } i \neq i'}\langle a_i|\hat{\mathcal{H}}'|a_{i'}\rangle \Rightarrow \langle a_i|\mathcal{H}'|a_{i'}\rangle = 0 \text{ when } i \neq i'.$$

$\Rightarrow [\mathcal{H}']$ is diagonal in this basis!

Example: Mixing degenerate and non-degenerate methods

Consider the unperturbed basis $\{|0\rangle, |1\rangle, |2\rangle\}$ with

$$H_0 = \begin{pmatrix} E_0^0 & 0 & 0 \\ 0 & E_0^0 & 0 \\ 0 & 0 & E_2^0 \end{pmatrix}, \quad H' = \begin{pmatrix} 0 & V & \Delta \\ V & 0 & 0 \\ \Delta & 0 & 0 \end{pmatrix}$$ where V, Δ are real and $E_2^0 > E_0^0$.

Calculate the energy levels up to 2^{nd} order in Δ and V.

First, we need to apply degenerate pert. theory to the $\{|0\rangle, |1\rangle\}$ subspace: Diagonalizing

$\begin{pmatrix} E_0^0 & V \\ V & E_0^0 \end{pmatrix}$ we get new states $|0'\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)$ with energy $\epsilon_0' = E_0^0 - V$.

$|1'\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ " " $\epsilon_1' = E_0^0 + V$.

(Why? See the example on page 7).

In this new basis we get

$$H_0 = \begin{pmatrix} E_0^0 & 0 & 0 \\ 0 & E_0^0 & 0 \\ 0 & 0 & E_2^0 \end{pmatrix} \quad \text{and} \quad H' = \left(\begin{array}{cc|c} -V & 0 & \langle 0'|H'|2\rangle \\ 0 & +V & \langle 1'|H'|2\rangle \\ \hline \langle 2|H'|0'\rangle & \langle 2|H'|1'\rangle & 0 \end{array}\right) = \begin{pmatrix} -V & 0 & \Delta/\sqrt{2} \\ 0 & +V & \Delta/\sqrt{2} \\ \Delta/\sqrt{2} & \Delta/\sqrt{2} & 0 \end{pmatrix}$$

$\uparrow$ unchanged because we only changed basis in the degenerate subspace!

$$\langle 0'|H'|2\rangle = \frac{1}{\sqrt{2}}(\langle 0| - \langle 1|)(\Delta|0\rangle) = \frac{\Delta}{\sqrt{2}}$$

$$\langle 1'|H'|2\rangle = \frac{1}{\sqrt{2}}(\langle 0| + \langle 1|)(\Delta|0\rangle) = \frac{\Delta}{\sqrt{2}}$$

or $$H_0 + H' = \underbrace{\begin{pmatrix} E_0^0 - V & 0 & 0 \\ 0 & E_0^0 + V & 0 \\ 0 & 0 & E_2^0 \end{pmatrix}}_{\tilde{H}_0} + \underbrace{\begin{pmatrix} 0 & 0 & \Delta/\sqrt{2} \\ 0 & 0 & \Delta/\sqrt{2} \\ \Delta/\sqrt{2} & \Delta/\sqrt{2} & 0 \end{pmatrix}}_{\tilde{H}'}$$

Now we can do nondegenerate pert theory! Note that 1^{st} order correction is zero; 2nd order: $E_n^2 = -\sum_{m \neq n} \frac{|\langle m^0|H'|n^0\rangle|^2}{E_m^0 - E_n^0}$

$$E_0 = E_0^0 - V - \left(\frac{|\langle 1'|\tilde{H}'|0'\rangle|^2}{\epsilon_1' - \epsilon_0'}^{\nearrow = 0} + \frac{|\langle 2|\tilde{H}'|0'\rangle|^2}{E_2^0 - \epsilon_0'} \right) = E_0^0 - V - \left(\frac{\Delta}{\sqrt{2}}\right)^2 \frac{1}{E_2^0 - (E_0^0 - V)} + \mathcal{O}(\Delta^3)$$

$$E_1 = E_0^0 + V - \left(\frac{|\langle 0'|\tilde{H}'|1'\rangle|^2}{\epsilon_0' - \epsilon_1'}^{\nearrow = 0} + \frac{|\langle 2|\tilde{H}'|1'\rangle|^2}{\epsilon_2' - \epsilon_1'} \right) = E_0^0 - V - \left(\frac{\Delta}{\sqrt{2}}\right)^2 \frac{1}{E_2^0 - (E_0^0 + V)} + \mathcal{O}(\Delta^3)$$

$$E_2 = E_2^0 - \left(\frac{|\langle 0'|\tilde{H}'|2\rangle|^2}{\epsilon_0' - E_2^0} + \frac{|\langle 1'|\tilde{H}'|2\rangle|^2}{\epsilon_1' - E_2^0} \right) = E_2^0 + \left(\frac{\Delta}{\sqrt{2}}\right)^2 \frac{1}{E_2^0 - (E_0^0 - V)} + \left(\frac{\Delta}{\sqrt{2}}\right)^2 \frac{1}{E_2^0 - (E_0^0 + V)} + \mathcal{O}(\Delta^3)$$