Lecture 13

Perturbation theory:

Expand energy eigenvalues as

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

Fails if $E_n^{(0)} = E_m^{(0)}$ for some $m \neq n$

Resolve using degenerate perturbation theory:

Collect all states with $E_n^{(0)} = E_m^{(0)}$

Set up matrix $H'_{mn} = \langle \phi_m^{(0)} | H' | \phi_n^{(0)} \rangle$

Griffiths calls this $W_{mn}$

Then need to exactly diagonalize matrix

Obtain eigenstates $| \phi_n^{(0)} \rangle$ (still eigenstates of $H^{(0)}$)

Since $\langle \phi_m^{(0)} | H' | \phi_n^{(0)} \rangle = 0$ for $m \neq n$,

we can now use regular perturbation theory formula (with sum extending over all $m$)

Example from Demetri: $E^{(1)}_\pm = -\frac{V_0 a}{L} \left( 1 \pm e^{-\frac{2\pi n a}{L}} \right)$
Diagonalization is easy enough if only two degenerate states

More than that, can't do analytically in general

But get help from powerful tool:

**Theorem:** Suppose operator $A$ commutes with $H^{(o)}$ & $H'$. Say $\phi_a^{(o)} \neq \phi_b^{(o)}$ are degenerate eigenstates of $H^{(o)}$ and also eigenstates of $A$ with distinct eigenvalues.

Then $\langle \phi_a^{(o)} | H' | \phi_b^{(o)} \rangle = 0$, so $\phi_a^{(o)} \neq \phi_b^{(o)}$ are good states to use for perturbation theory.

**Proof:** Say $A \phi_a^{(o)} = \mu \phi_a^{(o)}$ & $A \phi_b^{(o)} = \nu \phi_b^{(o)}$ with $\mu \neq \nu$

Have $[A, H'] = 0$

So $\langle \phi_a^{(o)} | A H' - H' A | \phi_b^{(o)} \rangle = 0$

$\langle \mu - \nu \rangle \langle \phi_a^{(o)} | H' | \phi_b^{(o)} \rangle = 0$

$\Rightarrow \langle \phi_a^{(o)} | H' | \phi_b^{(o)} \rangle = 0$

So we can avoid/simplify diagonalizing $H'$ matrix if we use eigenstates of $A$. 
Example: Ring problem

\( H^{(0)} \) & \( H' \) both symmetric under reflection \( \iff \)

Operator \( A \): \( A Z(x) = Z(L-x) \)

has \( \{ H^{(0)}, A \} = \{ H', A \} = 0 \)

Find eigenstates of \( H^{(0)} \)
that are also eigenstates of \( A \)

= symmetric and antisymmetric combos of \( e^{i n k x} \)

Know that these are \( \sin n k x, \cos n k x \)

\( = \) what we found by diagonalizing \( H^{(0)} \)& \( H' \! \)!

Another example:

Say \( H^{(0)} \): hydrogen atom
\( H' = \alpha \zeta \)

Then \( H^{(0)} \) & \( H' \) both have cylindrical symmetry
\( \Rightarrow \) \( \{ H', L_z \} = 0 \)

Check: \( \{ L_z, L_z \} = M \{ L_z, x p_y - y p_x \} = 0 \)

So states \( 2^+ \) with different \( m \)'s are not coupled!

For instance, \( n=2 \) level has four states \( (no \ spin) \)
\( l=0 \) \( m=0 \)
\( l=1 \) \( m=1 \)
\( l=1 \) \( m=0 \)
\( l=1 \) \( m=-1 \)
Theorem says only \( m = 0 \) states are coupled by \( H' \).

\( H' \) matrix has form

\[
\begin{bmatrix}
1 & 1 & 0 & 0 \\
0 & E_2 & 0 & 0 \\
0 & 0 & E_2 & U \\
0 & 0 & 0 & E_2
\end{bmatrix}
\]

for \( U = \left\langle \frac{3}{2}, 0 \right| x \left| \frac{3}{2}, 0 \right\rangle \).

Only need to diagonalize \( 2 \times 2 \) matrix, not \( 4 \times 4 \).

Most of the time, look for operators \( A \):
- spatial inversions (reflection symmetry)
- angular momenta (rotation symmetry)

Always look for symmetries before doing a big diagonalization.

Note general effect: perturbation breaks degeneracy.

Can be challenging when two different perturbations \( H' \), \( H'' \), similar sizes.

Say apply \( H' \), first... get states that are near... but not quite degenerate.

Then apply \( H'' \)... can't use plain perturbation theory because \( E_n - E_m \approx H'' \).

But can't use degenerate PT, because not degenerate: linear combos not eigenstates.
Generally, need to combine $H_1 + H_2$ as one perturbation and apply together.

Unless $H_1$ and $H_2$ have a symmetry in common, can't use operator A trick in stuck diagonalizing whole manifold.

Rest of CH 6: apply PT to hydrogen.

Several small effects in H left out of Bohr solution.

Road map:

Bohr energies: unperturbed states

Fine structure: relativistic correction to KE & spin-orbit coupling

(Zee man effect: Energy shifts in magnetic field

Hyperfine structure: coupling between electron & nuclear spin

Lamb shift: coupling of states to E+M field (we won't do this one!)