Optics & Spectroscopy — Lecture 13

- there are a number of "model" problems in QM. that can be solved exactly
  - harmonic oscillator
  - rigid rotor
  - H-atom
  - particle-in-a-box
- most real systems do not perfectly fit these model problems
- handle this through **Perturbation Theory**

real Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$

$\hat{H}_0$: model Hamiltonian that we can solve exactly

$\hat{H}'$: extra bit

goal: obtain estimates for the energy levels & wavefunctions of $\hat{H}$ in terms of our model problem

~ do this by expanding energies & wavefunctions in terms of a perturbation parameter "λ"

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \ldots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$

$|\psi^{(0)}\rangle$ & $E_n^{(0)}$ are the solutions of the model problem

"zeroth-order" solutions

i.e. $H_0 |\psi^{(0)}\rangle = E_n^{(0)} |\psi^{(0)}\rangle$

$|\psi^{(0)}\rangle$ & $E_n^{(0)}$ are known

$$\left.\begin{array}{l} E_n^{(1)},\ E_n^{(2)} \\ |\psi_n^{(1)}\rangle,\ |\psi_n^{(2)}\rangle \end{array}\right\}$$ 1st and 2nd order corrections to the wavefunction & energy

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write the S.E. $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ as

$$(\hat{H} - E_n)|\psi_n\rangle = 0$$

$$\Rightarrow \left\{\hat{H}_0 + \lambda\hat{H}' - (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)\right\}$$

$$\times\left\{|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right\}$$

$$= 0$$

~ expand & collect terms in λ

$$\{\hat{H}_0 - E_n^{(0)}\}|\psi_n^{(0)}\rangle$$

$$+ \lambda^1\left\{(\hat{H}_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + (\hat{H}' - E_n^{(1)})|\psi_n^{(0)}\rangle\right\}$$

$$+ \lambda^2\left\{(\hat{H}_0 - E_n^{(0)})|\psi_n^{(2)}\rangle + (\hat{H}' - E_n^{(1)})|\psi^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle\right\}$$

$$+ \lambda^3 \{ \} + \lambda^4 \{ \} + \dots = 0$$

~ now $\lambda \neq 0$ ($\lambda = 1$ ~ bookkeeping device)

$\Rightarrow$ each term that multiplies λ must be separately equal to zero

$$\Rightarrow \quad (\hat{H}^{(0)} - E_n^{(0)})|\psi_n^{(0)}\rangle = 0 \quad \leftarrow \text{model problem}$$

$$\lambda^1: \ (\hat{H}_0 - E_n^{(0)})|\psi_n^{(1)}\rangle + (\hat{H}' + E_n^{(1)})|\psi_n^{(0)}\rangle = 0$$

$$\lambda^2: \ (\hat{H}_0 - E_n^{(0)})|\psi_n^{(0)}\rangle + (\hat{H}' - E_n^{(1)})|\psi_n^{(1)}\rangle - E_n^{(2)}|\psi_n^{(0)}\rangle = 0$$

1st-order P.T.

$$(\hat{H}_0 - E_n^{(0)})|\psi_n^{(0)}\rangle + (\hat{H}' - E_n^{(1)})|\psi_n^{(0)}\rangle = 0$$

know $|\psi_n^{(0)}\rangle$ ~ complete basis set

$\Rightarrow$ expand $|\psi_n^{(1)}\rangle$ in terms of $\{|\psi_n^{(0)}\rangle\}$

$$|\psi_n^{(1)}\rangle = \sum_i C_{ni} |\psi_i^{(0)}\rangle$$

$$C_{ni} = \langle \psi_i^{(0)} | \psi_n^{(1)} \rangle$$

$$\Rightarrow (\hat{H}_0 - E_n^{(0)}) \sum_i C_{ni} |\psi_i^{(0)}\rangle + (\hat{H}' - E_n^{(1)}) |\psi_n^{(0)}\rangle = 0$$

~ multiply from the left by $\langle \psi_n^{(0)}|$

$$\langle \psi_n^{(0)} | (\hat{H}_0 - E_n^{(0)}) \sum_i C_{ni} |\psi_i^{(0)}\rangle = - \langle \psi_n^{(0)} | (\hat{H}' - E_n^{(1)}) | \psi_n^{(0)} \rangle$$

$$\langle \psi_n^{(0)} | (E_n^{(0)} - E_n^{(0)}) \sum C_{ni} |\psi_i^{(0)}\rangle = - \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle + E_n^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle}_{=1}$$

LHS $= 0$

$$\Rightarrow E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

~ 1st order correction to the energy is just an average of the perturbation over the zeroth-order wavefunctions.

Back to $(\hat{H}_0 - E_n^{(0)})|\psi_n^{(1)}\rangle = -(\hat{H}' - E_n^{(1)})|\psi_n^{(0)}\rangle$

~ again expand $|\psi_n^{(1)}\rangle = \sum_i c_{ni}|\psi_i^{(0)}\rangle$

$$(\hat{H}_0 - E_n^{(0)})\sum_i c_{ni}|\psi_i^{(0)}\rangle = -(\hat{H}' - E_n^{(1)})|\psi_n^{(0)}\rangle$$

~ now multiply from LHS by $\langle\psi_j^{(0)}|$ $j \neq n$

$$\langle\psi_j^{(0)}|(\hat{H}_0 - E_n^{(0)})\sum_i c_{ni}|\psi_i^{(0)}\rangle$$

$$= -\langle\psi_j^{(0)}|(\hat{H}' - E_n^{(0)}|\psi_n^{(0)}\rangle$$

$$LHS = \sum_i c_{ni}(E_j^{(0)} - E_n^{(0)})\langle\psi_j^{(0)}|\psi_i^{(0)}\rangle$$

$$= \sum_i c_{ni}(E_j^{(0)} - E_n^{(0)})\,\delta_{ji}$$

~ perform the sum over i, we pick out the term $i=j$

$$LHS = C_{nj}\,(E_j^{(0)} - E_n^{(0)})$$

$$RHS = -\langle \psi_j^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle + E_n^{(0)} \underbrace{\langle \psi_j^{(0)} | \psi_n^{(0)} \rangle}_{\substack{=0 \\ j \neq n}}$$

$$= -\langle \psi_j^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

$$\Rightarrow C_{nj}\,(E_j^{(0)} - E_n^{(0)}) = -\langle \psi_j^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

$$\Rightarrow C_{nj} = -\frac{\langle \psi_j^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_j^{(0)} - E_n^{(0)}}$$

$$\Rightarrow |\psi_n\rangle \simeq |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle$$

$$= |\psi_n^{(0)}\rangle + \sum_i C_{ni} |\psi_i^{(0)}\rangle$$

$$\Rightarrow |\psi_n\rangle \simeq |\psi_n^{(0)}\rangle + \sum_{i\neq n} -\frac{\langle\psi_i^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle}{E_i^{(0)} - E_n^{(0)}} |\psi_i^{(0)}\rangle$$

write in a more compact notation:

$$|n\rangle \simeq |n^\circ\rangle + \underbrace{\sum_{i\neq n} \frac{\langle i^\circ|\hat{H}'|n^\circ\rangle}{E_n^\circ - E_i^\circ} |i^\circ\rangle}_{\text{1st-order correction to the wavefunction}}$$

~ perturbation ($\hat{H}'$) mixes other states into the wavefunction

~ degree of mixing depends on coupling ($\langle i^\circ|\hat{H}'|n^\circ\rangle$) and how close the 2 states are in energy $\left(\frac{1}{E_n^{(0)} - E_i^{(0)}}\right)$

Two-level System:

$$\left.\begin{array}{l} \text{———}\ |2^\circ\rangle \\[2em] \text{———}\ |1^\circ\rangle \end{array}\right\} \text{coupled by "V"} \quad \hat{H} = \hat{H}_0 + \hat{V}$$

~ define $\Delta = E_2^\circ - E_1^\circ$

$$V_{12} = \langle 1^\circ | \hat{V} | 2^\circ \rangle$$

1st-order Perturbation Theory

$$|2\rangle \simeq |2^\circ\rangle + \frac{\langle 1^\circ|\hat{V}|2^\circ\rangle}{E_2^\circ - E_1^\circ}|1^\circ\rangle = |2^\circ\rangle + \frac{V_{12}}{\Delta}|1^\circ\rangle$$

$$|1\rangle \simeq |1^\circ\rangle + \frac{\langle 2^\circ|\hat{V}|1^\circ\rangle}{E_1^\circ - E_2^\circ}|2^\circ\rangle = |1^\circ\rangle - \frac{V_{21}}{\Delta}|2^\circ\rangle$$

$V_{21} = V_{12}^*$, assume V_{12} = real $\Rightarrow V_{12} = V_{21} = V$

$$|2\rangle = |2^\circ\rangle + \frac{V}{\Delta}|1^\circ\rangle \quad \& \quad |1\rangle = |1^\circ\rangle - \frac{V}{\Delta}|2^\circ\rangle$$

$|1\rangle$ + $|2\rangle$ are not normalized

$$\langle 1|1\rangle = \left\{\langle 1^0| - \frac{V}{\Delta}\langle 2^0|\right\}\left\{|1^0\rangle - \frac{V}{\Delta}|2^0\rangle\right\}$$

$$= 1 + \frac{V^2}{\Delta^2}$$

$$\langle 2|2\rangle = 1 + V^2/\Delta^2$$

$\Rightarrow$ normalized wavefunctions are

$$|1\rangle = \frac{1}{\sqrt{1+V^2/\Delta^2}}\left\{|1^0\rangle - \frac{V}{\Delta}|2^0\rangle\right\}$$

$$|2\rangle = \frac{1}{\sqrt{1+V^2/\Delta^2}}\left\{|2^0\rangle + \frac{V}{\Delta}|1^0\rangle\right\}$$

Note: $$\langle 1|2\rangle = \frac{1}{(1+V^2/\Delta^2)}\left\{\langle 1^0| - \frac{V}{\Delta}\langle 2^0|\right\} \times \left\{|2^0\rangle + \frac{V}{\Delta}|1^0\rangle\right\}$$

$$= \frac{1}{(\ \ )}\left(\frac{V}{\Delta} - \frac{V}{\Delta}\right) = 0$$