

Lecture 13

Recap perturbation theory

$$\text{Have } H = H^0 + H'$$

H' is in some sense small

Derived leading order corrections:

$$E_n \approx E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

$$E_n^{(1)} = W_{nn} \equiv \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$$

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

$$\text{and } \psi_n \approx \psi_n^{(0)} + \sum_{m \neq n} \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

Saw last time that we can think of these as leading order terms in re-diagonalization of H matrix

In particular, for two-level system, can solve exactly:

$$E_{\pm} = \frac{1}{2} \left[E_a^0 + E_b^0 + W_{aa} + W_{bb} \pm \sqrt{(E_a^0 - E_b^0 + W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]$$

Saw that this gives some leading order terms as above.

However, our perturbation expansion breaks down for degenerate states $E_n^0 = E_m^0$ for some n, m

Basic problem: premise that H' is small fails. Need H' small compared to ΔE , and it's not if $\Delta E = 0$.

Strategy: isolate degenerate levels

For instance, in hydrogen (no spin):

3s, 3p, 3d ————— 9 states

2s, 2p ————— 4 states

1s ————— 1 state

Treat each group of degenerate states by themselves.

If two states, already have answer.

If three states, proceed same way:

construct W_{ij} matrix, then diagonalize it

→ need to solve cubic equations. Kind of hard, but doable.

In general, if N degenerate states, need to diagonalize $N \times N$ W matrix

Eigenvalues are energy corrections

Not too hard for modest N

However, it's not so easy either.

Good to take advantage of symmetries in H^0 and H' .

Suppose some other operator Q commutes with H^0 & H' .

Then choose basis states as eigenstates of Q : ψ_{q_2}

Then we know $W_{q_2 q_1} = \langle \psi_{q_2} | H' | \psi_{q_1} \rangle = 0$ for $q_2 \neq q_1$.

Proof

$$\langle \psi_{q_2} | [Q, H'] | \psi_{q_1} \rangle = 0 \quad \text{since } [Q, H'] = 0$$

$$\langle \psi_{q_2} | QH' - H'Q | \psi_{q_1} \rangle = 0$$

$$= (q_2 - q_1) \langle \psi_{q_2} | H' | \psi_{q_1} \rangle = 0$$

$$= (q_2 - q_1) W_{q_2 q_1}$$

So if $q_2 - q_1 \neq 0$, must have $W_{q_2 q_1} = 0$.

This can eliminate many off-diagonal elements of W_{ij} ,
making diagonalization easier.

For instance, in hydrogen example, say we know $[H', L^2] = 0$.

Then $W_{ij} = 0$ for states with different l .

Thus $n=2$ level doesn't require diagonalization
of 4×4 matrix, but just a 1×1 and 3×3 .

Say that
 q is a
"good" quantum
number.

W matrix is "block diagonal"

$$W = \begin{matrix} & \begin{matrix} 2s & 2p & 2p & 2p \end{matrix} \\ \begin{matrix} 2s \\ 2p \\ 2p \\ 2p \end{matrix} & \begin{bmatrix} x & 0 & 0 & 0 \\ 0 & x & x & y \\ 0 & x & x & y \\ 0 & y & x & x \end{bmatrix} \end{matrix}$$

diagonalize blocks separately.

Or say $[H', L_z] = 0$. Then only states with same m 's are mixed

In $n=2$ level, have $l=1, m=-1, 0, 1$
 $l=0, m=0$

Only two $m=0$ states coupled
 $(lm) = \begin{matrix} 1-1 & 10 & 00 & 1+1 \end{matrix}$

Matrix

$$\begin{bmatrix} x & 0 & 0 & 0 \\ 0 & x & x & 0 \\ 0 & x & x & 0 \\ 0 & 0 & 0 & y \end{bmatrix}$$

If you can use this trick to isolate a single state [like $(1-1)$ and $(1+1)$ above]

then just use $E^{(1)} = W_{22} = \langle 2\psi_{\xi}^{(0)} | H' | 2\psi_{\xi}^{(0)} \rangle$

We'll get to see examples of this in next few lectures, should start to make sense.