Lecture #11

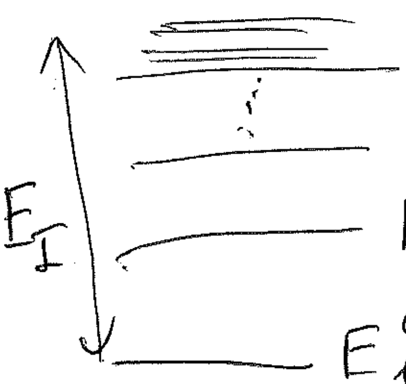
Degenerate perturbation theory

Motivation: recall non-degenerate pert. theory:

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

if $E_n^{(0)} = E_k^{(0)}$ ⇓ $E_n^{(2)} \to \infty$!

Ex. (H)-atom ⇒ $E_n^{(0)} = -\frac{E_I}{n^2}$ ← ionization energy 13.6 eV



E_I

$E_3^{(0)}$

$E_2^{(0)}$ 4-fold deg.: ⇒ $|200\rangle, |210\rangle, |21\pm1\rangle$

$E_1^{(0)}$ ⇒ $|100\rangle$ (non-deg.)

States: $|n^{(0)}\rangle \equiv |n l m^{(0)}\rangle$

principal quantum number; orb. ang. mom.; projection of orb. ang. mom.

⇓

energy levels are n^2-degenerate (if spin is included ⇒ $2n^2$)

So if we need to find a correction to $E_2^{(0)}$ ⇒ we have 4 states at this energy!

So how does one define $E_n^{(1)}$?

– what is $|n^{(0)}\rangle$ ⇒ $|200\rangle$, $|211\rangle$, ... or their combination?

⇓

need a method to deal with this!

Recall Lecture # 9:

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

(for non-deg. case, multiply by $\langle n^{(0)}|$)

Now multiply by $\langle n_i^{(0)}|$

$i = 1, 2, \ldots g$

$$\hat{H}_0 |n_i^{(0)}\rangle = E_n^{(0)} |n_i^{(0)}\rangle$$

$g = 4$ for $n=2$ energy of (H)-atom on p. 1

degeneracy of $n^{(0)}$th level

$\Downarrow$

$$\underbrace{\langle n_i^{(0)} | \hat{H}_0 - E_n^{(0)} | n^{(1)}\rangle}_{= 0} + \langle n_i^{(0)} | \hat{H}' | n^{(0)}\rangle = E_n^{(1)} \langle n_i^{(0)} | n^{(0)}\rangle$$

$$\langle n_i^{(0)} | H' | \underbrace{n^{(0)}}_{?} \rangle = E_n^{(1)} \langle n_i^{(0)} | n^{(0)}\rangle$$

? (could be any combination of $|n_i^{(0)}\rangle$?

Use closure:

$$\underbrace{\sum_{i'=1}^{g} \sum_{K}}_{} |K_{i'}^{(0)}\rangle\langle K_{i'}^{(0)}| = 1 \Rightarrow$$

sum over all states

$$\underbrace{\sum_{K}\sum_{i'}}_{} \langle n_i^{(0)}|\hat{H}'\underbrace{|K_{i'}^{(0)}\rangle\langle K_{i'}^{(0)}|}_{} \underbrace{}_{=\delta_{Kn}\langle n_{i'}|n^{(0)}\rangle} n^{(0)}\rangle =$$

$$= E_n^{(1)}\langle n_i^{(0)}|n^{(0)}\rangle$$

δ_{Kn} removes $\sum_K \Rightarrow$

$$\sum_{i'=1}^{g} \underbrace{\langle n_i^{(0)}|\hat{H}'|n_{i'}^{(0)}\rangle}_{\text{elements of } g\times g \text{ matrix } (H'_{ii'})} \langle n_{i'}^{(0)}|n^{(0)}\rangle = $$

$$= E_n^{(1)}\underbrace{\langle n_i^{(0)}|n^{(0)}\rangle}_{}$$

column

$$\Downarrow$$

$$\hat{H}'|n^{(0)}\rangle = E_n^{(1)}|n^{(0)}\rangle \qquad \begin{pmatrix} \langle n_1^{(0)}|n^{(0)}\rangle \\ \langle n_2^{(0)}|n^{(0)}\rangle \\ \vdots \\ \langle n_g^{(0)}|n^{(0)}\rangle \end{pmatrix}$$

$$\Downarrow$$

diagonalize H' in the degenerate subspace to find energy corrections $E_n^{(1)}$ ← will be g of those!

Example   Linear Stark effect

Consider a H-atom in the $n=2$ state. If it's placed in the $\mathcal{E}$-field $\parallel Oz$, how do the energy levels change? Neglect spin.

1. The degeneracy of $n=2$ level is $n^2=4$;
2. The perturbation is $H' = -\cancel{q}^{\,e}\,\mathcal{E} z$
   The unperturbed energy: $E^{(0)}_{n=2} = -\frac{E_I}{4}$
   The unperturbed states:

   $\underset{n\,\ell\,m}{|200\rangle}$; $|210\rangle$; $|211\rangle$; $|21\,-1\rangle$

   (The dimensionality of degenerate subspace is 4, so these unperturbed states span the basis)
3. Need to compose a 4×4 matrix H' & diagonalize to find $E^{(1)}_2$ corrections.
4. Define the basis:

$1 \Rightarrow |200^{(0)}\rangle$
$2 \Rightarrow |210^{(0)}\rangle$
$3 \Rightarrow |211^{(0)}\rangle$
$4 \Rightarrow |21-1^{(0)}\rangle$

So: $H'_{11} = \langle 200^{(0)}| + e\mathcal{E}z | 200^{(0)}\rangle$ (5)

$H'_{12} = \langle 200^{(0)}| + e\mathcal{E}z | 210^{(0)}\rangle$

$H'_{13} = \langle 200^{(0)}| + e\mathcal{E}z | 211^{(0)}\rangle$

$H'_{14} = \langle 200^{(0)}| + e\mathcal{E}z | 21-1^{(0)}\rangle$

$\vdots$

$H'_{44} = \langle 21-1^{(0)}| + e\mathcal{E}z | 21-1^{(0)}\rangle$

Recall: $|n\ell m\rangle \doteq R_{n\ell}(r) Y_{\ell m}(\theta,\varphi)$
(Ch. 8)

What properties can we use so we don't have to calculate 16 matrix elements?

- H' must be Hermitian so $H'_{mn} = H'^{*}_{nm}$
  (so need only half of matrix elements, but it's still a lot)
- Let's setup integrals for matrix elements & see if any obvious 0's show up!

Need:

(6)

$$\langle 2lm|+e\mathcal{E}\underset{\uparrow\atop r\cos\theta}{z}|2l'm'\rangle =$$

$$= e\mathcal{E}\int_0^\infty r R_{2l}^* R_{2l'} r^2 dr \int_0^{\pi}\int_0^{2\pi} Y_{lm}^* \cos\theta\, Y_{l'm'} \underbrace{d\Omega}_{\sin\theta d\theta d\varphi}$$

$$|200\rangle = \frac{2}{(2a_0)^{3/2}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}\cdot\frac{1}{\sqrt{4\pi}}$$

$$|210\rangle = \frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\sqrt{\frac{3}{4\pi}}\cos\theta$$

$$|21\pm1\rangle = \frac{\mp 1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\theta$$

Note: there is no φ-dep. in the perturbation $\Rightarrow$

$$\langle 2lm|z|2l'm'\rangle \sim \int_0^{2\pi} \underset{\uparrow\atop Y_{lm}^*}{e^{-im\varphi}}\,\underset{\uparrow\atop Y_{l'm'}}{e^{im'\varphi}}\,d\varphi =$$

(m is integer)

$$= \int_0^{2\pi} e^{i(m'-m)\varphi}d\varphi = \frac{e^{i(m'-m)2\pi}-1}{i(m'-m)} = e^{i\pi(m'-m)}\cdot 2i\cdot$$

$$\frac{\sin\pi(m'-m)}{i(m'-m)} = e^{i\pi(m'-m)}\cdot 2\frac{\sin\pi(m'-m)}{m'-m} = 2\pi\,\delta_{m'm}$$

So, $\langle 2lm | +e\mathcal{E}z | 2l'm' \rangle = 0$
unless $\underline{m = m'}$

e.g.
$\langle 200 | +e\mathcal{E}z | 211 \rangle$

Is there any requirement for l vs l'?

For example, use parity of Y_{lm}'s!

$\vec{r} \to -\vec{r} \Rightarrow$ if $\psi(\vec{r}) = \psi(-\vec{r})$ even
$\psi(\vec{r}) = -\psi(-\vec{r})$ odd

$\Downarrow$

In spherical coordinates $\Rightarrow$

$$r \to r$$
$$\theta \to \pi - \theta$$
$$\varphi \to \varphi + \pi$$

$$Y_{lm}(\theta, \varphi) = (-1)^l Y_{lm}(\pi - \theta, \varphi + \pi)$$

parity of spherical harmonics!
chapter 7
(eq. 7.167)

So if l is even / odd $\Rightarrow$ Y_{lm} is even / odd

Also note! $z = r\cos\theta = r\sqrt{\frac{4\pi}{3}}\, Y_{10}$

odd!

So, $\langle 2lm | +e\mathcal{E}z | 2l'm' \rangle \sim$

$$\sim \int_\Omega Y_{lm}^* \underset{\substack{\uparrow \\ \text{odd}}}{Y_{10}} Y_{l'm'} \, d\Omega$$

If $l = l' \Rightarrow \underset{(-1)^l}{Y_{lm}^*} \underset{(-1)^{l'}}{Y_{l'm'}}$ is even $\Rightarrow$ $\Rightarrow \underset{\substack{\uparrow \\ l=l'}}{(-1)^{2l}}$

$$\int_\Omega \underbrace{\text{even} \cdot \text{odd}}_{\text{odd}} \, d\Omega = 0$$

so all diagonal elements are 0!

e.g., $\int_{-L}^{L} \underset{\substack{\uparrow \\ \text{odd}}}{x} \, dx = 0$

So $l - l'$ should be $= \pm 1$ for the matrix element to be non-zero!

$$\hat{H}' \doteq \begin{array}{c} \begin{array}{cccc} |200\rangle & |210\rangle & |211\rangle & |21{-1}\rangle \end{array} \\ \begin{pmatrix} 0 & ? & 0 & 0 \\ ? & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{array}{l} \langle 200| \\ \langle 210| \\ \langle 211| \\ \langle 21{-1}| \end{array}$$

So $\Rightarrow$ need to calculate only 1 matrix element!