QM II
Phys 652

Lecture #21

Time-independent perturbation theory; perturbation of a degenerate level

Recall: $(H_0 + \lambda V)|n\rangle_\lambda = E_n^{(\lambda)}|n\rangle_\lambda$

V ← perturbation

$H_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$

$E_n^{(0)}$ ← unperturbed energy

$$E_n^{(\lambda)} = E_n^{(0)} + \lambda \underbrace{\langle n^{(0)}|V|n^{(0)}\rangle}_{V_{nn}} + \lambda^2 \sum_{k\neq n} \frac{|V_{kn}|^2}{E_n^{(0)}-E_k^{(0)}},$$

$$|n\rangle_\lambda = |n^{(0)}\rangle + \lambda \sum_{k\neq n} \frac{V_{kn}}{E_n^{(0)}-E_k^{(0)}} |k^{(0)}\rangle + \ldots \qquad (23.1)$$

What if we have a degenerate case, in which $|n^{(0)}\rangle$ & $|k^{(0)}\rangle$ are different states ($n\neq k$) with the same energy ($E_n^{(0)} = E_k^{(0)}$) $\Rightarrow$ can't use (23.1) since "corrections" blow up!

Let's say $E_n^{(0)}$ is g-fold degenerate $\Rightarrow \{|n_i^{(0)}\rangle\}$, $i = 1, 2, \ldots, g$

$$H_0|n_i^{(0)}\rangle = E_n^{(0)}|n_i^{(0)}\rangle$$

g equations like this

Back to Lecture # 21, p. 2:

$$\lambda^1: \quad H_0 |n^{(1)}\rangle + V|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle$$

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

$$\underbrace{\langle n_i^{(0)} | H_0}_{\langle n_i^{(0)}|E_n^{(0)}} - E_n^{(0)} |n^{(1)}\rangle + \langle n_i^{(0)}|V|n^{(0)}\rangle =$$

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

$\Downarrow$

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

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

$\Downarrow$

use closure $\Rightarrow \sum_{i'=1}^{g}\sum_{k} |k_{i'}^{(0)}\rangle\langle k_{i'}^{(0)}| = 1$

$\Downarrow$

$$\sum_k \sum_{i'} \langle n_i^{(0)}|V|k_{i'}^{(0)}\rangle \underbrace{\langle k_{i'}^{(0)}|n^{(0)}\rangle}_{\langle n_{i'}^{(0)}|n^{(0)}\rangle \delta_{kn}} = E_n^{(1)} \langle n_i^{(0)}|n^{(0)}\rangle$$

$\Rightarrow$ remove $\sum_k$

$\Downarrow$

$$\sum_{i'=1}^{g} \underbrace{\langle n_i^{(0)}|V|n_{i'}^{(0)}\rangle}_{\substack{\text{elements of}\\ g\times g \text{ matrix}}} \underbrace{\langle n_{i'}^{(0)}|n^{(0)}\rangle}_{\text{column}} = E_n^{(1)}\langle n_i^{(0)}|n^{(0)}\rangle$$

column $\begin{pmatrix} \langle n_1^{(0)}|n^{(0)}\rangle \\ \langle n_2^{(0)}|n^{(0)}\rangle \\ \vdots \\ \langle n_g^{(0)}|n^{(0)}\rangle \end{pmatrix}$

$\Updownarrow$

vector equation

$$\vec{V}|n^{(0)}\rangle = E_n^{(1)}|n^{(0)}\rangle \Rightarrow$$ (diagonalize $\vec{V}$ to find $E^{(1)}$)

3

Example: Linear Stark effect

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

1. If the spin is neglected $\Rightarrow$ the degeneracy of the nth level of the (H)-atom is $n^2 \Rightarrow$ 4-fold in our case

$E_{n=2} = -\frac{E_I}{4} \Leftarrow$

2. The perturbation is $(\lambda) V = -e\mathcal{E}z$

λ drop

3. The states corresponding to $n=2 \Rightarrow$

$|2,0,0\rangle$; $|2,1,0\rangle$; $|2,1,\pm1\rangle$

$n\ \ell\ m$

Need to compose 4×4 matrix $(\hat{V})$ and diagonalize.

4. Number the states :

$1 \Rightarrow |2,0,0\rangle$

$2 \Rightarrow |2,1,0\rangle$

$3 \Rightarrow |2,1,1\rangle$

$4 \Rightarrow |2,1,-1\rangle$

So,

$$V_{11} = \langle 2,0,0| -e\mathcal{E}z |2,0,0\rangle$$

$$V_{12} = \langle 2,0,0| -e\mathcal{E}z |2,1,0\rangle$$

$$V_{13} = \langle 2,0,0| -e\mathcal{E}z |2,1,1\rangle$$

$$V_{14} = \langle 2,0,0 | -e\mathcal{E}z | 2,1,-1 \rangle$$

$$V_{21} = \langle 2,1,0 | -e\mathcal{E}z | 2,0,0 \rangle$$

$$\vdots$$

$$V_{44} = \langle 2,1,-1 | -e\mathcal{E}_z | 2,1,-1 \rangle$$

Let's evaluate these matrix elements $\Rightarrow$

$$V_{11} = -e\mathcal{E} \int |R_{20}|^2 r\, r^2 dr \underbrace{\int |Y_0^0|^2 \cos\theta \sin\theta\, d\theta\, d\varphi}_{= 0}$$

Recall Lecture #19,
when we got selection rules for $\langle n, l', m' | \underbrace{z}_{\uparrow\, Y_1^0} | n, l, \ldots$

$$\underbrace{\Delta l}_{= l'-l} = \pm 1 \; ; \; \underbrace{\Delta m}_{= m'-m} = 0$$

$$\Downarrow$$

All diagonal elements are zero ($V_{11} = V_{22} = V_{33} = V_{44} = 0$)

Also, $V_{\substack{13\\31}} = V_{\substack{14\\41}} = V_{\substack{23\\32}} = V_{\substack{24\\42}} = 0 \leftarrow \Delta m \neq 0 \Rightarrow$ selection rules $\Downarrow$ 0

So, only V_{12}, V_{21} are non-zero

$$V_{12} = -e\mathcal{E}\int R_{20}^{*}\, r\, R_{21}\, r^2 dr \int Y_0^{0*} \cos\theta\, Y_1^0 \sin\theta\, d\theta\, d\varphi =$$

$$= -e\mathcal{E}\,\frac{1}{(2a_0)^3}\,\frac{1}{4\pi a_0}\,\cancel{2\pi}\int_0^\infty \left(2-\frac{r}{a_0}\right) r^4 e^{-\frac{r}{a_0}} dr \underbrace{\int_0^\pi \cos^2\theta \sin\theta\, d\theta}_{\frac{2}{3}}$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$R_{20} = \frac{1}{(2a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$$

$$R_{21} = \frac{1}{(2a_0)^{3/2}}\,\frac{r}{\sqrt{3}a_0}\,e^{-r/2a_0}$$

$$= \frac{-e\mathcal{E}}{24a_0^4}\left(\int_0^\infty 2r^4 e^{-r/a_0}dr - \frac{1}{a_0}\int_0^\infty r^5 e^{-r/a_0}dr\right) =$$

use Gamma-function properties

$$\Gamma(n) = \int_0^\infty x^{n-1}e^{-x}dx = (n-1)!$$

$$= -\frac{e\mathcal{E}}{24a_0^4}\left(2a_0^5\, 4! - a_0^6\, 5!\right) = -e\mathcal{E}a_0\left(\underbrace{\frac{4!}{12}}_{2} - \underbrace{\frac{5!}{24}}_{5}\right) =$$

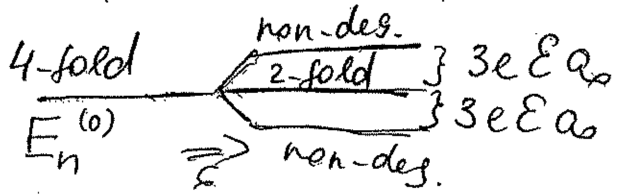
$$= 3e\mathcal{E}a_0 = V_{21}$$

So,
$$\hat{V} = \begin{pmatrix} 0 & 3e\mathcal{E}a_0 & 0 & 0 \\ 3e\mathcal{E}a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \Rightarrow$$

$$\det\begin{bmatrix} -\lambda & 3e\mathcal{E}a_0 & 0 & 0 \\ 3e\mathcal{E}a_0 & -\lambda & 0 & 0 \\ 0 & 0 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{bmatrix} = 0 \Rightarrow \lambda^2\left(\lambda^2 - (3e\mathcal{E}a_0)^2\right) = 0 \Rightarrow$$

1) $\underbrace{\lambda_{1,2}}_{=E^{(1)}_{n_{(1,2)}}} = 0$; 2) $\underbrace{\lambda_{3,4}}_{=E^{(1)}_{n_{(3,4)}}} = \pm 3e\mathcal{E}a_0$

$|2,1,\pm 1\rangle$



$$E^{(1)}_{n=2} = 3e\mathcal{E}a_0 \ : \quad \begin{pmatrix} -3e\mathcal{E}a_0 & 3e\mathcal{E}a_0 & 0 & 0 \\ 3e\mathcal{E}a_0 & -3e\mathcal{E}a_0 & 0 & 0 \\ 0 & 0 & -3e\mathcal{E}a_0 & 0 \\ 0 & 0 & 0 & -3e\mathcal{E}a_0 \end{pmatrix} \cdot \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = 0 \implies C_1 = C_2 \, , \quad C_3 = C_4 = 0$$

$$\Downarrow$$

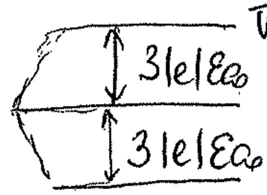
$$\underline{\frac{1}{\sqrt{2}}\left(|2,0,0\rangle + |2,1,0\rangle\right)}$$

$$E^{(1)}_{n=2} = -3e\mathcal{E}a_0 : \quad \underline{\frac{1}{\sqrt{2}}\left(|2,0,0\rangle - |2,1,0\rangle\right)}$$

<u>Energy diagram:</u> (note $e<0$)

$|2,1,\pm 1\rangle$
$|2,0,0\rangle, |2,1,0\rangle$
$n=2$

$\implies$ $\mathcal{E}$



$\frac{1}{\sqrt{2}}\left(|2,0,0\rangle - |2,1,0\rangle\right)$

$|2,1,\pm 1\rangle$

$\frac{1}{\sqrt{2}}\left(|2,0,0\rangle + |2,1,0\rangle\right)$

$\Downarrow$

<u>linear Stark effect</u> $\Leftarrow$ degeneracy is partially removed

So far, we didn't take into account spin $\Rightarrow$ if we do, then the degeneracy of the $n=2$ level is $\underbrace{4}_{n^2} \cdot \underbrace{2}_{\text{due to spin of the electron } \uparrow \downarrow} \cdot \underbrace{2}_{\text{due to spin of the proton } \uparrow\downarrow} = \underline{16}$

Can we still trust results obtained before; Should we consider 16×16 matrix instead of 4×4?

depends on $\hat{V}$!

If $\hat{V}$ does <u>not</u> involve spin operators $\Rightarrow$ acts only on $\mathcal{E}_{\vec{r}}$ space, then we are fine $\Leftarrow$ prove!

(consider as an example 8×8 matrix which takes into account spin of the electron and show that the result is the same as with 4×4 case)

If $\hat{V}$ mixes orbital & spin spaces (e.g. $\hat{V} = \vec{L} \cdot \vec{S}$) $\Rightarrow$ have to consider spin states.

<u>Also</u>:

in real systems, the degeneracy is typically removed due to some subtle interactions (next lectures!) $\Rightarrow$ can we still apply degenerate perturb. theory? $\Rightarrow$ depends on the perturbation! If $|V_{nk}| \ll |E_n - E_k|$ consider non-degenerate, if $|V_{nk}| \gg |E_n - E_k|$ $\Rightarrow$ close levels $\Rightarrow$ degenerate

E_k, E_n, Δ $\rightarrow$ count as $E_n = E_k$ or not?