Example : The stark effect in H atom

let us study the effect of an external electric field which is directed along the z axis ; $\vec{E} = E\hat{k}$, on the ground state $(n=1)$ and on the first excited state $(n=2)$ of the H atom

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} \; ; \quad m \text{ is the reduced mass}$$

the spectrum (unperturbed) of H_0 is given by

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi) \quad \text{with} \quad E_n^{(0)} = \frac{-13.6}{n^2}\ \text{eV}$$

i) Ground state $(n=1)$

$$H' = -\vec{P}\cdot\vec{E} \; ; \quad \vec{P} \text{ is the electric dipole moment}$$

$$\vec{P} = q\vec{r} = (-e)\vec{r}$$

$$H' = e\,\vec{r}\cdot\vec{E} = eEz \; ; \quad \text{G.S is } |100\rangle = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

$$E_n^{(1)} = \langle 100|H'|100\rangle = eE\langle 100|z|100\rangle = 0$$

this can be shown as follows

$$\langle 100|H'|100\rangle = eE\frac{1}{\pi a_0^3}\int_0^\infty r^3 e^{-2r/a_0}\,dr \int_0^{2\pi} d\phi \underbrace{\int_0^\pi \cos\theta \sin\theta\, d\theta}_{\frac{\sin^2\theta}{2}\Big|_0^\pi = 0}$$

$$= 0$$

so the G.S is Not affected by the perturbation H'. this is because the G.S has spherical charge distribution $(l=0)$ and hence has no dipole moment $H' = -\vec{P}\cdot\vec{E} = 0$. however if the H atom is in the first excited state $(n=2)$ it will have an electric dipole moment $\vec{P} \neq 0 \Rightarrow$ there will be a correction

ii) the first excited state ($n=2$)

this is a typical example of degenerate perturbation theory.

let us calculate the first order correction to the energy $E_n^{(1)}$ for the $n=2$ states of the H atom. for the unperturbed system there are 4 states (one 2s and 3 2p states). These are

$$|1\rangle = |200\rangle = \frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\left(1-\frac{r}{2a}\right)e^{-r/2a} \quad ; \; l=0, \; 2s, \; m=0$$

$$|2\rangle = |211\rangle = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}\, r\, e^{-r/2a}\sin\theta\, e^{i\phi} \quad , \; l=1, m=+1$$

$$|3\rangle = |210\rangle = \frac{1}{\sqrt{2\pi a}}\frac{1}{4a^2}\, r\, e^{-r/2a}\cos\theta \quad ; \; l=1, \; m=0$$

$$|4\rangle = |21-1\rangle = \frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}\, r\, e^{-r/2a}\sin\theta\, e^{-i\phi} \quad , \; l=1, \; m=-1$$

all the above states are degenerate ; $E_n = -\frac{R_y}{n^2} = -\frac{R_y}{4}$; $R_y = +13.6\,\text{eV}$

$$= -\frac{1}{4}\left(\frac{me^4}{2\hbar^2}\right) = -\frac{me^4}{8\hbar^2} = E_2^{(0)}$$

now when the atom is placed in an electric field, energy levels will split ($H' = eEz$)

so here the degenercy is 4 i.e $f=4 \Rightarrow$ we need to find and diagonalize the 4x4 matrix elements of the perturbation $\langle 2l'm'|H'|2lm\rangle = eE\langle 2l'm'|z|2lm\rangle$

$H' = eEz$ i.e

$$H' = eE\begin{pmatrix} \langle 200|z|200\rangle & \langle 200|z|211\rangle & \underbrace{\langle 200|z|210\rangle} & \langle 200|z|21-1\rangle \\ \langle 211|z|200\rangle & \langle 211|z|211\rangle & \langle 211|z|210\rangle & \langle 211|z|21-1\rangle \\ \underbrace{\langle 210|z|200\rangle} & \langle 210|z|211\rangle & \langle 210|z|210\rangle & \langle 210|z|21-1\rangle \\ \langle 21-1|z|200\rangle & \langle 21-1|z|211\rangle & \langle 21-1|z|210\rangle & \langle 21-1|z|21-1\rangle \end{pmatrix}$$

so we have 16 elements ; two of them only will survive and the rest will vanish

$\langle 1|eEz|1\rangle = eE\langle 200|z|200\rangle \quad ; \quad z = r\cos\theta$

$= eE\int d^3r\, |\Psi_{200}|^2 r\cos\theta$

$= eE\frac{1}{2\pi a}\frac{1}{4a^2}\int_0^\infty r^3(1-\frac{r}{2a})^2 e^{-r/a}dr \int_0^{2\pi} d\phi \underbrace{\int_0^\pi \cos\theta\sin\theta\, d\theta}_{\frac{\sin^2\theta}{2}\Big|_0^\pi = 0}$

$= 0$

similarly all the digonal elements vanish because of the θ integral vanish

$\therefore \langle 200|z|200\rangle = \langle 211|z|211\rangle = \langle 210|z|210\rangle = \langle 21\text{-}1|z|21\text{-}1\rangle = 0$

Now $\langle 1|eEz|2\rangle = eE\langle 200|z|211\rangle$

$= eE\{\underset{\theta \text{ and } r}{\cdots\cdots}\}\underbrace{\int_0^{2\pi} e^{i\phi}d\phi}_{0} = 0 = \langle 211|z|200\rangle^*$

$\langle 1|eEz|4\rangle = eE\langle 200|z|21\text{-}1\rangle$

$= eE\{\cdots\}\underbrace{\int_0^{2\pi} e^{-i\phi}d\phi}_{0} = 0 = \langle 21\text{-}1|z|200\rangle^*$

similarly

$\langle 211|ezE|210\rangle = eE\langle 211|z|210\rangle = 0 = \langle 210|z|211\rangle^* eE = 0$

$\langle 211|eEz|21\text{-}1\rangle = eE\langle 211|z|21\text{-}1\rangle = 0 = eE\langle 21\text{-}1|z|211\rangle^*$

$\langle 210|eEz|21\text{-}1\rangle = eE\langle 210|z|21\text{-}1\rangle = 0 = eE\langle 21\text{-}1|z|210\rangle^*$

so the above 14 elements vanish, and the only survive tow elements which are a combination of $|200\rangle$ and $|210\rangle$

$\langle 200|eEz|210\rangle$ and $\langle 210|eEz|200\rangle$; it is enough to find one of them as the second is a complex conjugate of the first

$eE\langle 200|z|210\rangle$

$$= eE\,\frac{1}{2\pi a}\,\frac{1}{8a^3}\underbrace{\int_0^\infty dr\, r^4 e^{-r/a}\left(1-r/2a\right)}\ \underbrace{\int_0^{2\pi} d\phi}_{2\pi}\ \underbrace{\int_0^{\pi}\sin\theta\cos^2\theta\, d\theta}_{\frac{\cos^3\theta}{3}\Big|_0^{\pi}=\frac{2}{3}}$$

$$\int_0^\infty r^4 e^{-r/a}\,dr-\frac{1}{2a}\int_0^\infty r^5 e^{-r/a}\,dr$$

$$\frac{4!}{(1/a)^5}\quad-\frac{1}{2a}\,\frac{5!}{(1/a)^6}$$

$$\Rightarrow\ = -3eaE\ = eE\langle 210|z|200\rangle$$

$$\therefore\ H' = -3eaE\underbrace{\begin{pmatrix} 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\end{pmatrix}}$$

we need to find the four eigenvalue of this matrix of H'

$$\begin{vmatrix} -\lambda & 0 & 1 & 0\\ 0 & -\lambda & 0 & 0\\ 1 & 0 & -\lambda & 0\\ 0 & 0 & 0 & -\lambda\end{vmatrix} = 0$$

$$\Rightarrow -\lambda(-\lambda)^3-\lambda^2=\lambda^4-\lambda^2=0$$

$$\lambda^2(\lambda^2-1)=0$$

$$\lambda = 0,\ 0,\ +1,\ -1$$

$$\Rightarrow E_2^{(1)} = 0(-3eaE),\ 0(-3eaE),\ +1(-3eaE),\ -1(-3eaE)$$

$$= 0\ ,\ 0\ ,\ -3eaE\ ,\ +3eaE$$

the perturbed energies are

$E_2^{(0)}$, $E_2^{(0)}$, $E_2^{(0)}+3eaE$, $E_2^{(0)}-3eaE$

still degenerate

so degeneracy is partially lifted.

to find the eigenvectors of the non-degenerate levels with energies $\pm 3eaE$

i) $E_2^{(1)} = +3eaE$

$$\begin{pmatrix} 0 & -3eaE \\ -3eaE & 0 \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 3eaE\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \Rightarrow a_2 = -a_1$$

$\begin{pmatrix} a_1 \\ -a_1 \end{pmatrix} \rightarrow$ normalize $2a_1^2 = 1 \Rightarrow a_1 = 1/\sqrt{2}$

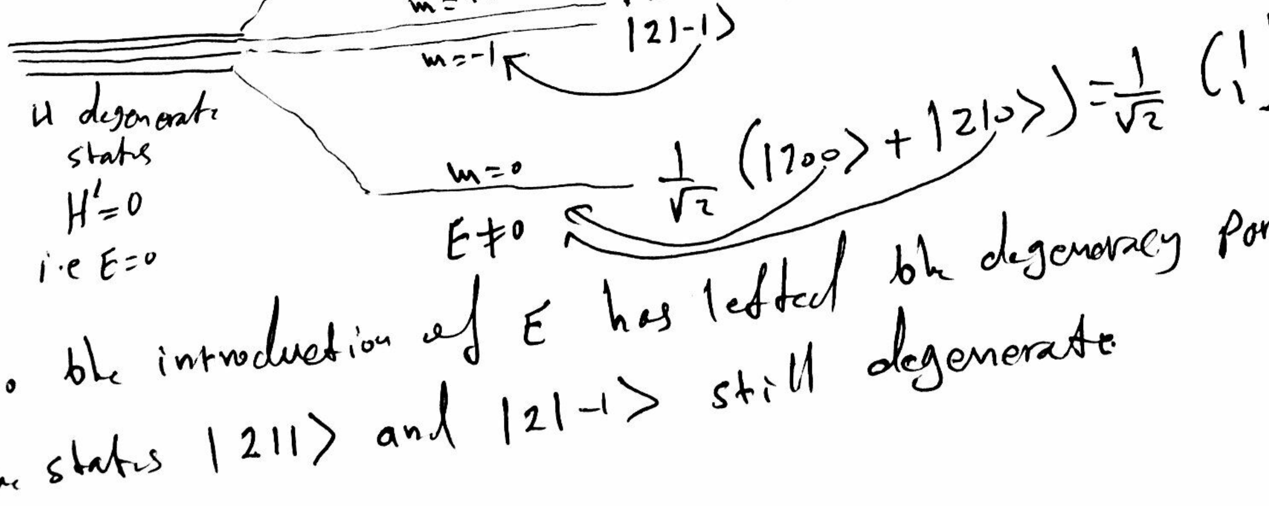
$\Rightarrow |\Phi_1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

ii) $E_2^{(1)} = -3eaE$

$$\begin{pmatrix} 0 & -3eaE \\ -3eaE & 0 \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = -3eaE\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \Rightarrow a_1 = a_2$$

$\begin{pmatrix} a_1 \\ a_1 \end{pmatrix} \rightarrow$ normalize $2a_1^2 = 1 \Rightarrow a_1 = 1/\sqrt{2}$

$\Rightarrow |\Phi_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$



so the introduction of E has lifted the degeneracy partially

the states $|211\rangle$ and $|21-1\rangle$ still degenerate

Notice that the four eigenvectors can be written as

$$|211\rangle, \ |21-1\rangle, \ \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right), \ \frac{1}{\sqrt{2}}\left(|200\rangle - |210\rangle\right)$$

or $$\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \ \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \ \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \ \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \\ 0 \end{pmatrix}$$