① —

② $(\hat{H}' - E_{1n})|\phi_{0n}\rangle = \sum_k a_{nk}(E_{0n} - E_{0k})|\phi_{0k}\rangle$

Start with $\left(\hat{H}' - E_{1n}\right)|\phi_{0n}\rangle = \sum_k a_{nk}\left(E_{0n} - E_{0k}\right)|\phi_{0k}\rangle$ and close with $\langle\phi_{0m}|$.

Because $m \neq n$ the left-hand side gives $\langle\phi_{0m}|\hat{H}'|\phi_{0n}\rangle$.

The right-hand side gives $\sum_k a_{nk}\left(E_{0n} - E_{0k}\right)\delta_{mk} = a_{nm}\left(E_{0n} - E_{0m}\right)$.

Equating these gives the required result $a_{nm} = \dfrac{\langle\phi_{0m}|\hat{H}'|\phi_{0n}\rangle}{E_{0n} - E_{0m}}$ for $m \neq n$.

③ $$E_{2n} = \sum_{k \neq n} \frac{\langle\phi_{0n}|\hat{H}'|\phi_{0k}\rangle\langle\phi_{0k}|\hat{H}'|\phi_{0n}\rangle}{E_{0n} - E_{0k}}$$

$|\phi_{1n}\rangle = \sum_k a_{nk}|\phi_{0k}\rangle$

$|\phi_{2n}\rangle = \sum_k b_{nk}|\phi_{0k}\rangle$

Equation (8) in the lecture notes is $\hat{H}'|\phi_{1n}\rangle + \hat{H}_0|\phi_{2n}\rangle = E_{0n}|\phi_{2n}\rangle + E_{1n}|\phi_{1n}\rangle + E_{2n}|\phi_{0n}\rangle$.

We write $|\phi_{1n}\rangle = \sum_k a_{nk}|\phi_{0k}\rangle$ and $|\phi_{2n}\rangle = \sum_k b_{nk}|\phi_{0k}\rangle$ and substitute these in to give
$\sum_k a_{nk}\hat{H}'|\phi_{0k}\rangle + \sum_k b_{nk}E_{0k}|\phi_{0k}\rangle = E_{0n}\sum_k b_{nk}|\phi_{0k}\rangle + E_{1n}\sum_k a_{nk}|\phi_{0k}\rangle + E_{2n}|\phi_{0n}\rangle$.

Re-arranging this gives $\sum_k a_{nk}\left(\hat{H}' - E_{1n}\right)|\phi_{0k}\rangle + \sum_k b_{nk}\left(E_{0k} - E_{0n}\right)|\phi_{0k}\rangle = E_{2n}|\phi_{0n}\rangle$.

We now close with $\langle\phi_{0n}|$.

The second sum on the left-hand side gives zero.

In the first sum, the term with $k = n$ gives zero, because $E_{1n} = \langle\phi_{0n}|\hat{H}'|\phi_{0n}\rangle$.

We therefore get $E_{2n} = \sum_{k \neq n} a_{nk}\langle\phi_{0n}|\hat{H}'|\phi_{0k}\rangle$.

Combining this with the result of question 2 gives the required result

$$E_{2n} = \sum_{k \neq n} \frac{\langle\phi_{0k}|\hat{H}'|\phi_{0n}\rangle\langle\phi_{0n}|\hat{H}'|\phi_{0k}\rangle}{E_{0n} - E_{0k}}.$$

④ A1!

1st order correct°: $E_{1n} = \langle\phi_{0n}|\hat{H}'|\phi_{0n}\rangle$

$|\phi_{0n}\rangle$ = 1st state hydrogen atom : $\phi_{0n} = \sqrt{\frac{1}{\pi a_0^3}}\exp(-r/a_0)$

Perturbat° $\hat{H}' = V = e\mathcal{E}r\cos\theta$

$$E_1 = \frac{1}{\pi a_0^3} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e\varepsilon r \cos\theta \, r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$= 0 \Rightarrow 1^{st}$ order correct° is zero

(5) $E_{1n} = \langle \phi_{on} | \hat{H} | \phi_{on} \rangle$

$$\phi_n = \sqrt{\frac{1}{\pi a^3}} \exp(-r/a_0)$$

$$\hat{H}' = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{r^2}{2R_N^3} + \frac{1}{2R_N} - \frac{1}{r}\right)$$

$$E_1 = \frac{1}{\pi a_0^3} \int_0^{2\pi}\int_0^{\pi}\int_0^{R_N} -\frac{e^2}{4\pi\epsilon_0}\left(\frac{r^2}{2R_N^3} + \frac{1}{2R_N} - \frac{1}{r}\right) r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$= \frac{-e^2}{4\pi^2 a_0^3 \epsilon_0} \int_0^{2\pi}\int_0^{\pi}\int_0^{R_N} \left(\frac{r^2}{2R_N^3} + \frac{1}{2R_N} - \frac{1}{r}\right) r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$= \frac{-e^2}{4\pi^2 a_0^3 \epsilon_0} \int_0^{2\pi}\int_0^{\pi}\int_0^{R_N} \left(\frac{r^2}{2R_N^3} + \frac{1}{2R_N} - \frac{1}{r}\right) r^2 \sin\theta \, dr\, d\theta\, d\phi$$

$$\Big| \frac{1}{2R_N^3} r^4 + \frac{1}{2R_N} r^2 - r$$

$$\frac{r^5}{} + \frac{r^3}{} - \frac{r^2}{}$$

$$\downarrow \quad 10R_N^3 \qquad 6R_N \qquad 2$$

$$= \frac{-e^2}{4\pi^2 a_0^3 \epsilon_0}\left[\int_0^{2\pi} d\phi + \int_0^{\pi} \sin\theta \, d\theta + \left[\frac{r^5}{10R_N^3} + \frac{r^3}{6R_N} - \frac{r^2}{2}\right]_0^{R_N}\right]$$

$$= \frac{-e^2}{4\pi^2 a_0^3 \epsilon_0}\left[\int_0^{2\pi} d\phi + \int_0^{\pi} \sin\theta \, d\theta \left[\frac{R_N^2}{10} + \frac{R_N^2}{6} - \frac{R_N^2}{2}\right]\right]$$

$$= \frac{e^2}{\cancel{4}\pi^2 a_0^3 \epsilon_0}\left[\cancel{4}\,\cancel{\pi}\left(-\frac{14 R_N^2}{60}\right)\right]$$

$$E_1 = \frac{-e^2}{4a_0^3 \pi \epsilon_0} \frac{14}{15} R_N^2$$

↳ estimate magnitude correct° in eV

$E_0 = -\frac{\hbar^2}{2\mu}\frac{1}{a_0^2} = -\frac{\hbar^2}{2\mu}\frac{e^2\mu}{4\pi\varepsilon_0\hbar^2}\frac{1}{a_0} = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{a_0}$ since the Bohr radius $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2\mu}$.

Hence, $\frac{e^2}{4\pi\epsilon_0 a_0}$ is $-2\times$ the energy of the 1s state, i.e., $-2\times(-13.6) = 27.2$ eV.

$(R_N/a_0)^2$ is of the order of 10^{-10}.

So, E_1 is of the order of 10^{-9} eV.

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$$H_{11}' = H_{22}'$$

$$E = E_0 + H_{11}' \pm |H_{12}'|$$

Assuming H_{12}' & H_{21}' are both real : $H_{12}' = H_{21}'$

Governing eqt°:

$$\begin{pmatrix} (E_0 + H_{11}') - E & H_{12}' \\ H_{12} & (E_0 + H_{11}') - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

eigenvals : $E = E_0 + H_{11}' \pm H_{12}'$

$$\begin{pmatrix} \mp H_{12}' & H_{12}' \\ H_{12}' & \mp H_{12}' \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

$$\oplus \rightarrow \begin{pmatrix} -H_{12}' & H_{12}' \\ H_{12}' & -H_{12}' \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

normalised eigenvector $\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$

z
recall that

eigenf° $\frac{1}{\sqrt{2}} |\phi_{01}\rangle + \frac{1}{\sqrt{2}} |\phi_{02}\rangle$

$$\ominus \rightarrow \begin{pmatrix} H & H \\ H & H \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

eigenvector $\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

eigenf° $\frac{1}{\sqrt{2}}|\phi_{01}\rangle - \frac{1}{\sqrt{2}}|\phi_{01}\rangle$

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single degen electron

$|\phi_{01}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $|\phi_{02}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

mag field = perturbat° $\hat{H}' = \frac{e}{mc}\underline{B}\cdot\underline{\hat{S}}$

Apply magnetic field in z direct°

What happens E levels?

$$\hat{H}' = \frac{e}{mc}\underline{B}\cdot\underline{\hat{S}} = \frac{eB}{mc}\hat{S}_z = \frac{eB}{mc}\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$H'_{11} = \frac{e\hbar B}{2mc}|\phi_{01}\rangle\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}|\phi_{01}\rangle$$

$$= \frac{e\hbar B}{2mc}(0\ 1)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= -\frac{e\hbar B}{2mc}$$

$$H'_{22} = \frac{e\hbar B}{2mc}|\phi_{02}\rangle\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}|\phi_{02}\rangle = 0$$

$$H'_{12} = \frac{e\hbar B}{2mc} |\phi_{01}\rangle \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} |\phi_{02}\rangle = 0$$

$$\therefore E = E_0 \pm \frac{e\hbar B}{2mc}$$

Spacing btw 2 spin states $= \left| -\frac{e\hbar B}{mc} - 0 \right|$

$$= e\hbar B / mc$$

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$$\hat{H}' = \frac{e}{mc} \underline{B} \cdot \underline{\hat{S}} = \frac{eB}{mc} \hat{S}_x = \frac{eB}{mc} \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$H'_{11} = \frac{e\hat{B}}{mc} \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= 0$$

$$H'_{22} = \frac{e\hat{B}}{mc} \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= 0$$

$$H'_{12} = \frac{e\hat{B}}{mc} \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= \frac{e\hat{B}}{mc} \frac{\hbar}{2}$$

$$\therefore\ E = E_0 \pm \frac{e\hbar B}{2mc}$$

ΔE btw 2 spin states $= \dfrac{e\hbar B}{mc}$