14. For electron to be in classically forbidden Region, the Potential Energy has to be greater than the total energy

i.e. $V(r) > E$

Let us apply this to the H-atom

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r} \quad [Z=1]$$

$$E = -\frac{Z^2 \mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}\cdot\frac{1}{n^2} = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\cdot\frac{1}{n^2}$$

[replaced μ by m_e as discussed in class]

also $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ [m_e = mass of electron]

Using $V(r) \geq E$

$$-\frac{e^2}{4\pi\varepsilon_0 r} \geq -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\cdot\frac{1}{1^2}$$ [n=1 for ground state of H-atom]

$$\therefore \frac{e^2}{4\pi\varepsilon_0 r} \leq \frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

$$\therefore r \geq \frac{8\pi\varepsilon_0\hbar^2}{m_e e^2}$$

$$\therefore r \geq 2a_0$$ ← lower limit of 'r'

The probability is given by

$$\int_{2a_0}^{\infty}\int_0^{\pi}\int_0^{2\pi} |\psi_{100}|^2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi a_0^3} \int_{2a_0}^{\infty} r^2 e^{-2r/a_0} \, dr \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

[we have used $\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$]

$$= \frac{4\pi}{\pi a_0^3} \int_{2a_0}^{\infty} r^2 e^{-2r/a_0} \, dr$$

$$= \underline{\underline{0.238}}$$

~~15.~~ This question is pretty straightforward.

Just do the following integral

$$\int_0^{a_0} \int_0^{\pi} \int_0^{2\pi} \psi_{1s}^* \psi_{1s} \; r^2 \sin\theta \, dr \, d\theta \, d\phi$$

Now use the wavefunction of ψ_{1s}

~~16.~~ H-like atom refers to a one-electron species where there is no interelectronic repulsion.

For example: He^+, Li^{2+} are one-electron H-like species

In these cases, the Z varies and cannot be equated to 1

$Z=1$ only for H-atom

Solving the problem using 2 different approaches.

(a) $$\psi_{1s} = R_{10}(r)\, Y_{00}(\theta,\phi)$$

$$= 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2} \cdot \frac{1}{\sqrt{4\pi}}$$

Remember how we described the radial distribution function (RDF)

$$P(r)\,dr = R_{10}^2(r)\, r^2\, dr \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi\, |Y_{lm_l}|^2_{(00)}$$

$$= R_{10}^2(r)\, r^2\, dr \cdot \frac{1}{4\pi} \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi$$

$$= R_{10}^2(r)\, r^2\, dr \cdot \frac{4\pi}{4\pi}$$

$$= R_{10}^2(r)\, r^2 dr \cdot 1$$

Spherical harmonics are normalized (here I just showed it again)

$\therefore \quad P(r) = r^2 R_{10}^2(r)$

$$= r^2 \cdot 4 \cdot \left(\frac{Z}{a_0}\right)^3 e^{-2r/a_0}$$

$$= 4\left(\frac{Z}{a_0}\right)^3 r^2 e^{-2Zr/a_0}$$

$$\frac{dP(r)}{dr} = \frac{d}{dr}\left[4\left(\frac{Z}{a_0}\right)^3 r^2 e^{-2Zr/a_0}\right] = 0$$

$$\therefore \quad 4\left(\frac{Z}{a_0}\right)^3 \left[2r - \frac{2Zr^2}{a_0}\right] e^{-2Zr/a_0} = 0$$

$$\therefore \quad r - \frac{Zr^2}{a_0} = 0$$

$$\therefore \quad r = \frac{Zr^2}{a_0}$$

$$\therefore \quad r_{mp} = \frac{a_0}{Z}$$

as atomic number increases, r_{mp} therefore decreases

Alternate approach

This time I just write down the total wave fn. of ψ_{1s}

$$\psi_{1s} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}$$

$P(r)\,dr$

$$= \int_0^\infty r^2 dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; |\psi_{1s}|^2$$

$$= \left(\frac{Z^3}{\pi a_0^3}\right) \int_0^\infty r^2 e^{-2Zr/a_0} dr \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi$$

$$\approx \left(\frac{Z^3}{\pi a_0^3}\right) r^2 e^{-2Zr/a_0} \cdot 2 \cdot 2\pi$$

[removed the integral for 'r'; if I had done it through I would have obtained 1 $\Rightarrow$ simple normalization of wavefunctions]

$$= 4\left(\frac{Z}{a_0}\right)^3 r^2 e^{-2Zr/a_0}$$

$$= \underline{4\left(\frac{Z}{a_0}\right)^3 r^2 \exp(-2Zr/a_0)}$$

← exactly the same expression as I got before

The idea behind the RDF is to integrate out the angular dependence.

17.

$$\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

$$\langle r \rangle = \int_{\text{all space}} \psi^*_{1s}\, r\, \psi_{1s}\, d\tau$$

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

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

$$= \frac{4\pi}{\pi a_0^3} \int_0^\infty r^3 e^{-2r/a_0}\, dr \qquad \left[\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \right]$$

$$= \frac{3}{2} a_0$$

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[redacted]

$$\psi_{2p_x} = -\frac{Y_{1,1}(\theta,\phi) - Y_{1,-1}(\theta,\phi)}{\sqrt{2}}$$

To show that ψ_{2p_x} is normalized

$$\int \psi^*_{2p_x} \psi_{2p_x} \, d\tau$$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \left\{ -\frac{Y^*_{1,1}(\theta,\phi) - Y^*_{1,-1}(\theta,\phi)}{\sqrt{2}} \right\} \left\{ -\frac{Y_{1,1}(\theta,\phi) - Y_{1,-1}(\theta,\phi)}{\sqrt{2}} \right\}$$

$$= \frac{1}{2} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \left\{ Y^*_{1,1} - Y^*_{1,-1} \right\} \left\{ Y_{1,1} - Y_{1,-1} \right\}$$

where $Y_{1,1}$ represents $Y_{1,1}(\theta,\phi)$

$$= \frac{1}{2} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \left\{ Y^*_{1,1} Y_{1,1} - Y^*_{1,1} Y_{1,-1} - Y^*_{1,-1} Y_{1,1} + Y^*_{1,-1} Y_{1,-1} \right\}$$

$$= \frac{1}{2} \Big[\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, Y^*_{1,1} Y_{1,1} - \int_0^{2\pi} d\theta \int_0^{\pi} d\theta \sin\theta \, Y^*_{1,1} Y_{1,-1}$$
$$- \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, Y^*_{1,-1} Y_{1,1} + \int_0^{2\pi} d\theta \int_0^{\pi} d\theta \sin\theta \, Y^*_{1,-1} Y_{1,-1} \Big] \quad \text{------ (1)}$$

normalization

$$= \frac{1}{2} \Big[\underset{=1}{I_1} - I_2 - I_3 + \underset{=1}{I_4} \Big] \quad \text{...... (2)}$$

where the total integral has been split up into 4 parts.

I_2 and I_3 are automatically $=$ zero [orthogonality of spherical harmonics]

$$= \frac{1}{2} [I_1 + I_4] = \frac{1}{2} [1+1] = 1$$ (hence normalized)

(b) for this part use

$$L^2 Y_{1,1}(\theta,\phi) = \hbar^2 1(1+1) Y_{1,1}(\theta,\phi)$$

[because $L^2 Y_{l,m}(\theta,\phi) = \hbar^2 l(l+1) Y_{l,m}(\theta,\phi)$]

$$\therefore \underline{L^2 Y_{1,1}(\theta,\phi) = 2\hbar^2 Y_{1,1}(\theta,\phi)}$$

Similarly $L^2 Y_{1,-1}(\theta,\phi) = 2\hbar^2 Y_{1,1}(\theta,\phi)$

{ eigen value of L^2 <u>does not</u> depend on m }

$$\therefore L^2 \Psi_{2p_x} = -\frac{1}{\sqrt{2}}\left\{ L^2 Y_{1,1} - L^2 Y_{1,-1} \right\}$$

$$= -\frac{1}{\sqrt{2}}\left\{ 2\hbar^2 Y_{1,1} - 2\hbar^2 Y_{1,-1} \right\}$$

$$= 2\hbar^2 \left\{ -\frac{Y_{1,1} - Y_{1,-1}}{\sqrt{2}} \right\}$$

$$= \underline{2\hbar^2 \Psi_{2p_x}}$$

hence Ψ_{2p_x} is an eigenfunction of L^2 with the eigenvalue $\underline{\underline{2\hbar^2}}$

(c) use $L_z Y_{1,m}(\theta,\phi) = m\hbar \, Y_{1,m}(\theta,\phi)$

$$L_z Y_{1,-1}(\theta,\phi) = -1\hbar \, Y_{1,-1}(\theta,\phi)$$
$$= -\hbar \, Y_{1,-1}(\theta,\phi)$$

and $L_z Y_{1,1}(\theta,\phi) = \hbar \, Y_{1,1}(\theta,\phi)$

$$L_z \Psi_{2p_x} = -\frac{1}{\sqrt{2}} \left\{ L_z Y_{1,1} - L_z Y_{1,-1} \right\}$$

use the above relations and see whether you get the same eigenfunction back.

You will see that Ψ_{2p_x} is not an eigenfunction of L_z

(This is left as an exercise)

20.

$$\langle V\rangle = \left\langle -\frac{e^2}{4\pi\varepsilon_0 r}\right\rangle = -\frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r}\right\rangle$$

$$\psi_{2s} = \psi_{200} = R_{20}(r)\,Y_{00}(\theta,\phi)$$

$$= \frac{1}{\sqrt{8}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)\,e^{-\rho/2}\cdot\frac{1}{\sqrt{4\pi}} \qquad \rho = \frac{2Zr}{na_0}$$

$n=2$
$Z=1$

$$\therefore \langle V\rangle = \int_{\text{all space}} \psi_{2s}^*\left(-\frac{e^2}{4\pi\varepsilon_0 r}\right)\psi_{2s}\,d\tau$$

$$= -\frac{1}{8}\frac{1}{a_0^3}\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{4\pi}\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\int_0^{\infty}r^2\left(2-\frac{r}{a_0}\right)^2\cdot\frac{1}{r}e^{-r/a_0}\,dr$$

$$= -\frac{e^2}{32\pi\varepsilon_0}\cdot\frac{1}{a_0^3}\cdot\frac{4\pi}{4\pi}\int_0^{\infty}r\left(2-\frac{r}{a_0}\right)^2e^{-r/a_0}\,dr$$

$$= -\frac{e^2}{16\pi\varepsilon_0 a_0}$$

Now $$E_n = -\frac{Z^2e^4\mu}{32\pi^2\varepsilon_0^2\hbar^2}\cdot\frac{1}{n^2} = -\frac{Ze^2}{8\pi\varepsilon_0 a_0}\cdot\frac{1}{n^2}$$

$$= -\frac{Ze^2}{8\pi\varepsilon_0 a_0}\cdot\frac{1}{4} \qquad [n=2;\ Z=1]$$

$$= -\frac{Ze^2}{32\pi\varepsilon_0 a_0} = \frac{1}{2}\langle V\rangle$$

Since $\langle V\rangle = 2\langle E_n\rangle$

$$\langle E_{\text{kinetic}}\rangle = -\langle E_n\rangle = -\frac{1}{2}\langle V\rangle \quad \in \boxed{\text{Virial theorem}}\ !!$$

Q2.

$r^2 \psi_{2s}^2(r)$ ⇒ has the form of radial distribution fn. as shown ~~below~~ in class.

Using the expression of ψ_{2s} from the previous problem,

$$f(r) = r^2 \cdot \frac{1}{32\pi} \cdot \left(\frac{1}{a_0}\right)^3 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}$$

To derive the maxima, use $\frac{df(r)}{dr} = 0$

$$\frac{df(r)}{dr} = \frac{1}{32\pi a_0^3} \frac{d}{dr}\left[r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} \right]$$

$$= \frac{1}{32\pi a_0^3} \left[2r\left(2 - \frac{r}{a_0}\right) e^{-r/a_0} - \frac{2r^2}{a_0}\left(2 - \frac{r}{a_0}\right) e^{-r/a_0} - \frac{r^2}{a_0}\left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} \right] = 0$$

Simplifying $\quad r_{max}^2 - 6a_0 r_{max} + 4a_0^2 = 0$

$$\therefore \quad r_{max} = (3 \pm \sqrt{5})\, a_0$$