775(12): The H Atom

The orbitals are well known to be:

$$\phi(r, \theta, \phi) = R_{nl}(r) Y(\theta, \phi) \quad -(1)$$

where $Y(\theta, \phi)$ are the spherical harmonics and

$$R_{nl}(r) = -\left(\frac{2}{na}\right)\left[\frac{(n-l-1)!}{2n[(n+l)!]^3}\right] \rho^l L_{n+l}^{2l+1}(\rho) e^{-\rho/2} \quad -(2)$$

and

$$\rho = \frac{2r}{na}, \quad -(3)$$

where a is the Bohr radius. For example, using the fact that $L_{n+l}^{2l+1}(\rho)$ are the associated Laguerre polynomials, the following is a table of the first few orbitals' radial part:

n	l	$R_{nl}(r)$
1	0 (1s)	$2\left(\frac{1}{a}\right)^{3/2} \exp(-\rho/2)$
2	0 (2s)	$\frac{1}{2\sqrt{2}}\left(\frac{1}{a}\right)^{3/2}(2-\rho)\exp(-\rho/2)$
2	1 (2p)	$\frac{1}{2\sqrt{6}}\left(\frac{1}{a}\right)^{3/2}\rho\exp(-\rho/2)$

The H atom orbital for $n = 1, l = 0, m = 0$

is therefore:

$$\phi = \frac{1}{(\pi a^3)^{1/2}} \exp\left(-\frac{r}{a}\right) \quad -(3)$$

2) The normalization is:

$$\int \psi^* \psi \, d\tau = 1 \quad -(4)$$

This is evaluated using the volume element of the spherical polar coordinate:

$$dV = r^2 \sin\theta \, dr \, d\theta \, d\phi . \quad -(5)$$

Therefore:

$$\int \psi^* \psi \, d\tau = \frac{1}{\pi a^3} \int_0^\infty r^2 e^{-2r/a} \int_0^{2\pi} \int_0^\pi \sin\theta \, d\theta \, d\phi \, dr \quad -(6)$$

where:

$$\int_0^{2\pi} \int_0^\pi \sin\theta \, d\theta \, d\phi = 4\pi . \quad -(7)$$

So

$$\int \psi^* \psi \, d\tau = \frac{4}{a^3} \int_0^\infty r^2 \exp\left(-\frac{2r}{a}\right) dr . \quad -(8)$$

Now use:

$$\int x^2 e^{-\alpha x} dx = e^{-\alpha x} \left(-\frac{x^2}{\alpha} - \frac{2x}{\alpha^2} - \frac{2}{\alpha^3} \right) \quad -(9)$$

to find:

$$\int_0^\infty r^2 e^{-2r/a} dr = \frac{a^3}{4} \quad -(10)$$

Therefore:

$$\int \psi^* \psi \, d\tau = \underline{1} \quad -(11)$$

Q.E.D.

The gradient of ϕ is:

$$\underline{\nabla}\phi = \frac{\partial\phi}{\partial r}\underline{e}_r + \frac{1}{r}\frac{\partial\phi}{\partial\theta}\underline{e}_\theta + \frac{1}{r\sin\phi}\frac{\partial\phi}{\partial\phi}\underline{e}_\phi \quad -(12)$$

so:

$$\hat{p}\phi = -i\hbar\underline{\nabla}\phi \quad -(13)$$

Therefore

$$\boxed{\underline{\nabla}\phi = -\frac{\underline{e}_r}{(\pi a^5)^{1/2}}\exp\left(-\frac{r}{a}\right)} \quad -(14)$$

and

$$\hat{p}\phi = \frac{i\hbar\,\underline{e}_r}{(\pi a^5)^{1/2}}\exp\left(-\frac{r}{a}\right) \quad -(15)$$

and

$$\frac{\partial\phi}{\partial r} = -\frac{1}{(\pi a^5)^{1/2}}\exp\left(-\frac{r}{a}\right) \quad -(16)$$

Now use:

$$\underset{\sim}{r} = X\underline{i} + Y\underline{j} + Z\underline{k} \quad -(17)$$

where:

$$\left.\begin{aligned} X &= r\sin\theta\cos\phi \\ Y &= r\sin\theta\sin\phi \\ Z &= r\cos\theta \end{aligned}\right\} \quad -(18)$$

$$\left.\begin{aligned} \underline{i} &= \sin\theta\cos\phi\,\underline{e}_r + \cos\theta\cos\phi\,\underline{e}_\theta - \sin\phi\,\underline{e}_\phi \\ \underline{j} &= \sin\theta\sin\phi\,\underline{e}_r + \cos\theta\sin\phi\,\underline{e}_\theta + \cos\phi\,\underline{e}_\phi \\ \underline{k} &= \cos\theta\,\underline{e}_r - \sin\theta\,\underline{e}_\theta \end{aligned}\right\} \quad -(19)$$

to find that:

$$\underset{\sim}{r} = r\left(\cos^2\theta + \sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi\right)\underline{e}_r$$
$$+ r\left(\cos^2\theta + \sin^2\theta\cos^2\phi + \sin\theta\cos\theta\sin^2\phi\right)\underline{e}_\theta$$
$$+ r\left(-\cos\theta\sin\theta + \sin\theta\cos\theta\cos^2\phi\right.$$

$$+ i r\left(-\sin\theta\cos\phi\sin\phi+\sin\theta\sin\phi\cos\phi\right)\underline{e}_\phi$$

$$= r\underline{e}_r \quad -(20)$$

So:

$$\boxed{\begin{aligned}\hat{p}\,\psi &= \frac{i\hbar}{(\pi a^5)^{1/2}}\exp\left(-\frac{r}{a}\right)\underline{e}_r &-(21)\\ \underline{r} &= r\underline{e}_r &-(22)\end{aligned}}$$

Therefore it is convenient to work out:

$$\left[r, \frac{\partial}{\partial r}\right]\psi = r\frac{\partial\psi}{\partial r} - \frac{\partial}{\partial r}(r\psi)$$

$$= r\frac{\partial\psi}{\partial r} - r\frac{\partial\psi}{\partial r} - \psi \quad -(23)$$

and

$$\left\{r, \frac{\partial}{\partial r}\right\}\psi = 2r\frac{\partial\psi}{\partial r} + \psi. \quad -(24)$$

For this purely radial wave function:

$$\left[r, \hat{p}_r\right]\psi = i\hbar\psi \quad -(25)$$

and

$$\left\{r, \hat{p}_r\right\}\psi = -i\hbar\left(\psi + 2r\frac{\partial\psi}{\partial r}\right) \quad -(26)$$

with

$$\boxed{\begin{aligned}\left[r^2, \hat{p}_r^2\right]\psi &= 2i\hbar\left\{r, \hat{p}_r\right\}\psi \\ &= 2\hbar^2\left(\psi + 2r\frac{\partial\psi}{\partial r}\right)\end{aligned}} \quad -(27)$$

? e expectation value can now be worked out.