Problem 6: The hydrogen atom (10 points)

The figure below shows the radial function $R_{n,\ell}(r)$ for a stationary state of atomic hydrogen. The normalized Hamiltonian eigenfunction for this state, in atomic units, is

$$\psi_{n,\ell,m_\ell}(\boldsymbol{r}) = \frac{1}{81}\sqrt{\frac{2}{\pi}}(6-r)\; e^{-r/3}\;\cos\theta. \tag{1}$$

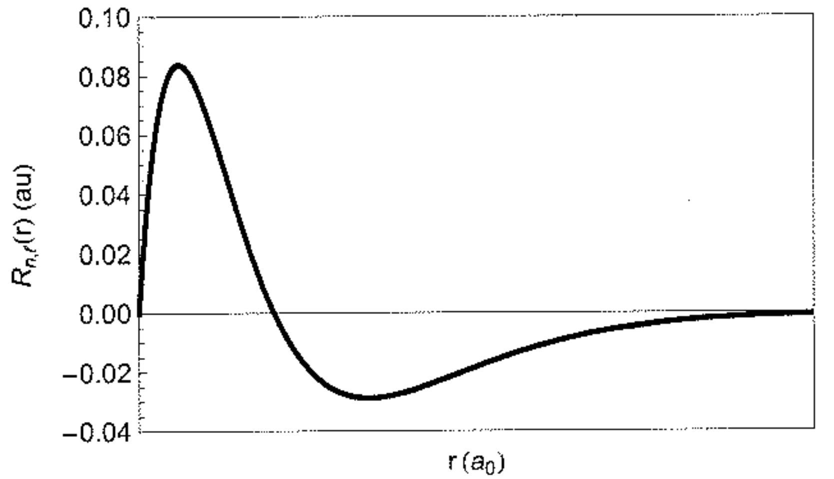

Figure 1: A radial function for a stationary state of atomic hydrogen.

1. **3 points.** What are the values of the quantum numbers n, ℓ, and m_ℓ for this state? To receive any credit, you must fully justify your answer.
2. **1 points.** What is the energy (in eV) of this state?
3. **2 points.** What are the mean value and uncertainty in r (in atomic units) for this state?
4. **2 points.** Calculate the value of r (in atomic units) at which a position measurement would be most likely to find the electron if the atom is in this state.
5. **2 points.** From Eq. 1, generate the normalized eigenfunction $\psi_{n,\ell,m_\ell+1}(\boldsymbol{r})$.

Hint:

$$\int_0^\infty e^{-2r/3} r^n\, \mathrm{d}r = n!\left(\frac{3}{2}\right)^{n+1} \tag{2}$$

Hint: *The following table gives the orbital-angular-momentum operators in Cartesian and spherical coordinates.*

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Component	Cartesian coordinates	Spherical coordinates
$\widehat{L}_x$	$-\imath\hbar\left(y\dfrac{\partial}{\partial z}-z\dfrac{\partial}{\partial y}\right)$	$\imath\hbar\left(\sin\varphi\dfrac{\partial}{\partial\theta}+\cot\theta\cos\varphi\,\dfrac{\partial}{\partial\varphi}\right)$
$\widehat{L}_y$	$-\imath\hbar\left(z\dfrac{\partial}{\partial x}-x\dfrac{\partial}{\partial z}\right)$	$-\imath\hbar\left(\cos\varphi\dfrac{\partial}{\partial\theta}-\cot\theta\sin\varphi\,\dfrac{\partial}{\partial\varphi}\right)$
$\widehat{L}_z$	$-\imath\hbar\left(x\dfrac{\partial}{\partial y}-y\dfrac{\partial}{\partial x}\right)$	$-\imath\hbar\dfrac{\partial}{\partial\varphi}$
$\widehat{\boldsymbol{L}}^2$	$\widehat{L}_x^2+\widehat{L}_y^2+\widehat{L}_z^2$	$-\hbar^2\left[\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial}{\partial\theta}\right)+\dfrac{1}{\sin^2\theta}\dfrac{\partial^2}{\partial\varphi^2}\right]$

Table 1: Components and square of the orbital angular momentum operator in Cartesian and spherical coordinates.

(a)

In general, we know $\ell = 0, \ldots, n-1$ and $m_\ell = -\ell, \ldots, \ell$. Since there is no ϕ dependence, we know $\boxed{m_\ell = 0}$. Our Legendre polynomial is $P = \cos\theta$, which corresponds to $m_\ell = 0$ and $\boxed{\ell = 1}$. So we know we must have $n > 1$.

In general, the exponential portion of the radial equation is given by

$$e^{-x/2},$$

where

$$x = \frac{2r}{a_0}.$$

So

$$e^{-x/2} = e^{-\frac{1}{2}\left(\frac{2r}{na_0}\right)} = e^{-r/na_0}.$$

In atomic units, $a_0 = 1$, so since our exponential portion is

$$e^{-r/3},$$

we must have $\boxed{n = 3}$. Thus,

$$|n\,\ell\,m_\ell\rangle = |3\;1\;0\rangle.$$

(b)

The energy is given by

$$E_n = \frac{E_1}{n^2},$$

where

$$E_1 = -13.6\,\text{eV}.$$

So since $n = 3$, we have

$$E_3 = \frac{-13.6\,\text{eV}}{(3)^2}$$

$$= \frac{-13.6\,\text{eV}}{9}$$

$$\boxed{E_3 \approx -1.51\,\text{eV}}$$

(c)

We want to determine $\langle r \rangle$ and Δr. So

$$\langle r \rangle = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \left(\frac{1}{81}\sqrt{\frac{2}{\pi}}\right)^2 r(6-r)^2 e^{-2r/3} \cos^2\theta \, r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{4\pi}{3}\left(\frac{1}{81}\sqrt{\frac{2}{\pi}}\right)^2 \int_0^{\infty} \left(r^5 - 12r^4 + 36r^3\right) e^{-2r/3} dr$$

$$= \frac{8}{3^9}\left[\frac{5!}{(2/3)^6} - 12\frac{4!}{(2/3)^5} + 36\frac{3!}{(2/3)^4}\right]$$

$$= \frac{8}{3^9}\left[\frac{5\cdot\cancel{4}\cdot 3\cdot\cancel{2}\cdot 3^6}{\cancel{2^2}\cdot\cancel{2}\cdot 2^3} - 12\,\frac{\cancel{4}\cdot 3\cdot\cancel{2}\cdot 3^5}{\cancel{2^2}\cdot\cancel{2}\cdot 2^2} + 36\,\frac{3\cdot\cancel{2}\cdot 3^4}{\cancel{2}\cdot 2^3}\right]$$

$$= \frac{2^3}{3^9}\left[\frac{5\cdot 3^7}{2^3} - \frac{\cancel{2^4}\cdot 3^7}{\cancel{2^2}} + \frac{2^2\cdot 3^7}{2^3}\right]$$

$$= \frac{1}{3^9}\left[5\cdot 3^7 - 2^3\cdot 3^7 + 2^2\cdot 3^7\right]$$

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

$$= \frac{5}{9} - \frac{8}{9} + \frac{4}{9}$$

$$\boxed{\langle r \rangle = \frac{1}{9}}.$$

(c), cont'd...

We know

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2},$$

so we need to determine $\langle r^2 \rangle$. Then

$$\langle r^2 \rangle = \frac{2}{3} \cdot 2\pi \left(\frac{1}{81}\sqrt{\frac{2}{\pi}}\right)^2 \int_0^\infty \left[\left(r^6 - 12r^5 + 36r^4\right) e^{-2r/3} dr\right]$$

$$= \frac{4\pi}{3}\left(\frac{1}{81}\sqrt{\frac{2}{\pi}}\right)^2 \left[\frac{6!}{(2/3)^7} - 12\frac{5!}{(2/3)^6} + 36\frac{4!}{(2/3)^5}\right]$$

$$= \frac{8}{3^9}\left[\frac{6\cdot5\cdot\cancel{4}\cdot3\cdot\cancel{2}\cdot3^7}{\cancel{2}\cdot\cancel{2^2}\cdot\cancel{2}\cdot2^3} - \frac{5\cdot\cancel{4}\cdot3\cdot\cancel{2}\cdot\cancel{2^2}\cdot3\cdot3^6}{\cancel{2^2}\cdot\cancel{2}\cdot\cancel{2^2}\cdot2} + \frac{\cancel{4}\cdot3\cdot\cancel{2}\cdot3^2\cdot\cancel{2^2}\cdot3^5}{\cancel{2^2}\cdot\cancel{2}\cdot\cancel{2^2}}\right]$$

$$= \frac{2^3}{3^9}\left[\frac{3\cdot5\cdot3\cdot3^7}{2^3} - \frac{5\cdot3\cdot3\cdot3^6}{2} + 3\cdot3^2\cdot3^5\right]$$

$$= \frac{2^3}{3^9}\left[\frac{5\cdot3^9}{2^3} - \frac{5\cdot3^8}{2} + 3^8\right]$$

$$= 5 - \frac{2^2\cdot5}{3} + \frac{2^3}{3}$$

$$= 5 - \frac{20}{3} + \frac{8}{3}$$

$$= 1$$

and thus,

$$\Delta r = \sqrt{1 - (1/9)^2}$$

$$= \sqrt{\frac{80}{81}}$$

$$\boxed{\Delta r = \frac{4\sqrt{5}}{9}}$$

(d)

We want to determine the most probable radius. The radial probability density is

$$\rho = 4\pi r^2 |\psi_r|^2$$
$$= 4\pi r^2 \left(\frac{1}{81}\sqrt{\frac{2}{\pi}}\right)^2 (r^2 - 12r + 36) e^{-2r/3}$$

We want to maximize this. So

$$\frac{d\rho}{dr} = \frac{d}{dr}\left[\frac{8}{81^2}(r^4 - 12r^3 + 36r^2) e^{-2r/3}\right] = 0$$

$$= \frac{8}{81^2}\left[-\frac{2}{3}e^{-2r/3}(r^4 - 12r^3 + 36r^2) + e^{-2r/3}(4r^3 - 36r^2 + 72r)\right] = 0$$

$$+\frac{2}{3}(r^4 - 12r^3 + 36r^2) = 4r^3 - 36r^2 + 72r$$
$$r^4 - 12r^3 + 36r^2 = 6r^3 - 54r^2 + 108r$$
$$r^3 - 12r^2 + 36r = 6r^2 - 54r + 108$$
$$r^3 - 18r^2 + 90r - 108 = 0$$

The roots are

$$r = -3(\sqrt{2} - 2),\ 3(\sqrt{2} + 2),\ 6$$

Based on the plot, it seems as though our most probable radius is

$$r = 3(2 - \sqrt{2})$$
$$\boxed{r = 6 - 3\sqrt{2}},$$

which is verified by plugging each of our choices into ψ_r.

(e)

In order to find $\psi_{n,\ell,m_\ell+1}$, we want to apply the raising operator

$$L_+ = L_x + iL_y .$$

We have

$$L_+ = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) + \hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

Since ψ_{n,ℓ,m_ℓ} does not depend on ϕ, we can eliminate those derivatives
Then

$$L_+ = i\hbar\sin\phi\frac{\partial}{\partial\theta} + \hbar\cos\phi\frac{\partial}{\partial\theta} .$$

We want to determine

$$\psi_{n,\ell,m_\ell+1} = L_+\psi_{n,\ell,m_\ell} .$$

So

$$L_+\psi_{n,\ell,m_\ell} = \left(i\hbar\sin\phi\frac{\partial}{\partial\theta} + \hbar\cos\phi\frac{\partial}{\partial\theta}\right)\left(\frac{1}{81}\sqrt{\frac{2}{\pi}}(6-r)e^{-r/3}\cos\theta\right)$$

$$= \frac{\hbar}{81}\sqrt{\frac{2}{\pi}}\left(i\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\frac{\partial}{\partial\theta}\right)\left((6-r)e^{-r/3}\cos\theta\right)$$

$$= \frac{\hbar}{81}\sqrt{\frac{2}{\pi}}\left[-i\sin\theta\sin\phi(6-r)e^{-r/3} - \sin\theta\cos\phi(6-r)e^{-r/3}\right]$$

$$= -\frac{\hbar}{81}\sqrt{\frac{2}{\pi}}(6-r)e^{-r/3}\left[\sin\theta(\cos\phi + i\sin\phi)\right]$$

$$\boxed{\psi_{n,\ell,m_\ell+1}(\vec{r}) = -\frac{\hbar}{81}\sqrt{\frac{2}{\pi}}(6-r)e^{-r/3}\sin\theta\, e^{i\phi}}.$$