The radial equation

Recall that

$$-\frac{\hbar^2}{2\mu}\left(\partial_r^2 R + \frac{2}{r}\partial_r R\right) + \left(V + \frac{a}{r^2}\right)R = ER$$ and we found $a = \frac{\hbar^2}{2\mu} l(l+1)$, so:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}(E - V)R = l(l+1)\frac{R}{r^2}$$

To solve this equation, we need to specify $V(r)$. Let's consider the case of one-electron atoms, so $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$, where Z is the nuclear charge ($Z=1$ for hydrogen, $Z=2$ for ionized helium), $-e$ = electron charge = 1.6×10^{-19} C, ε_0 = vacuum permittivity = 8.85×10^{-12} F/m (Faraday/meters)

This $V(r)$ is called the Coulomb potential

Note that at this point we know nothing about E other than it is constant. Let us show that E cannot be complex. Let R^* be the complex conjugate of R (we don't know yet if R is real or complex; of course, if R is real then $R^* = R$), write $V(r) = -\frac{K}{r}$, $K > 0$, and multiply the equation by $r^2 R^*$:

$$R^* \frac{d}{dr}\left(r^2 R\right) + \frac{2\mu}{\hbar^2} r^2 E R^* R + \frac{2\mu}{\hbar^2} K r R^* R = \ell(\ell+1) R^* R .$$

Integrate this equation from 0 to ∞, and assume that the integrals converge:

$$\int_0^\infty R^* \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) dr + \frac{2\mu E}{\hbar^2} \int_0^\infty r^2 |R|^2 dr + \frac{2\mu K}{\hbar^2} \int_0^\infty r |R|^2 dr = \ell(\ell+1) \int_0^\infty |R|^2 dr$$

where we used that $R^* R = |R|^2$ which is real. Integrating by parts:

$$\int_0^\infty R^* \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) dr = -\int_0^\infty \frac{dR^*}{dr} r^2 \frac{dR}{dr} dr + R^* r^2 \frac{dR}{dr}\Big|_0^\infty = -\int_0^\infty r^2 \left|\frac{dR}{dr}\right|^2 dr + R^* r^2 \frac{dR}{dr}\Big|_0^\infty$$

The function R and its derivatives should not be singular at $r=0$, so $R^* r^2 \frac{dR}{dr} \longrightarrow 0$ as $r \to 0$. Since under our assumptions the integrals $\int_0^\infty r^2 \left|\frac{dR}{dr}\right|^2 dr$ and $\int_0^\infty r^2 |R|^2 dr$ converge, we have that $r\frac{dR}{dr}$ and rR have to go to zero when $r \to \infty$. Thus $R^* r^2 \frac{dR}{dr} = (R^* r)(r\frac{dR}{dr}) \to 0$ as $r \to \infty$, and we conclude that $R^* r^2 \frac{dR}{dr}\Big|_0^\infty = 0$. We obtain

$$- \int_0^\infty r^2 \left|\frac{dR}{dr}\right|^2 dr + \frac{2\mu E}{\hbar^2}\int_0^\infty r^2 |R|^2 dr + \frac{2\mu K}{\hbar^2}\int_0^\infty r |R|^2 dr = l(l+1)\int_0^\infty |R|^2 dr .$$

All terms in this expression are real. Solving for E, we conclude that E must be real as well.

E being real implies that R is a real function.

Now that we know E to be a real number, let us show that it is negative.

To analyze the equation, let us investigate its behavior when $r \gg 1$. Since $V \sim \frac{1}{r}$, we then get $\frac{d^2R}{dr} + \frac{2\mu}{\hbar^2} E R \approx 0$. Multiply by r and note that $\partial_r^2(rR) = \partial_r(R + r\partial_r R) = 2\partial_r R + r\partial_r^2 R \simeq r\partial_r^2 R$ for $r \gg 1$, so we can write $\partial_r^2(rR) \simeq -\frac{2\mu}{\hbar^2} E(rR)$, which has the (approximate) solutions (solve for rR): $rR \simeq e^{\pm \frac{\sqrt{-2\mu E}}{\hbar} r}$. If $E \geq 0$, then this solution is complex of the form $rR \simeq e^{\pm i \xi r}$, $\xi = \frac{\sqrt{2\mu E}}{\hbar}$, so that $|rR| \simeq 1$ for $r \gg 1$. But then $\int_{\mathbb{R}^3} |R|^2 \, dx = \int_{\mathbb{R}^3} \underbrace{|R|^2 r^2}_{\simeq 1 \text{ for } r \gg 1} \sin\varphi \, dr \, d\varphi \, d\theta$ and the integral diverges. So does $\int_{\mathbb{R}^3} |\Psi|^2$ but $\int_{\mathbb{R}^3} |\Psi|^2$ must be finite to allow $\int_{\mathbb{R}^3} |\Psi|^2 = 1$. Hence $E < 0$.

As $E < 0$, $-\frac{2\mu E}{\hbar^2} > 0$, thus we can set $\beta^2 = -\frac{2\mu E}{\hbar^2}$. We also introduce $\gamma = \frac{\mu Z e^2}{4\pi\varepsilon_0 \hbar^2 \beta}$ and $\varrho = 2\beta r$. Using this definitions into the R equation gives:

$$\frac{1}{\varrho^2}\frac{d}{d\varrho}\left(\varrho^2 \frac{dR}{d\varrho}\right) + \left(-\frac{1}{4} - \frac{l(l+1)}{\varrho^2} + \frac{\gamma}{\varrho}\right) R = 0$$

Note that we do not know what β and γ are since we don't know E.

We will solve this equation using power series techniques. A simple power series of the form $R(\varrho) = \sum_{k=0}^{\infty} a_k \varrho^k$, however, will not work. To see this, compute $\frac{1}{\varrho^2}\frac{d}{d\varrho}\left(\varrho^2 \frac{d}{d\varrho}\sum_{k=0}^{\infty} a_k \varrho^k\right) = \frac{1}{\varrho^2}\frac{d}{d\varrho}\left(\sum_{k=0}^{\infty} k a_k \varrho^{k+1}\right) = \sum_{k=0}^{\infty} k(k+1) a_k \varrho^{k-2}$, so

$$\sum_{k=0}^{\infty}(k+1) k a_k \varrho^{k-2} - \frac{1}{4}\sum_{k=0}^{\infty} a_k \varrho^k - l(l+1)\sum_{k=0}^{\infty} a_k \varrho^{k-2} + \gamma \sum_{k=0}^{\infty} a_k \varrho^{k-1} = 0$$

Expanding:

$$2\cdot 1\, a_1 \varrho^{-1} + \overbrace{\sum_{k=2}^{\infty}(k+1)k\, a_k \varrho^{k-2}}^{=\sum_{k=0}^{\infty}(k+3)(k+2)a_{k+2}\varrho^{k}} - \frac{1}{4}\sum_{k=0}^{\infty} a_k \varrho^{k} - l(l+1)a_0\varrho^{-2} - l(l+1)a_1\varrho^{-1} - l(l+1)\overbrace{\sum_{k=2}^{\infty} a_k \varrho^{k-2}}^{=\sum_{k=0}^{\infty} a_{k+2}\varrho^{k}}$$

$$+ \rho a_0 \varrho^{-1} + \underbrace{\rho \sum_{k=1}^{\infty} a_k \varrho^{k-1}}_{=\sum_{k=0}^{\infty} a_{k+1}\varrho^{k}} = 0$$

$$-l(l+1)a_0\varrho^{-2} + \left(\left(2-l(l+1)\right)a_1 + \rho a_0\right)\varrho^{-1} + \sum_{k=0}^{\infty}\left[\left((k+3)(k+2)-l(l+1)\right)a_{k+2} + \rho a_{k+1} - \frac{1}{4}a_k\right]\varrho^{k} = 0$$

This leads to $a_0 = 0$, $a_1 = 0$ and then $a_k = 0$ for all k, so $R = 0$.

Therefore, we need a more elaborated approach to find R.

For $\varrho \gg 1$, the equation gives

$\frac{dR}{d\varrho} - \frac{1}{4}R \approx 0$. Seeking an approximate solution of the form $e^{\lambda\varrho}$, we find $R(\varrho) \approx e^{-\frac{1}{2}\varrho}$.

This suggest looking for solutions of the form $R(\rho) = e^{-\frac{\rho}{2}} F(\rho)$ for some function F to be determined. Plugging in we obtain that F must satisfy:

$$\frac{d^2 F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left(\frac{\gamma - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) F = 0$$

The presence of the terms $\frac{1}{\rho}$ and $\frac{1}{\rho^2}$ suggest that we should try

$$F(\rho) = \rho^s \sum_{k=0}^{\infty} a_k \rho^k = \sum_{k=0}^{\infty} a_k \rho^{s+k}.$$

We need $s \geq 0$ in order to guarantee that F is finite when $\rho \to 0^+$.

We can also assume that $a_0 \neq 0$ (otherwise we could just relabel the coefficients)

Plugging in:

$$\sum_{k=0}^{\infty} (s+k)(s+k-1) a_k \rho^{s+k-2} + \underbrace{\left(\frac{2}{\rho} - 1\right)\sum_{k=0}^{\infty} (s+k) a_k \rho^{s+k-1}}_{= 2\sum_{k=0}^{\infty} (s+k) a_k \rho^{s+k-2} - \sum_{k=0}^{\infty} (s+k) a_k \rho^{s+k-1}} + \overbrace{\left(\frac{\gamma-1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)\sum_{k=0}^{\infty} a_k \rho^{s+k}}^{(\gamma-1)\sum_{k=0}^{\infty} a_k \rho^{s+k-1} - \ell(\ell+1)\sum_{k=0}^{\infty} a_k \rho^{s+k-2}} = 0$$

Regrouping:

$$\sum_{k=0}^{\infty}\Big(\underbrace{(s+k)(s+k-1)+2(s+k)-l(l+1)}_{=(s+k)(s+k+1)-l(l+1)}\Big)a_k\,\rho^{s+k-2}+\sum_{k=0}^{\infty}\Big(\overbrace{(\rho-1)-(s+k)}^{=-(s+k+1-\rho)}\Big)a_k\,\rho^{s+k-1}=0$$

Expanding

$$\big(s(s+1)-l(l+1)\big)a_0\,\rho^{s-2}+\underbrace{\sum_{k=1}^{\infty}\big((s+k)(s+k+1)-l(l+1)\big)a_k\,\rho^{s+k-2}}_{=\sum_{k=0}^{\infty}\left((s+k+1)(s+k+2)-l(l+1)\right)a_{k+1}\,\rho^{s+k-1}}-\sum_{k=0}^{\infty}(s+k+1-\rho)a_k\,\rho^{s+k-1}=0$$

$$\big(s(s+1)-l(l+1)\big)a_0\,\rho^{s-2}+\sum_{k=0}^{\infty}\Big[\big((s+k+1)(s+k+2)-l(l+1)\big)a_{k+1}-(s+k+1-\rho)a_k\Big]\rho^{s+k-1}=0$$

The first term must vanish for any ρ and $a_0\neq 0$, thus

$s(s+1)-l(l+1)=0$. This has two solutions: $s=l$

$s=-(l+1)$

But recall that we must have $s \geq 0$ (if we use $s = -(l+1)$, then we get $F(\rho) = \rho^{-(l+1)} \sum_{k=0}^{\infty} a_k \rho^k$ which blows-up when $\rho \to 0^+$) Therefore we take

$s = l$. Now that we have determined s, we obtain the following recurrence relation:
$$a_{k+1} = \frac{l+k+1-r}{(l+k+1)(l+k+2)-l(l+1)} a_k$$

We next investigate the convergence of this series. We have:
$$a_{k+1} = \frac{k+\cdots}{k^2+\cdots} a_k = \frac{k+\cdots}{k^2+\cdots} \frac{k-1+\cdots}{(k-1)^2+\cdots} a_{k-1} = \frac{k+\cdots}{k^2+\cdots} \frac{k-1+\cdots}{(k-1)^2+\cdots} \frac{k-2+\cdots}{(k-2)^2+\cdots} a_{k-2},$$
i.e., for k very large $a_k \approx \frac{k(k-1)(k-2)\cdots}{k^2(k-1)^2(k-2)^2} \approx \frac{1}{k!}$. This means that the series $\sum_{k=0}^{\infty} a_k \rho^{s+k}$ behaves like $\rho^s e^{\rho}$. But recalling that $R(\rho) = e^{-\frac{\rho}{2}} F(\rho)$, we then have $R(\rho) \approx \rho^s e^{-\frac{\rho}{2}} e^{\rho} = \rho^s e^{\frac{\rho}{2}}$. Since $\rho^s e^{\frac{\rho}{2}} \to \infty$ as $\rho \to \infty$,

The integral $\int_0^\infty R^2(\rho)\,d\rho$ thus diverges, implying that $\int_{\mathbb{R}^3} |\Psi|^2\,dx$ diverges as well, which cannot be the case. Therefore, the series for F,

$$F(\rho) = \sum_{k=0}^{\infty} a_k \rho^{s+k} = \sum_{k=0}^{\infty} a_k \rho^{\ell+k}$$ can have only finitely many terms. From the recurrence relation we thus conclude that for some k:

$$\ell + k + 1 - p = 0$$

This means that p must be an integer. Recall that p was undetermined up to this point since it involves β which in turn involves E. In other words,

$p = n$, with $n = \ell+1, \ell+2, \ldots$. With $p = n$ the series terminates at the $(n-(\ell+1))$-th term and $F(\rho)$ is then a polynomial of degree $n-1$.

Thus we have

$$F_n(\rho) = \sum_{k=0}^{\infty} a_{k,n}\,\rho^{\ell+k}$$ with $a_{k,n}$ given by the recurrence relation with $p = n$; $n = 1, 2, \ldots$

Hence $R_n(\rho) = e^{-\frac{\rho}{2}} F_n(\rho)$, or $R_{n,\ell}(\rho) = e^{-\frac{\rho}{2}} F_{n,\ell}(\rho)$ to indicate the dependence on ℓ

Using the definitions of ρ and β we can now write $E = E_n$. We find

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\cdot\frac{1}{n^2}, \quad n = 1, 2, \ldots$$

We can also write: $R_{n,\ell}(r) = e^{-\frac{Zr}{n\alpha}}\left(\frac{Zr}{n\alpha}\right)^{\ell} F_{n,\ell}\left(\frac{Zr}{n\alpha}\right)$, $\alpha = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$

Combining everything, we finally obtain $\psi = R\,\Phi\,\Theta$ and $\Psi = e^{-\frac{iEt}{\hbar}} R\,Y$.

Since the equation is linear, $A e^{-\frac{iEt}{\hbar}} R\,Y$ is also a solution for any constant A.

Writing the dependence on n, ℓ, m, we have

$$\Psi_{n,\ell,m}(t,x) = A_{n,\ell,m}\, e^{-\frac{iE_n t}{\hbar}} R_{n,\ell}(r)\, Y_{\ell,m}(\theta,\varphi), \text{ where } \begin{cases} n = 1, 2, 3, \ldots \\ \ell = 0, 1, 2, \ldots, n-1 \\ m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell. \end{cases}$$

We choose the constant $A_{n,\ell,m}$ so that $\int_{\mathbb{R}^3} |\Psi|^2\, dx = 1$. Explicitly:

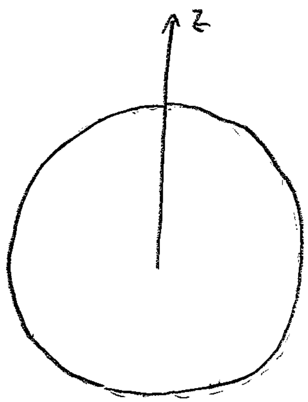
$$A_{n,\ell,m} = \left[\left(\int_0^\infty |R_{n,\ell}(r)|^2 r^2\, dr\right)\left(\int_0^{2\pi}\int_0^{\pi} |Y_{\ell,m}(\theta,\varphi)|^2 \sin\varphi\, d\varphi\, d\theta\right)\right]^{-1/2}$$

Physical interpretation: We changed $m \mapsto \mu$ because the motion of the electron around the nucleous happens about the center of mass of the system. We take r to be not the distance between the electron and (the center of) the nucleous but rather its distance to the center of mass. But then we must use the reduced mass μ given by $\mu = \dfrac{Mm}{M+m}$ where M is the mass of the nucleous (but $\mu \simeq m$ if $M \gg m$).

The values E_n are the energy levels of the electron, the values of l and m are associated, respectively, to the magnitude of the orbital angular momentum and m to the x_3-component of the angular momentum. Note that all these values are quantized.

General nomenclature: one-electron atoms with $l = 0, 1, 2, 3$ are labeled s, p, d, f. In hydrogen and hydrogen-like atoms, this letter is preceded by a number giving the energy level (n). Thus, the lowest energy state of the hydrogen is 1s, the next to the lowest 2s and 2p, the next 3s, 3p, 3d, and so on (see Weinberg p. 43).

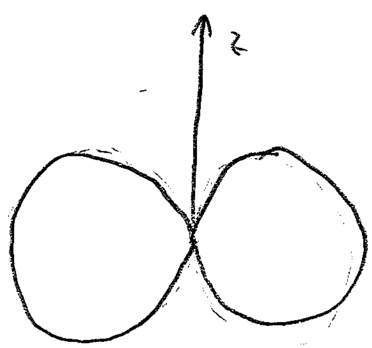
Polar diagrams of probabilities ($\Phi^* \Phi$)



$l = 0,\ m_l = 0$

($n = 1$)

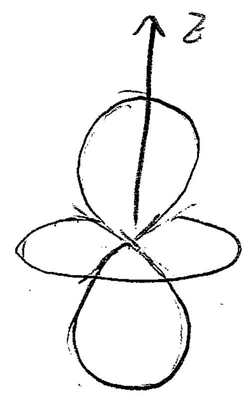
s



$l = 1,\ m_l = \pm 1$

($n = 2$)

p



$l = 3,\ m_l = 0$

($n = 3$)

d