However, not that we need $P_l^m(\cos\theta)$ which is always a polynomial in $\cos\theta$ or $\sin\theta$. Note that l must be nonnegative and integer to make sense. Also note that if $|m| > l$ then $P_l^m = 0$. Thus, for any given l, there are $2l+1$ possible values of m

$$m = -l, -l_1 + 1, \dots, l_1 - 1, l$$

We initially assumed that m and l can be any complex number. What happened? Well, all other solutions exist, but they blow up at $\theta = 0$ or $\theta = \pi$.

The last thing we need to do is to look at the normalization.

$$1 = \int |\psi|^2 d^3r = \int |\psi|^2 r^2 \sin\theta dr\, d\theta\, d\phi = \int |R|^2 r^2 dr \quad \int |Y|^2 \sin\theta d\theta\, d\phi$$

Let's normalize them separately

$$\begin{aligned} 1 &= \int |R|^2 r^2 dr \\ 1 &= \int |Y|^2 \sin\theta d\theta\, d\phi \end{aligned}$$

Let's not do the calculation and rather quote the result. The normalized functions are the spherical harmonics

$$Y_l^m(\theta\phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos\theta)$$

where

$$\epsilon = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m \leq 0 \end{cases}$$

These functions are orthogonal:

$$\int_0^{2pi} \int_0^{\pi} [Y_l^m(\theta,\phi)]^* [Y_{l'}^{m'}(\theta,\phi)]^* \sin\theta d\theta\, d\phi = \delta_{ll'} \delta_{mm'}$$

For purely historical reasons we define two names for the two integers:

Definition 37. l is the azimuthal quantum number

Definition 38. m is the magnetic quantum number

9.4 The radial equation

We still need to look at the radial equation.

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} R \right) - \frac{2mr^2}{\hbar^2} (V - E) \quad = \quad -l(l+1)$$

Let's multiply this with R to get

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} R \right) - \frac{2mr^2}{\hbar^2} (V - E) R \quad = \quad -l(l+1) R$$

and make the Ansatz $u(r) \equiv rR(r)$. We have

$$\begin{aligned} R &= \frac{u}{r} \\ \frac{\partial}{\partial r} R &= \frac{r \frac{\partial}{\partial r} u}{r^2} \\ \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} R\right) &= r \frac{\partial^2}{\partial r^2} u \end{aligned}$$

This gives us

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} u + \left(V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right) u = Eu$$

The bracket term is called the effective potencial, which includes the potential itself ans the centrifigual term. The normalization condition becomes

$$\int_0^\infty |u|^2 dr = 1$$

To go any further, we need to specify the potential $V(r)$.

10 Hydrogen Atom

We now move on the solve the hydrogen atom. Finally! In the hydrogen atom's centre, there is a heavy charged nucleus, the proton. The potential is given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

The radial equation of the spherical time-independent Schroedinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} u + \left(-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right) u = Eu$$

We will basically follow the approach we used for the harmonic oscillator. Just the form of the potential is different. Note that there is also one qualitative difference. The potential allows for continuum states ($E > 0$). These describe electron-positron scattering. The discrete states describe the bound states of the hydrogen atom.

10.1 The Radial Wave Function

Let us tidy up the radial equation by defining

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$$

Then, we have

$$\frac{1}{\kappa^2}\frac{\partial^2}{\partial r^2} u = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\kappa r} + \frac{l(l+1)}{\kappa^2 r^2}\right] u$$

Let's further rescale the radios and define ρ_0

$$\begin{aligned} \rho &\equiv \kappa r \\ \rho_0 &\equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \end{aligned}$$

Then we have a *nice* equation

$$\frac{\partial^2}{\partial\rho^2}\,u = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right] u$$

As in the harmonic oscillator case, we look at the limit for $\rho \to \infty$. The equation reduces to

$$\frac{\partial^2}{\partial\rho^2}\,u = u$$

Which has the solution

$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

The B term blows up, so the state would be unnormalizable. Thus the A term is the physical one.

Let's look at the other limit $\rho \to 0$

$$\frac{\partial^2}{\partial\rho^2}\,u = \frac{l(l+1)}{\rho^2}u$$

Thegeneral solution is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l}$$

Here, the D term blows up near the origin, so the C term must be the physical solution.

This motives the following Ansatz:

$$u(\rho) = \rho^{l+1}e^{-l}v(\rho)$$

Let's calculate the derivatives.

$$\begin{aligned}
\frac{\partial}{\partial\rho}\,u(\rho) &= (l+1)\rho^l e^{-l}v(\rho) - \rho^{l+1}e^{-l}v(\rho) + \rho^{l+1}e^{-l}\,\frac{\partial}{\partial\rho}\,v(\rho) \\
&= \rho^l e^{-\rho}\left[(l+1-\rho)v(\rho) + \rho\,\frac{\partial}{\partial\rho}\,v(\rho)\right] \\
\frac{\partial^2}{\partial\rho^2}\,u(\rho) &= \rho^l e^{-\rho}\left\{\left[-2l - 2 + \rho + \frac{l(l+1)}{\rho}\right]v(\rho) + 2(l+1-\rho)\,\frac{\partial}{\partial\rho}\,v(r) + \rho\,\frac{\partial^2}{\partial\rho^2}\,v(r)\right\}
\end{aligned}$$

Putting this into the radial equation simplifies it to

$$\rho\,\frac{\partial^2}{\partial\rho^2}\,v(r) + 2(l+1-\rho)\,\frac{\partial}{\partial\rho}\,v(r) + \left[\rho_0 - 2(l+1)\right]v(r) = 0$$

Now, let's make a Taylor series Ansatz

$$v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$$

Putting this in the radial equations gives us an equation for the coefficients c_j

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]c_j = 0$$

or, writing it as recursion

$$c_{j+1} = \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)}c_j$$

Let's look at those coefficients for $j \to \infty$. We have

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$$

This gives us the asymptotic behaviour of

$$c_j \approx \frac{2^j}{j!} c_0$$

And thus

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

or

$$u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

Surprise! It blows up. There is something wrong. As in the harmonic oscillator case, this can only we solved if the series terminates. Thus there is a j_{max} such that $c_j = 0$ for all $j > j_{max}$. This condition equals

$$2(j_{max} + l + 1) - \rho_0 = 0$$

Let us define the principle quantum number

$$n = j_{max} + l + 1$$

Then

$$\rho_0 = 2n$$

Because

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

the energy levels are then

$$E_n = -\left(\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon} \right)^2 \right) \frac{1}{n^2} = \frac{E_1}{n^2} \qquad n = 1, 2, 3, \ldots$$

This is called the Bohr Formula, obtained by Bohr in 1913. He used some primitive form of quantum mechanics which did not yet include the Schroedinger Equation (which was first written down in 1924). The lowest energy state is E_1 with a numerical value of -13.6 eV.

The constant κ can be written as

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0 \hbar^2} \right) \frac{1}{n} = \frac{1}{an}$$

Here, a is the Bohr radius

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 5.929 \cdot 10^{-11}\text{m}$$

With this quantity we can write

$$\rho = \frac{r}{an}$$

We can now label the position space wave function using the three quantum numbers

$$\psi n, l, m(r, \theta\phi) = R_{n,l}(r) Y_l^m(\theta, \phi)$$

where

$$R_{n,l}(r) = \frac{1}{r}\rho^{l+1} e^{-\rho} v(\rho)$$

The function v is a polynomial pf degree $j_{max} = n - l - 1$ in ρ, whose coefficients are given by the recursion formula

$$c_{j+1} = 2c_j \frac{j + l + 1 - n}{(j+1)(j+2l+2)}$$

Let's look at the ground state. We have

$$n = 1$$

which forces us to set

$$l = 0 \qquad m = 0.$$

So we have

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi)$$

The recursion forula truncates after the first term. Thus we only have one constant c_0 and we have a very simple function R:

$$R_{10}(r) = \frac{c_0}{a} e^{-r/a}$$

Normalizing it

$$\int |R_{01}(r)|^2 r^2 dr = \frac{|c_0|^2}{a^2} \int e^{-2r/a} r^2 dr = |c_0|^2 \frac{a}{4} = 1$$

Thus

$$c_0 = \frac{2}{\sqrt{a}}$$

The Y function is also simple

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

The the final functional form looks like

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

For the first excited state, $n = 2$, we can have $l = 0$ or $l = 1$. We have four degenerate states

$$\begin{aligned} l &= 0 \qquad m = 0 \\ l &= 1 \qquad m = -1, 0, 1 \end{aligned}$$

The radial functions look like

$$\begin{aligned} R_{20}(r) &= \frac{c_0}{2a}\left(1-\frac{r}{2a}\right)e^{-r/2a} \\ R_{21}(r) &= \frac{c_0}{4a^2} r e^{-r/2a} \end{aligned}$$

up to a normalization. In generaral, the radial polynomial can be described with the associated Laguerre polynomical

$$L^{p}_{p-q}(x) \equiv (-1)^p \left(\frac{\partial}{\partial x}\right)^p L_q(x)$$

where

$$L_q(x) \equiv e^x \left(\frac{\partial}{\partial x}\right)^q (e^{-x}x^q)$$

is the q-th Laguerre polynomial. If we would work out all the normalization, we would get

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l \ L^{2l+1}_{n-l-1}(2r/na)\ Y^m_l(\theta,\phi)$$

These functions are orthognal

$$\int\int\int \psi^*_{nlm}\psi_{n'l'm'} r^2 \sin\theta dr d\theta d\phi = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$