THE LEGENDRE AND LAGUERRE POLYNOMIALS & THE ELEMENTARY QUANTUM MECHANICAL MODEL OF THE HYDROGEN ATOM

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Abstract. In this report, we explore the basic Quantum Mechanical analysis of hydrogen. In the process we come across the Legendre and Laguerre polynomials, and present an informal derivation of these functions and their normalization.

1. The Bohr model

We first consider an early model of the hydrogen atom, (Thompson 1903) [1]. In this model, the atom is a blob of uniformly distributed positive charge, a sphere of radius $1\mathring{A}$ and charge $+e$. The electron is considered to exist as a point like particle within this sphere. Breaking the sphere up into infinitesimal shells, each shell will contribute a potential to the electron of

$$dV = \frac{-e\rho 2\pi r^2 dr}{4\pi\epsilon_0}\int_0^\pi \frac{\sin\theta d\theta}{r^2 + r'^2 - 2rr'\cos\theta} \tag{1.1}$$

Where $\rho = e/(4\pi R^3/3)$, r is the radius of the shell, and r' is the location of the electron relative to the center of the sphere. Considering shells of radius less than the position of the electron, and those greater, the potential is

$$V = \frac{-e4\pi\rho}{4\pi\epsilon_0}\left(\int_0^{r'} \frac{r^2 dr}{r'} + \int_{r'}^{R} \frac{r^2 dr}{r}\right) = \frac{-e\rho 4\pi}{4\pi\epsilon_0}\left(\frac{-r'^2}{6} + \frac{R^2}{2}\right) \Rightarrow F = \frac{-e^2}{4\pi\epsilon_0 R^3} r \tag{1.2}$$

Similar in form to the harmonic potential, $F = -kr$, we have,

$$\omega = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{e^2}{4\pi\epsilon_0 R^3 m_e}} \tag{1.3}$$

We divide by 2π and use known constants to find that we expect a frequency of 2.43×10^{15}Hz corresponding to 123 nm wavelength. This is approximately the Lyman-alpha wavelength (121.5 nm), but does not account for the infinite spectrum that Hydrogen actually exhibits. Nor does this model incorporate Planck's discovery of quantization of radiation.

The earliest model of the hydrogen atom that accounted for Planck's discovery that a proper explanation of the blackbody radiation spectrum could only be achieved through quantization of the energy released by atoms was achieved by Niels Bohr. The model had the following properties, as summarized by Bohr [2, 3]:

(1) The electron emits radiation when transitioning from one discreet state to the next.
(2) Classical mechanics is valid when the electron is not transitioning.
(3) In transition from a state to another, energy differences being ΔE, a photon of frequency $\nu = \Delta E/h$ is emitted.
(4) Angular momentum is quantized and identifies permitted orbits. It is always a natural number multiple of $h/2\pi$.

The model is amazingly simple, but manages to correctly predict the ground state energy level. It goes as follows. Since we assume the laws of classical mechanics hold in non-transition periods, the electron obeys the Coulomb force law and the centripetal acceleration formulation:

$$\frac{m_e v^2}{r} = \frac{1}{4\pi\epsilon_o}\frac{e^2}{r^2} \tag{1.4}$$

Under the quantization of orbital angular momentum, we can write $L = m_e v r = n\hbar, n \in \mathbb{Z} > 0$. This number, n, will be seen throughout this derivation as a key and important variable, the angular momentum quantum number. From our definition of L, we find that,

$$\frac{m_e v^2}{r} = \frac{m_e}{r}\left(\frac{n^2\hbar^2}{m_e^2 r^2}\right) = \frac{1}{4\pi\epsilon_o}\frac{e^2}{r^2} \longrightarrow r = \frac{4\pi\epsilon_o n^2\hbar^2}{e^2 m_e} \tag{1.5}$$

The smallest possible orbit is when $n = 1$. This is called the Bohr radius, and is given as

$$a_o = \frac{4\pi\epsilon_o\hbar^2}{e^2 m_e} \tag{1.6}$$

Energy is the sum of its Kinetic and Potential partitions, and given our previous results,

$$E_n = \frac{m_e v_e^2}{2} - \frac{e^2}{4\pi\epsilon_o r} = -\frac{m_e}{2}\left(\frac{e^2}{4\pi\epsilon_o\hbar n}\right)^2 \tag{1.7}$$

It was a great result that this formula predicts the ground state energy and excited energy states of the electron:

$$E_1 = -\frac{m_e}{2}\left(\frac{e^2}{4\pi\epsilon_o\hbar}\right)^2 = -2.18E - 18J = -13.6ev \tag{1.8}$$

The model also gives a more accurate picture of the spectrum of hydrogen, where we can use $E_n = \hbar\nu$ to find the corresponding frequencies. But this is not good enough. This model tells us nothing about why and how the transitions are made. It is rather ad hoc.

Bohr also introduced a helpful principle in Quantum Mechanics, the Correspondence Principle, the idea that Quantum Mechanical calculations must limit to classical results when the census of quantum numbers tends towards infinity.

2. The Hydrogen Calculation using Schrödinger's equation

Enter Schrödinger. He proposed that an object in quantum mechanics obeys the wave equation,

$$\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t} \tag{2.1}$$

But of course, the Hydrogen atom does not live in one dimension. We must move to three dimensions, using spherical coordinates as the most natural setting for our derivation.

In spherical coordinates the Laplacian becomes:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{2.2}$$

Schrödinger's equation becomes:

$$\begin{aligned} -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial\psi}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right)\right.\\ \left. + \frac{1}{r^2\sin^2(\theta)}\left(\frac{\partial^2}{\partial\phi^2}\right)\right) + V\psi = E\psi \end{aligned} \tag{2.3}$$

If we assume that the solutions can be found through separation of variables:

$$
\begin{aligned}
\psi(r,\theta,\phi) &= R(r)Y(\theta,\phi) \rightarrow \\
-\frac{\hbar^2}{2m}\left(\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) + \frac{1}{Y\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) & \\
+\frac{1}{Y\sin(\theta)}\frac{\partial^2}{\partial\psi^2} + r^2(V-E) &= 0 \\
\Longrightarrow \frac{1}{R}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V-E) &= \Delta, \\
\frac{1}{Y}\left(\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}\right) &= -\Delta \qquad (2.4)
\end{aligned}
$$

We have divided, and now we are ready to solve. The radial term contains the potential V, which is a function of r for hydrogen. It is the more complex of the two, and so we seek to explore the angular term first. Our analysis will find the Δ constant of separation in its exact form, enabling a strong attempt at solving the radial equation.

3. The Angular Component

Once again, it is reasonable to assume a certain dimensional independence which enables separation of variables in terms of the θ and ϕ components. Under this regime:

$$
\begin{aligned}
Y(\theta,\phi) &= \Theta(\theta)\Phi(\phi) \Longrightarrow \\
\frac{1}{\Theta}\left(\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) + \Delta\sin^2\theta\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} &= 0 \ \ni \\
\frac{1}{\Theta}\left(\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) + \Delta\sin^2\theta\right) &= m^2, \\
\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \Longrightarrow \Phi(\phi) &= e^{im\phi},\ m \in \mathbb{Z} \qquad (3.1)
\end{aligned}
$$

The Φ side of the equation was quickly solved. We can recast this equation in the following variations, where we let C represent $x = \cos(\theta)$ and S $\sqrt{1-x^2} = \sin(\theta)$; we introduce the notation ▼ which represents an introduction of a new idea into the stream of derivation, and ► is followed by the immediate consequence of this new idea; we then consider the $m = 0$ case.

$$
\begin{aligned}
S\frac{d}{d\theta}\left(S\frac{d\Theta}{d\theta}\right) + (\Delta S^2\theta)\Theta &= 0 \\
x = C(\theta) \rightarrow \frac{dx}{d\theta} &= -S(\theta) \Longrightarrow S\frac{\partial}{\partial\theta}\left(S\frac{d\Theta}{dx}\frac{dx}{d\theta}\right) \\
= S\frac{d}{d\theta}\left(-S^2\frac{d\Theta}{dx}\right) &= -2S^2C\frac{d\Theta}{dx} + \left(-S^3\frac{d}{dx}\frac{d\Theta}{d\theta} = S^4\frac{d^2\Theta}{dx^2}\right) \ni \\
\blacktriangledown\Theta = y \blacktriangleright S^2y'' - 2Cy' + \Delta y & \\
= (1-x^2)y'' - 2xy' + \Delta y &= \frac{d}{dx}\left((1-x^2)y'\right) + \Delta y = 0
\end{aligned}
$$

As we further press on this equation, we shall find it suggesting its own solution, even betraying the separation constant Δ.

3.1. **A closer look.** Let us take a careful look at the equation,

$$(1-x^2)y'' - 2xy' + \Delta y = 0 \tag{3.2}$$

We note that the x derivative of $(1-x^2)$ is $-2x$. This is highly suggestive that the kernel of our function is $(1-x^2)$ itself. The multiple derivatives suggest something a la $w = (1-x^2)^n$. So let us explore this kernel. Its first derivative is $w' = -2xn(1-x^2)^{n-1}$ or $w'(1-x^2) + 2nxw = 0$ Define D_n to be the nth derivative of this latter equation. Then we have the following formulation:

$$\begin{aligned}
D_0 : \quad & (1-x^2)w' + 2nxw && = 0 \\
D_1 : \quad & (1-x^2)w'' - 2xw' + 2nxw' + 2nw && \\
& = (1-x^2)w'' + 2x(n-1)w' + 2nw && = 0 \\
D_2 : \quad & (1-x^2)w''' - 2xw'' + 2x(n-1)w'' + 2(N-1)w' + 2nw' && \\
& = (1-x^2)w''' + 2x(n-2)w'' + (4n-2)w' && = 0 \\
D_3 : \quad & (1-x^2)w^{(4)} - 2xw^{(3)} + 2x(n-2)w^{(3)} + 2(n-2)w(2) + (rn-2)w^{(2)} && \\
& = (1-x^2)w^{(4)} + 2x(n-3)w^{(3)} + (6n-6)w^{(2)} && = 0
\end{aligned} \tag{3.3}$$

If we have instead $w = (x^2-1)^n$:

$$\begin{aligned}
D_0 : \quad & (x^2-1)w' - 2nxw && = 0 \\
D_1 : \quad & (x^2-1)w'' - 2(n-1)xw' - 2nxw && = 0 \\
D_2 : \quad & (x^2-1)w^{(3)} - 2(n-2)xw^{(2)} - 2(2n-1)w' && = 0 \\
D_3 : \quad & (x^2-1)w^{(4)} - 2(n-3)xw^{(3)} - 2(3n-3)w^{(2)} && = 0 \\
\vdots \quad & \qquad \vdots && = \vdots \\
D_{(n+1)} : \quad & (x^2-1)w''^{(n)} + 2xw'^{(n)} - 2\left(n^2 - \textstyle\sum_{m=0}^{n}(m-1)\right)w^n && = 0 \\
& (x^2-1)w''^{(n)} + 2xw'^{(n)} - 2\left(n^2 - \tfrac{n(n-1)}{2}\right)w^n && = 0 \\
& (x^2-1)w''^{(n)} + 2xw'^{(n)} - n(n+1)w^n && = 0
\end{aligned} \tag{3.4}$$

This latter equation is in the same form as our original equation. That is,

$$y = \frac{d^2}{dx^n}(x^2-1)^n \tag{3.5}$$

Or, if we so choose,

$$y = \frac{1}{2^n n!}\frac{d^2}{dx^n}(x^2-1)^n \tag{3.6}$$

This is the so called Legendre Polynomial, denoted by $P_n(x)$ We so assign $\Delta = l(l+1)$. But what of the $m \neq 0$ cases? In such a situation, our equation of interest can be cast as:

$$(1-x^2)y'' - 2xy' + \left(l(l+1) - \frac{m^2}{1-x^2}\right)y = 0 \tag{3.7}$$

Let us continue the derivation series from above; Recall that

$$D_{(n+1)} : \quad (x^2-1)w''^{(n)} + 2xw'^{(n)} - n(n+1)w^n = 0 \tag{3.8}$$

Continuing the process we get,

$$D_{k,n+1} : \quad (1-x^2)y^{(2+k)} - x(2+2k)y^{(k+1)} + (l(l+1) - k(k+1))\,y^{(k)} = 0 \tag{3.9}$$

Or, in the spirit of what we have done thus far, write:

$$z = \left(\frac{d^k}{dx^k}\right) y \rightarrow (1-x^2)z'' - 2x(k+1)z' + \left(l(l+1) - k(k+1)\right) z = 0 \tag{3.10}$$

This does not yield the correct formulation. When we recast the original equation as:

$$(1-x)^2 y'' - 2x(1-x^2)y' + \left(l(l+1)(1-x^2) - m^2\right) y = 0 \tag{3.11}$$

This easily suggests the following form for our final function:

$$\zeta = (1-x^2)^a \left(\frac{d}{dx}\right)^b y_n \tag{3.12}$$

To find what form a and b take, we consider $y_1 = x$ with $b = 1$ since clearly b must be be a positive integer:

$$\begin{aligned}
\zeta &= (1-x^2)^a \frac{d}{dx}(x) \rightarrow \zeta = (1-x^2)^a \\
\zeta' &= -2ax(1-x^2)^{a-1} \\
\zeta'' &= -2a(1-x^2)^{a-1} + a(a-1)(4x^2)(1-x^2)^{a-2} \\
&\ni \quad (1-x^2)\zeta'' - 2x\zeta' + \left(l(l+1) - \frac{m^2}{(1-x^2)}\right)\zeta \\
&= -2a(1-x^2)^a + a(a-1)(4x^2)(1-x^2)^{a-1} + yx^2 a(1-x^2)^{a-1} \\
&\quad +l(l+1)(1-x^2)^a - m^2(1-x^2)^{a-1} = 0
\end{aligned} \tag{3.13}$$

Upon the expansion of the latter equation for x, we can match each term with its coefficients. These coefficients must equal zero to satisfy the equation. It is easiest to take the highest coefficients of x:

$$\begin{aligned}
a(a-1)4x^2(1-x^2)^{a-1} + 4x^2 a(1-x^2)^{a-1} - m^2(1-x^2)^{a-1} &= 0 \\
a^2 = \frac{m^2}{4} \rightarrow a &= \frac{|m|}{2}
\end{aligned} \tag{3.14}$$

Here m=1, but we assume the ansazts of generalization whereby, sans a normalization constant, the full solution of our angular equation is the associated Legendre Function,

$$P_l^m(x) = (1-x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx}\right)^{|m|} \left(\frac{1}{2^l l!}\right) \left(\frac{d}{dx}\right)^l (x^2-1)^l \tag{3.15}$$

3.2. **Normalization for final result.** Define $A_{n,s}^k = \int_1^1 P_n^k(x) P_s^k(x) dx$, then by separation of variables:

$$\begin{aligned}
A_{n,s}^k &= \int_1^1 (1-x^2)^k \left(\frac{d^k}{dx^k} P_n(x)\right) \left(\frac{d^k}{dx^k} P_s(x)\right) dx \\
&= \int_1^1 (1-x^2)^k \left(\frac{d^k}{dx^k} P_n(x)\right) \left(\frac{d^{k-1}}{dx^{k-1}} P_s(x)\right) dx \\
&\quad - \int \left(\frac{d^{k-1}}{dx^{k-1}} P_s(x)\right) \frac{d}{dx} \left((1-x^2)^k \frac{d^k}{dx^k} P_n(x)\right) dx
\end{aligned} \tag{3.16}$$

Introduce $z' = \frac{d^k}{dx^k} P_n(x)$. From our previous discussion, we find that,

$$\frac{d}{dx}\left((1-x^2)z'\right) = \left((k(k+1) - l(l+1)\right) z = 0 \tag{3.17}$$

Or just as easily,

$$\begin{aligned}\frac{d}{dx}\left((1-x^2)^{k+1}z'\right) &= \left(k(k+1)-l(l+1)\right)(1-x^2)^k z \\ &= (k-l)(k+l+1)(1-x^2)^k z = 0\end{aligned}$$

(3.18)

Here we need to compensate for the following: The z used in this previous equation was built with:

$$z' = \frac{d^k}{dx^k}P_n(x) \;\rightarrow\; z = \frac{d^{k-1}}{dx^{k-1}}P_n(x) \tag{3.19}$$

Thus we must shift $k \;\rightarrow\; k-1$. Thus,

$$\begin{aligned}A^k_{n,s} = \int_{-1}^{1} P^k_n(x)P^k_s(x)dx &= (n-k+1)(n+k)\int_{-}^{1} 1P^{k-1}_s P^{k-1}_n dx \\ A^k_{n,s} &= (n-k+1)(n+k)A^{k-1}_{n,s} \\ A^k_{n,s} &= (n-k+1)(n+k)(n-k+2)(n+k-1)A^{k-2}_{n,s} \\ \cdots &= \cdots \\ A^k_{n,s} = \frac{(n+k)!}{(n-k)!}A^0_{n,s} &= \frac{(n+k)!}{(n-k)!}\int_{-1}^{1} P_n P_s dx = \delta_{ns}||P_n||^2\end{aligned}$$

We can find $||P_n||^2$ as another separation of variables chain:

$$\begin{aligned}\int_{-1}^{1} P_n(x)dx &= \left(\frac{1}{2^n n!}\right)\int_{-1}^{1}\left(\frac{d}{dx}\right)^n (1-x^2)^n \left(\frac{d}{dx}\right)^m (1-x^2)^m dx \\ &= \left(\frac{1}{2^n n!}\right)\left(\frac{d}{dx}\right)(1-x^2)^n\left(\frac{d}{dx}^{m+1}(1-x^2)^m|^1_{-1}\right) \\ &\quad -\left(\frac{1}{2^n n!}\right)\int_{-1}^{1}\left(\frac{d}{dx}\right)^{m-1}(1-x^2)^m\left(\frac{d}{dx}\right)^{n+1}(1-x^2)dx\end{aligned} \tag{3.20}$$

The non-integral part equals zero, the integral component cycles up on the n derivative and down on the m derivative. Of course, $m = n$, but we maintain the separation for the sake of derivation. The final result of the cycle gives:

$$\int_{-1}^{1} ||P_n(x)||^2 dx = \frac{(2n)!}{(2^n n!)^2}\int_{-1}^{1}\left(\frac{d}{dx}^0 (x^2-1)^m\right)dx \tag{3.21}$$

To solve the latter integral, we introduce two identities:

$$\begin{aligned}(1-x^2)^m &= \left(\int_0^x\right)^m P_m(x')\,(dx')^m \\ &\quad \frac{1}{2n+1}\left(P'_{n+1}(x)-P'_{n-1}\right) \\ &= \frac{1}{2n+1}\frac{1}{2^n n!}\frac{d^n}{dx^n}\left(\frac{1}{2(n+1)}\frac{d^2}{dx^2}(x^2-1)^{n+1} - 2n(x^2-1)^{n-1}\right) \\ &\quad \blacktriangledown \frac{1}{2(n+1)}\frac{d^2}{dx^2}(x^2-1)^{n+1} = (x^2-1)^n + 2x^2 n(x^2-1)^{n-1} \\ &\quad \blacktriangleright \frac{1}{2n+1}\left(P'_{n+1}(x)-P'_{n-1}(x)\right) \\ &= \frac{1}{2n+1}\frac{1}{2^n n!}\frac{d^n}{dx^n}\left((x^2-1)^n + 2n(x^2-1)(x^2-1)^{n-1}\right) \\ &= \frac{1}{2^n n!}\frac{d^n}{dx^n}(x^2-1) = P_n(x)\end{aligned} \tag{3.22}$$

So we follow through,

$$\begin{aligned}
P_n(x) &= \frac{1}{2n+1}\left(P'_{n+1}(x) - P'_{n-1}(x)\right)\\
\int_0^x P_n(x)dx &= \frac{1}{2n+1}\left(P_{n+1}(x) - P_{n-1}(x)\right)\\
\int_0^x \int_0^x P_n(x)dx\ dx &= \frac{1}{2n+1}\left(\frac{1}{2n+3}\left(P_{n+2}(x) - P_n\right) - \frac{1}{2n-1}\left(P_n(x) - P_{n-2}(x)\right)\right)
\end{aligned}$$

We follow through this derivation cycle n times, splitting each P value as per the above identity. The $P_n(x)$ integral becomes the $(1-x^2)^n$ as identified above and he array P_n will be spread from values of $P_{2n} \rightarrow P_0$. If we integrate both sides of the equation over the Legendre function range, [-1,1], all said values of P_n will vanish except P_0. The prefactors from the expansion give:

$$2^n n! \int_{-1}^{1} (1-x^2)^n dx$$

$$= \int_{-1}^{1} 2^n n! \left(\left(\int_0^x\right)^n P_n(x)\,(dx)^n\right) dx = \frac{(2n)!}{(2n+1)!}\int_{-1}^{1} P_0(x)dx \tag{3.23}$$

But properly,

$$\begin{aligned}
\int_{-1}^{1} |P_n|^2 dx &= \frac{(2n)!}{(2^n n!)^2}\int_{-1}^{1}(1-x^2)^n dx\\
&= \frac{(2n)!}{(2^n n!)^2}\int_{-1}^{1} 2^n n! \left(\int_0^x P_n(x)\,(dx)^n\right) dx\\
&= \frac{(2n)!}{(2^n n!)^2}\int_{-1}^{1} 2^n n! \frac{2^n n!}{(2n+1)!} dx\\
&= \frac{2}{2n+1} \qquad (3.24)
\end{aligned}$$

From this we conclude,

$$A^k_{n,s} = \left(\frac{(n+k)!}{(n-k)!}\frac{2}{2n+1}\right) \tag{3.25}$$

Of course, we cannot neglect the symmetric components of theta, which give us an additional normalization of 2π, thus the final normalization condition,

$$\int_0^{2\pi}\int_0^{\pi} ||Y^k_n| \sin(\theta) d\theta d\phi \tag{3.26}$$

Re-tagging our variables appropriately, the normalized Associated Legendre Polynomial is,

$$Y^k_n(\theta,\phi) = \sqrt{\frac{2n+1}{4\pi}\frac{(n-k)!}{(n+k)!}} e^{im\phi}(1-x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx}\right)^{|m|}\left(\frac{1}{2^l l!}\right)\left(\frac{d}{dx}\right)^l (x^2-1)^l$$

Or in simplified notation,

$$Y^m_n(\theta,\phi) = \sqrt{\frac{2n+1}{4\pi}\frac{(n-m)!}{(n+m)!}} e^{im\phi} P^m_l(cos(\theta)) \tag{3.27}$$

.

4. Radial side

Granted that $\Delta = l(l+1)$, the radial equation becomes simply:

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left(V(r)-E\right)R = l(l+1)R \tag{4.1}$$

When finding solutions to such equations, it is generally in our best interest to isolate the leading derivatives. We can do so with the substitution:

$$\begin{aligned}
u(r) = rR(r) \rightarrow R = \frac{u}{r},\ \frac{dR}{dr} = \frac{r\frac{du}{dr}-u}{r^2} \quad &\ni \quad \frac{d}{dr}(r^2\frac{dR}{dr}) = r\frac{d^2u}{dr^2} \\
\therefore\ -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left(V - E + \frac{\hbar^2 l(l+1)}{2mr^2}\right)u \quad &= \quad 0 \\
\blacktriangledown\ V = -\frac{e^2}{4\pi\epsilon_o r}\ ,\ \ \zeta \quad &= \quad \frac{\sqrt{-2mE}}{\hbar}\ \blacktriangleright \\
-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left(-\frac{e^2}{4\pi\epsilon_o r} + \frac{\zeta^2\hbar^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2}\right)u \quad &= \quad 0 \\
\frac{1}{\zeta^2}\frac{d^2u}{dr^2} \quad &= \quad \left(1 - \frac{me^2}{2\pi\epsilon_o\hbar^2\zeta^2 r} + \frac{l(l+1)}{\zeta^2 r^2}\right)u \\
\blacktriangledown\ \rho = \zeta r\ ,\ \ \rho_o = \frac{me^2}{2\pi\epsilon_o\hbar^2\zeta}\ \blacktriangleright\ \frac{d^2u}{d\rho^2} \quad &= \quad \left(1 - \frac{\rho_o}{\rho} + \frac{l(l+1)}{\rho^2}\right)u \qquad (4.2)
\end{aligned}$$

Here we have considered the bound states of the electron (of course) where $E < 0$.

Typically, one looks and supposes asymptotic solutions. For $\rho \rightarrow \infty$,

$$\frac{d^2u}{d\rho^2} = u \ \longrightarrow\ u(\rho) = \alpha e^{-\rho} + \beta e^{\rho} \tag{4.3}$$

But of course, finiteness requires that $\beta = 0$ As $\rho \rightarrow 0$, the ρ^{-2} term dominates $\ni$

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)u}{\rho^2} \tag{4.4}$$

The solution to this equation is interesting to derive. We suppose the existence of some function $z(\rho)$, and rewrite the equation thereby:

$$\begin{aligned}
\frac{du}{d\rho} &= \frac{du}{dz}\frac{dz}{d\rho} \\
\frac{d^2u}{d\rho^2} &= \frac{d}{d\rho}\left(\frac{d}{dz}u\frac{dz}{d\rho}\right) \\
&= \frac{dz}{d\rho}\frac{d}{dz}\left(\frac{du}{dz}\right) + \frac{du}{dz}\frac{d^2z}{d\rho^2} \\
&= \frac{d^2u}{dz^2}\left(\frac{dz}{d\rho}\right)^2 + \frac{du}{dz}\frac{d^2z}{d\rho^2} \\
\therefore\ \frac{d^2u}{d\rho^2} &= \frac{l(l+1)u}{\rho^2}\ \blacktriangleright \\
0 &= \frac{d^2u}{dz^2}\left(\frac{dz}{d\rho}\right)^2 + \frac{du}{dz}\frac{d^2z}{d\rho^2} - \frac{l(l+1)u}{\rho^2} \qquad (4.5)
\end{aligned}$$

The trick here is to assume that there exist a $z(\rho)$ such that the previous equation is a differential equation with constant coefficients, i.e.:

$$\begin{aligned}
\frac{\left(\frac{dz}{d\rho}\right)^2}{\frac{l(l+1)}{\rho^2}} &= 1 \\
\frac{dz}{d\rho} &= \frac{\sqrt{l(l+1)}}{\rho} \\
z = \sqrt{l(l+1)}\ln(\rho) &= \ln(p^{\sqrt{l(l+1)}}) \qquad (4.6)
\end{aligned}$$

Our characteristic equation follows from:

$$\frac{l(l+1)}{\rho^2}u'' - \frac{\sqrt{l(l+1)}}{\rho^2}u' - \frac{l(l+1)}{\rho^2} = 0 \qquad (4.7)$$

It is easy to show the resulting characteristic is $(1 \pm (2l+1))/(2\sqrt{l(l+1)})$ with solutions:

$$\begin{aligned}
u &= \gamma exp(\frac{2(l+1)z}{2\sqrt{l(l+1)}}) + \beth exp(\frac{-2lz}{2\sqrt{l(l+1)}}) \\
&= \gamma exp(\frac{2(l+1)\sqrt{l(l+1)}ln\rho}{2\sqrt{l(l+1)}}) + \beth exp(\frac{-2l\sqrt{l(l+1)}ln\rho}{2\sqrt{l(l+1)}}) \\
&= \gamma exp(ln\rho^{(l+1)}) + \beth exp(ln\rho^{-l}) \\
&= \gamma\rho^{l+1} + \beth\rho^{-l} \qquad (4.8)
\end{aligned}$$

Since this solution contains the zero point, $\beth = 0$, and we can write our asymptotic general solution in total as $u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$, where $v(\rho)$ is some unknown function which properly completes the radial function and is to be found. Reformulating the equation thus far,

$$\begin{aligned}
u(\rho) &= \rho^{l+1}e^{-\rho}v(\rho) \\
\frac{du}{d\rho} &= \rho^l e^{-\rho}\left((l+1-\rho)v + \rho\frac{dv}{dp}\right) \\
\frac{d^2u}{d\rho^2} &= \rho^l e^{-\rho}\left(\left(-2l-2+\rho+\frac{l(l+1)}{\rho}\right)v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right)
\end{aligned}$$

With the radial equation as,

$$\frac{d^2u}{d\rho^2} = \left(1 - \frac{\rho_o}{\rho} + \frac{l(l+1)}{\rho^2}\right)u \qquad (4.9)$$

We can plug in the values we found above to reformulate the equation in terms of v. Via algebra which can be easily done in mind, we find:

$$\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + (\rho_o - 2(l+1))v = 0 \qquad (4.10)$$

Following typical derivations (though we will part with it eventually), we assume a solution of a series solution form, $v(\rho) = \sum_{j=0}^{\infty} a_j p^j$. Done so, the prior equation becomes,

$$\begin{aligned}
\sum^{\infty} j(j+1)a_{j+1}p^j + 2(l+1)\sum_{j=0}^{\infty} a_{j+1}p^j - 2\sum_{j=0}^{\infty} ja_jp^j & & \\
+ (p_o - 2(l+1))\sum_{j=0}^{\infty} a_jp^j &=& 0 \longrightarrow \\
j(j+1)a_{j+1} + 2(l+1)(j+1)a_{j+1} - 2ja_j + (p_o - 2(l+1))\,a_j &=& 0 \\
\therefore\ a_{j+1} &=& \left(\frac{2(j+l+1)-\rho_o}{(j+1)(j+2l+2)}\right)a_j \\
\blacktriangledown \lim_{j\to\infty}\left(\frac{2(j+l+1)-\rho_o}{(j+1)(j+2l+2)}\right)a_j &\approx& \frac{2^j}{j!}\gamma \\
\blacktriangleright\ \mu(\rho) = \sum_{j=0}^{\infty}\frac{2^j}{j!}p^j = \epsilon e^{2p} &\rightarrow& \infty \text{ @ } \rho\rightarrow\infty
\end{aligned} \tag{4.11}$$

Obviously the series must terminate dynamically, i.e.

$$\exists\ j_{max} \ni a_{j_{max}+1} = 0 \rightarrow 2(j_{max}+l+1) - \rho_o = 0\ \blacktriangledown\ n = j_{max}+l+1\ \blacktriangleright\ \rho_o = 2n$$

Our new recursion equation is:

$$a_{j+1} = \frac{2(j+l+1-2n)}{(j+1)(j+2l+2)}a_j \tag{4.12}$$

We consider a few sample results of v_n^l. E.g.

$$\begin{aligned}
v_2^0 &=& a_o - a_ox \\
v_3^1 &=& a_o - \frac{a_o}{2}x \\
v_3^o &=& a_o - 2a_ox + \frac{2a_o}{3}x^2 \\
v_4^l &=& a_o - a_ox + \frac{2a_o}{10}
\end{aligned}$$

We can go on ad infinitum, but we seek an analytical solution to this equation. The asymptotically suggested form gives us a starting point for its completing function. We also suspect that the solution might follow the onion-derivative similar to that of the angular solution. With these educated guesses, we start as follows: We assume the solution has a kernel $w = e^{-x}x^q$

$$\begin{aligned}
w' = -e^{-x}x^q + qe^{-x}x^{q-1} \\
w'' = e^{-x}x^q - qe^{-x}x^{q-1} + q(q-1)e^{-x}x^{q-2} - qe^{-x}x^{q-1} \\
\text{e.g. @ } q = 2\ w'' = 2e^{-x} - 4e^{-x}x + e^{-x}x^2, \\
e^xw''(q=2) = 2 - 4x + x^2
\end{aligned} \tag{4.13}$$

We had plugged in $p = 2$ as a simple test of low level results. Take the derivative of the latter equation and find, $2x - 4$ a la $v_1^3 = a_o - \frac{a_o}{2}x$. One could follow through this examination ad infinitum, but we already know the ending to this story so we assume immediately that we have happened upon the correct solution form, i.e.

$$v_{q-p}^p(x) = \daleth\left(\frac{d}{dx}\right)^p\left(e^x\left(\frac{d}{dx}\right)^q e^{-x}x^q\right) \tag{4.14}$$

When $\daleth = (-1)^p$, the above equation is the associated Laguerre Polynomial, L_{q-p}^p. We can bring this all home as follows. We consider our v_1^3 example. In that case, for $n = 3$, $l = 1$, we can write the the v completing function with coefficients in terms of the recursion variables. Using $v(\rho) = L^{2l+1}_{n-l-1}(2\rho)$, which, due to the multiplication by two matches our v_1^3 example,

Now $R = \frac{u(\rho)}{r}$, where:

$$u(\rho) = \rho^{l+1} e^{-\rho} L^{2l+1}_{n-l-1}(2\rho) \tag{4.15}$$

But with $\rho_o = 2n$, and

$$\rho_o = \frac{me^2}{2\pi\epsilon_o \hbar^2 \kappa}$$

$$\kappa = \frac{me^2}{4\pi n \epsilon_o \hbar^2} \tag{4.16}$$

Let

$$a = \frac{4\pi\epsilon_o \hbar^2}{me^2}$$

which is the Bohr Radius we had previously derived. Then we write $\kappa = \frac{1}{an}$. Thus $\rho = \kappa r = \frac{r}{an}$. Ergo

$$R(r) = \frac{N}{an}\left(\frac{r}{an}\right)^l \exp(-\frac{r}{na}) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) \tag{4.17}$$

The normalization factor N is determined as follows.

4.1. **Normalization of the Radial Term.** Key to normalizing the radial term is the normalization of the Laguerre Polynomials. This task will not be as facile as was normalization for the Legendre Polynomials.

Given that $L_n(x) = \frac{e^x}{n!}\frac{d^n}{dx^2}(x^n e^{-x})$, we note the following:

$$\begin{aligned}
nL_{n-1}(x) &= \frac{ne^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}} x^{n-1} e^{-x} \\
&= \frac{e^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}} (nx^{n-1} e^{-x}) \\
&= \frac{e^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}} (\frac{d}{dx} x^n e^{-x} + x^n e^{-x}) \\
&= \frac{ne^x}{n!}\frac{d^n}{dx^n} x^n e^{-x} + \frac{e^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}} x^n e^{-x} \\
&= nL_n(x) + \frac{e^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}} x^n e^{-x} && (4.18)
\end{aligned}$$

In the same way, we find that:

$$\begin{aligned}
(n+1)L_{n+1}(x) &= (n+1)\frac{e^x}{(n+1)!}\frac{d^{n+1}}{dx^{n+1}} x^{n+1} e^{-x} \\
\blacktriangledown \ \frac{d}{dx} x^{n+1} e^{-x} &= (n+1)x^n e^{-x} - x^{n+1} e^{-x} \\
\blacktriangleright \ (n+1)L_{n+1}(x) &= \frac{e^x}{n!}\frac{d^n}{dx^n}\left((n+1)x^n e^{-x} - x^{n+1} e^{-x}\right) \\
&= \frac{e^x}{n!}\frac{d^n}{dx^n}\left((n+1)x^n e^{-x}\right) - \frac{e^x}{n!}\frac{d^n}{dx^n}(x^{n+1} e^{-x}) \\
&= (n+1)L_n(x) - \frac{e^x}{n!}\frac{d^n}{dx^n}(x^{n+1} e^{-x}) && (4.19)
\end{aligned}$$

One final note is to demonstrate the following for one case and assume the rest of the cases by assumed induction:

$$\frac{e^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}}(x^n e^{-x}) - \frac{e^x}{n!}\frac{d^n}{dx^n}(x^{n+1}e^{-x}) = ?$$

$$n = 1 \rightarrow e^x(xe^{-x}) - e^x\frac{d}{dx}(x^2e^{-x}) = e^x\left(xe^{-x} - 2xe^{-x} + x^2e^{-x}\right)$$

$$= x^2 - x = -xL_1$$

$$\text{Generally:}\quad \frac{e^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}}(x^n e^{-x}) - \frac{e^x}{n!}\frac{d^n}{dx^n}(x^{n+1}e^{-x}) = -xL_n(x)$$

Putting the above three results into place, we find that:

$$(n+1)L_{n+1}(x) = (2n+1-x)L_n(x) - nL_{n-1}(x) \tag{4.20}$$

We can derive another important and useful identity as follows:

$$\begin{aligned}
-xL_n(x) &= \frac{e^x}{(n-1)!}\frac{d^{n-1}}{dx^{n-1}}(x^n e^{-x}) - \frac{e^x}{n!}\frac{d^n}{dx^n}(x^{n+1}e^{-x}) \\
\rightarrow\ -xL_n'(x) - L_n &= -xL_n + nL_n - (n+1)L_{n+1}(x) \\
\blacktriangledown\ -xL_n(x) &= (n+1)L_{n+1}(x) + nL_{n-1}(x) - (2n+1)L_n(x) \\
\blacktriangleright\ xL_n'(x) &= nL_n(x) - nL_{n-1}(x) \qquad (4.21)
\end{aligned}$$

But we are using associated Laguerre Polynomials, so we need to extend these identities. We will not work out the details, but taking the derivatives of the previous identities gives us the associated identities:

$$\begin{aligned}
(n+1)L_{n+1}^k(x) &= (2n+k+1-x)L_n^k(x) - (n+k)L_{n-1}^k(x) \\
x\frac{d}{dx}L_n^k(x) &= nL_n^k(x) - (n+k)L_{n-1}^k(x) \qquad (4.22)
\end{aligned}$$

The solution we found for the radial equation took the form $\exp(-x/2)x^{(k+1)/2}L_n^k(x)$. The normalization equation for this formulation gives:

$$\int_0^\infty e^{-x}x^{k+1}(L_n^k(x))^2dx = \int_0^\infty \frac{x}{n!}\frac{d^n}{dx^n}\left(e^{-x}x^{n+k}\right)\left(L_n^k(x)\right)dx \tag{4.23}$$

Applying integration by parts n times, cycling up on the left derivative and down on the right Laguerre, using the derivative formula above, we land at:

$$\int_0^\infty e^{-x}x^{k+1}(L_n^k(x))^2dx = \int_0^\infty \frac{x^{-(n-1)}}{n!}(e^{-x}x^{n+k})(n+k)!L_0^k(x)dx \tag{4.24}$$

$$\int_0^\infty e^{-x}x^{k+1}(L_n^k(x))^2dx = \int_0^\infty \frac{(n+k)!}{n!}(e^{-x}x^k)L_0^k(x)dx \tag{4.25}$$

From the identity, we have:

$$xL_0^k(x) = (2n+k+1)L_0^k(x) + (n+1)L_1^k(x) - (n+k)L_{-1}^k(x) \tag{4.26}$$

When we plug this into the integral to wash away the x, all terms integrate to zero except L_0^k, and our integral becomes:

$$\int_0^\infty e^{-x}x^{k+1}(L_n^k(x))^2dx = (2n+k+1)\frac{(n+k)!}{n!}\int_0^\infty e^{-x}x^kL_0^k(x)dx \tag{4.27}$$

With $L_0^k(x) = k!$, and a integration by parts performed on the remaining integral (cycling down the x^k so that the $k!$ values cancel, we get:

$$\int_0^\infty e^{-x}x^{k+1}(L_n^k(x))^2dx$$

$$= (2n+k+1)\frac{(n+k)!}{n!}\int_0^\infty e^{-x}dx = \frac{(n+k)!}{n!}(2n+k+1) \tag{4.28}$$

Now when we adjust this representation for our own, i.e. $n \to n-l-1$ and $k \to 2l+1$, the normalization constant becomes $\frac{(n+l)!}{(n-l-1)!}(2n)$. Incorporating the fact that we must convert $x \to \frac{2}{na}$, this calls upon an additional normalization factor of $\left(\frac{2}{na}\right)^{3/2}$

Thus the radial normalization is:

$$N = \sqrt{\frac{(n-l-1)!}{2n(n+l)!}\left(\frac{2}{na}\right)^3} \tag{4.29}$$

Our final radial equation becomes:

$$R(r) = \sqrt{\frac{(n-l-1)!}{2n(n+l)!}\left(\frac{2}{na}\right)^3}\, e^{-\frac{r}{na}}\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}(\frac{2r}{na}) \tag{4.30}$$

5. Final Form

Putting these pieces together, the full function that describes the most basic hydrogen quantum model is given as,

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n((n+1)!)}}e^{-\frac{4}{na}}\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)Y_l^m(\theta,\phi) \tag{5.1}$$

We present this equation in full below.

References

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$$\psi_{nlm} = \sqrt{\frac{(n-l-1)!}{2n(n+l)!}\left(\frac{2}{na}\right)^3} e^{-\frac{r}{na}}\left(\frac{2r}{na}\right)^l \frac{e^{\left(\frac{2r}{na}\right)}\left(\frac{2r}{na}\right)^{-(2l+1)}}{(n-l-1)!}\frac{d^{(n-l-1)}}{d\left(\frac{2r}{na}\right)^{(n-l-1)}}\left(e^{-\left(\frac{2r}{na}\right)}\left(\frac{2r}{na}\right)^{n+l}\right)\sqrt{\frac{2n+1}{4\pi}\frac{(n-m)!}{(n+m)!}}e^{im\phi}(1-\cos(\theta)^2)^{\frac{|m|}{2}}\left(\frac{d}{d\cos(\theta)}\right)^{|m|}\frac{1}{2^l l!}\left(\frac{d}{d\cos(\theta)}\right)^l(\cos(\theta)^2-1)^l$$