Modern Physics

Unit 5: Schrödinger’s Equation and the Hydrogen Atom
Lecture 5.5: Eigenfunctions of Schrödinger’s Equation for the Hydrogen Atom

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From last lecture, Schrödinger’s Equation reduces to three separate equations

I. \[ \frac{d^2}{d\phi^2} \Phi(\phi) + m^2 \Phi(\phi) = 0 \]

II. \[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) \Theta(\theta) + \left[ \ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = 0 \]

III. \[ \frac{d^2}{dr^2} (rR(r)) - \frac{2m_e}{\hbar^2} \left[ U(r) + \frac{\ell(\ell + 1) \hbar^2}{2m_e r^2} - E_n \right] (rR(r)) = 0 \]

where \( \ell(\ell+1) \) and \( m^2 \) are separation constants
I. The Equation for $\Phi$

The $\Phi(\varphi)$ equation:

$$-rac{1}{\Phi(\varphi)} \frac{d^2 \Phi(\varphi)}{d\varphi^2} = m^2 = \text{constant (independent of } r \text{ and } \theta)$$

try $\Phi(\varphi) = Ae^{im\varphi}$

$$\frac{d^2 \Phi(\varphi)}{d\varphi^2} = A(im)^2 e^{im\varphi} = -Am^2 e^{im\varphi} = -m^2 \Phi(\varphi) \quad \text{what is value of } m^2 \text{?}$$

Require $\Phi$ to be single valued:

$$\Phi(\varphi + 2\pi) = \Phi(\varphi)$$

$$Ae^{im(\varphi+2\pi)} = Ae^{im\varphi} e^{i2\pi m} = Ae^{im\varphi} \Rightarrow e^{i2\pi m} = 1$$

$$\cos(2\pi m) + i \sin(2\pi m) = 1 \Rightarrow m = 0, \pm 1, \pm 2, \ldots$$

always 1 always 0

$m$ is known as the magnetic quantum number

$$\Phi_m(\varphi) = Ae^{im\varphi} ; \quad m = 0, \pm 1, \pm 2, \ldots$$
Physical significance of the $\Phi$ wavefunction

Classically, there is a strong parallel between linear and circular motion (see Lecture 1.02). Expect the same for the quantum case.

For some fixed $r$ and $\theta$:

\[ r_\perp = r \sin \theta \]

<table>
<thead>
<tr>
<th>Displacement</th>
<th>Linear Motion</th>
<th>Orbital Motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavefunction</td>
<td>$\Psi_k(x) = A e^{i(k)x}$</td>
<td>$\Phi_m(\phi) = e^{i(m/r_\perp)s}$</td>
</tr>
<tr>
<td>Quantum Number</td>
<td>none</td>
<td>$m = 0, \pm 1, \pm 2, \ldots$</td>
</tr>
<tr>
<td>Dynamical variable</td>
<td>Momentum in $x$</td>
<td>Momentum in $\phi$</td>
</tr>
<tr>
<td>Quantum operator</td>
<td>$-i\hbar \frac{\partial}{\partial x}$</td>
<td>$-i\hbar \frac{\partial}{\partial \phi}$</td>
</tr>
<tr>
<td>Eigenvalue</td>
<td>$\hbar k$</td>
<td>$m\hbar$</td>
</tr>
<tr>
<td>Physical meaning</td>
<td>Linear momentum in $x$-direction</td>
<td>Angular momentum in $z$-direction</td>
</tr>
</tbody>
</table>

The $z$ component of angular momentum is quantized!
II. The Equation for $\Theta$

\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) \Theta(\theta) + \left[ \ell (\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = 0
\]

• The $\Theta$ equation can be transformed to match the associated Legendre (1752-1833) Equation (see Math Note 1 in Appendix to this lecture).

• There are solutions for **ALL** values of $\ell(\ell+1)$

• Most solutions are **infinite** when $\theta=0$ or $\theta=\pi$ - not good!

• There are unique solutions that do NOT diverge when

  $\ell=+\text{integer AND } \ell \geq |m|$

• The eigenfunctions are indexed by the two quantum numbers $m$ and $\ell$

• These acceptable solutions are written as $\Theta_{\ell m}(\theta)$

• The solutions to the $\Theta$ equation are often combined with the solutions for the $\Phi$ equation and written in terms of the spherical harmonics $Y_{\ell m}$

\[
Y_{\ell,m}(\theta, \phi) \equiv \text{const} \times \Theta_{\ell m}(\theta)\Phi_m(\phi) = \text{const} \times \Theta_{\ell m}(\theta)e^{im\phi}
\]
Listing of $\Theta_{\ell m}(\theta)$, $\Phi_m(\phi)$ and $Y_{\ell m}(\theta, \phi)$.

<table>
<thead>
<tr>
<th>$l$</th>
<th>$m_l$</th>
<th>$\Theta_{l m_l}(\theta)$</th>
<th>$\Phi_{m_l}(\phi)$</th>
<th>$Y_{l m_l}(\theta, \phi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$\frac{1}{\sqrt{2}}$</td>
<td>$\frac{1}{\sqrt{2\pi}}$</td>
<td>$\frac{1}{\sqrt{4\pi}}$</td>
</tr>
<tr>
<td>1</td>
<td>$\pm 1$</td>
<td>$\mp \frac{\sqrt{3}}{2} \sin \theta$</td>
<td>$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$</td>
<td>$\mp \frac{\sqrt{3}}{\sqrt{3\pi}} \sin \theta e^{\pm i\phi}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\sqrt{\frac{3}{2}} \cos \theta$</td>
<td>$\frac{1}{\sqrt{2\pi}}$</td>
<td>$\sqrt{\frac{3}{4\pi}} \cos \theta$</td>
</tr>
<tr>
<td>2</td>
<td>$\pm 2$</td>
<td>$\frac{\sqrt{15}}{4} \sin^2 \theta$</td>
<td>$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$</td>
<td>$\sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>$\pm 1$</td>
<td>$\mp \frac{\sqrt{15}}{2} \sin \theta \cos \theta$</td>
<td>$\frac{1}{\sqrt{2\pi}} e^{i\phi}$</td>
<td>$\mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\sqrt{\frac{5}{2}} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right)$</td>
<td>$\frac{1}{\sqrt{2\pi}}$</td>
<td>$\sqrt{\frac{5}{4\pi}} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2}\right)$</td>
</tr>
</tbody>
</table>

Notes:
Some of the $\Phi_m$ have imaginary components.
The functions are normalized: $\int_0^\pi \int_0^{2\pi} Y_{\ell m}^2(\theta, \phi) \sin \theta d\theta d\phi = 1$
Physical significance of the \( \Psi \) wavefunction

Schrodinger's equation is often rewritten by defining a new operator

\[
\frac{-\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Psi + U(r)\Psi = E\Psi
\]

rearranging gives

\[
\frac{-\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{2m_e r^2} \right] - \hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \Psi + U(r)\Psi = E\Psi
\]

define

\[
\hat{L}^2 \equiv -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]

where the operator \( \hat{L}^2 \) is defined as the square of the angular momentum.

\[
\left[ \frac{p_r^2}{2m_e} + \frac{\hat{L}^2}{2m_e r^2} + U(r) \right] \Psi = E\Psi
\]

where \( \Psi = R_n(r)Y_{\ell,m}(\theta,\phi) \)

You can show that

\[
\hat{L}^2 Y_{\ell,m}(\theta,\phi) = \ell(\ell + 1)\hbar^2 \ Y_{\ell,m}(\theta,\phi)
\]

which justifies the choice of the separation constant as \( \ell(\ell+1) \).
III. The Equation for $R(r)$

$$\frac{d^2}{dr^2}(rR(r)) - \frac{2m_e}{\hbar^2} \left[ U(r) + \frac{\ell(\ell + 1)\hbar^2}{2m_e r^2} - E \right](rR(r)) = 0$$

where (for the hydrogen atom), $U(r)$ is the electrostatic potential energy between an electron and a proton

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

- The $R(r)$ equation can be transformed to match a differential equation with known solutions given by the associated Laguerre (1834-1886) Polynomials (see Math Note 2 attached to this lecture).
- The quantization of the energy eigenvalues follows from the $R(r)$ equation.
- The allowed eigenvalues $E$ are indexed by integer $n$.
- The eigenfunctions are in turn indexed by the two quantum numbers $n$ and $\ell$. 
The $R(r)$ equation can be written in either of two ways

\[
\frac{d^2}{dr^2}(rR_{n,\ell}(r)) - \frac{2m_e}{\hbar^2}\left[U(r) + \frac{\ell(\ell + 1)\hbar^2}{2m_e r^2} - E_n\right](rR_{n,\ell}(r)) = 0
\]

OR

\[
\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dR_{n,\ell}(r)}{dr}\right) - \frac{2m_e}{\hbar^2}\left[U(r) + \frac{\ell(\ell + 1)\hbar^2}{2m_e r^2} - E_n\right](rR_{n,\ell}(r)) = 0
\]

If a new function is defined as $P_{n\ell}(r) \equiv rR_{n\ell}(r)$

then the first equation above is often written as

\[
\frac{d^2}{dr^2}(P_{n,\ell}(r)) - \frac{2m_e}{\hbar^2}\left[U(r) + \frac{\ell(\ell + 1)\hbar^2}{2m_e r^2} - E_n\right](P_{n,\ell}(r)) = 0
\]
### Listing of $P_{nl}(r)$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$P_{nl}(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$\sqrt{\frac{Z}{a_0}} \frac{2}{2} \left( \frac{Zr}{a_0} \right) e^{-\frac{Zr}{a_0}}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\sqrt{\frac{Z}{a_0}} \frac{1}{\sqrt{2}} \left( \frac{Zr}{a_0} \right) \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\sqrt{\frac{Z}{a_0}} \frac{2}{\sqrt{6}} \left( \frac{Zr}{a_0} \right)^2 e^{-\frac{Zr}{2a_0}}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\sqrt{\frac{Z}{a_0}} \frac{2}{3\sqrt{3}} \left( \frac{Zr}{a_0} \right) \left[1 - \frac{2Zr}{3a_0} + \frac{2}{27} \left( \frac{Zr}{a_0} \right)^2 \right] e^{-\frac{Zr}{3a_0}}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\sqrt{\frac{Z}{a_0}} \frac{4}{27\sqrt{3}} \left( \frac{Zr}{a_0} \right)^2 \left(1 - \frac{Zr}{6a_0}\right) e^{-\frac{Zr}{3a_0}}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$\sqrt{\frac{Z}{a_0}} \frac{2\sqrt{2}}{81\sqrt{15}} \left( \frac{Zr}{a_0} \right)^3 e^{-\frac{Zr}{3a_0}}$</td>
</tr>
</tbody>
</table>

### Things to Note:

- $R_{nl} = \frac{P_{nl}}{r}$
- The functions $R_{nl}$ are normalized: $\int_0^\infty r^2 R_{n,l}^2 \, dr = 1$
- For hydrogen, $Z=1$
- Each $P_{nl}$ has a common factor of $(a_o)^{-3/2}$
- The radial parameter $r$ is always normalized by $a_o$
- The argument of the exponential is $[-r/(n\,a_o)]$
If \( \ell > 0 \), all the \( \Psi(r=0) = 0 \)

Phase of wavefunction (R>0, R<0): important for chemical bonding

Radial nodes
The principal quantum number $n$ is an integer that determines the allowed (quantized) energy level; its value runs from 1, 2, 3, ...

For each $n$, the orbital quantum number $\ell = 0, 1, 2, \ldots (n-1)$; we will show that $\ell$ is related to the magnitude of angular momentum.

For each $\ell$, the magnetic quantum number $m$ can be

$$-\ell, -\ell + 1, \ldots \ell - 1, \ell$$

we will show that $m$ specifies the $z$ component of the angular momentum.

IMPORTANT
There are a chain of restrictions on $n$, $\ell$ and $m$ imposed by the desire for solutions that do not diverge

• The principal quantum number $n$ is an integer that determines the allowed (quantized) energy level; its value runs from 1, 2, 3, ...

• For each $n$, the orbital quantum number $\ell = 0, 1, 2, \ldots (n-1)$; we will show that $\ell$ is related to the magnitude of angular momentum.

• For each $\ell$, the magnetic quantum number $m$ can be

$$-\ell, -\ell + 1, \ldots \ell - 1, \ell$$

we will show that $m$ specifies the $z$ component of the angular momentum.

We will introduce one more quantum number later this semester to account for the intrinsic spin of an electron.
Physically speaking, why are there restrictions on \( n \), \( \ell \) and \( m \)?

• “\( n \)” specifies how much of the electron’s energy is due to the electron’s potential energy of interaction with the positive nucleus.

• “\( \ell \)” specifies how much of the electron’s energy is tied up in angular motion. Since some of the energy is ‘kinetic’ and some is ‘potential’, “\( \ell \)” must be less than “\( n \)”.

• “\( m \)” specifies the projection of angular momentum (often called the z-component). This projection must always be equal or less than the total angular momentum, so “\( m \)” must be less than or equal to “\( \ell \)”.
Up next . . . the quantized energy spectrum
Math Appendices

An extended discussion of the eigenfunctions for the angular and radial wave equations.

Background: Historically, the solutions of certain differential equations were discovered by 18th century math geniuses, mostly as a mathematical exercise. These ‘special’ differential equations (along with their solutions known as orthogonal polynomials) were written down, published in books, and stored in libraries, waiting for an application. Just as a Fourier series provides a convenient method of expanding a periodic function in a series of linearly independent terms, orthogonal polynomials provide a way to solve and expand solutions to many differential equations.
Math Note 1: Legendre’s Equation

Legendre functions were first introduced by Legendre in 1784. They are important for problems involving spheres or spherical coordinates. Legendre’s functions are also called zonal harmonics or spherical harmonics.

Legendre’s Differential Equation can be written as

\[(1 - x^2) \frac{d^2 y}{dx^2} - 2xy \frac{dy}{dx} + \ell (\ell + 1) y = 0\]

Solutions to this equation are called Legendre functions of order \(\ell\)

IF \(\ell=0,1,2,3\ldots\), the solution to Legendre’s Differential Equation are given by the Legendre polynomials \(P_\ell(x)\)

\[P_\ell (x) = \frac{1}{2^\ell \ell!} \frac{d^\ell}{dx^\ell} (x^2 - 1)^\ell; \quad -1 \leq x \leq +1\]
the first few Legendre polynomials $P_\ell(x)$ are plotted and listed below

http://mathworld.wolfram.com/LegendrePolynomial.html

Easy to check: choose a value for $\ell$, find the corresponding $P_\ell(x)$ and substitute into Legendre’s Differential Equation.
Legendre’s Equation is a special case of a differential equation known as the associated Legendre Equation which is written as

\[(1 - x^2) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + \left[ \ell(\ell + 1) - \frac{m^2}{1 - x^2} \right] y = 0\]

Solutions to this equation are called the associated Legendre functions of the first kind. The solutions depend on BOTH \( \ell \) and \( m \). The solutions are often written as

\[P_\ell^m(x) = (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_\ell(x)\]

Note that since \( P_\ell \) is generally a polynomial in \( x \) of order \( \ell \), the derivatives are equal to zero when \( m > \ell \). This implies that

\[P_\ell^m(x) = 0 \quad \text{if} \quad m > \ell\]

This simple realization places a restriction on \( m \) wrt \( \ell \).
List of first few associated Legendre functions in terms of $x$ and $\theta$

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$m$</th>
<th>$P_l^m(x)$</th>
<th>$P_l^m(\cos \theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>any $\ell$</td>
<td>0</td>
<td>$P_\ell(x)$</td>
<td>$P_\ell(\cos \theta)$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>$-\sqrt{1-x^2}$</td>
<td>$-\sin \theta$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$-3x\sqrt{1-x^2}$</td>
<td>$-3 \sin \theta \cos \theta$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\frac{3}{2}(1-5x^2)\sqrt{1-x^2}$</td>
<td>$-\frac{3}{2}(5 \cos^2 \theta - 1) \sin \theta$</td>
</tr>
</tbody>
</table>

Diagram: Associated Legendre functions (normalized)

To understand why this discussion of Legendre’s equation is relevant, we must transform Legendre’s associated equation into polar coordinates. In what follows, we set the dummy parameter \( x \) used in the pervious slides equal to \( z \).

\[
\begin{align*}
  x &= r \sin \theta \cos \phi \\
  y &= r \sin \theta \sin \phi \\
  z &= r \cos \theta
\end{align*}
\]

**Handy lookup table**

<table>
<thead>
<tr>
<th>( z = \cos \theta )</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>( \pi )</td>
</tr>
<tr>
<td>0</td>
<td>( \pi/2 )</td>
</tr>
<tr>
<td>+1</td>
<td>0</td>
</tr>
</tbody>
</table>
\[(1 - z^2) \frac{d^2 P^m_\ell(z)}{dz^2} - 2z \frac{dP^m_\ell(z)}{dz} + \left[ l(l + 1) - \frac{m^2}{1 - z^2} \right] P^m_\ell(z) = 0 \]

The solutions \( P^m_\ell(z) \) = associated Legendre functions

Let: \( z = \cos \theta \quad \theta = \cos^{-1} z \)

\[
\frac{d\theta}{dz} = \frac{d}{dz} \left( \cos^{-1} z \right) = -\frac{1}{\sqrt{1 - z^2}} = -\frac{1}{\sin \theta}
\]

\[
\frac{d^2\theta}{dz^2} = \frac{d}{dz} \left( \frac{d\theta}{dz} \right) = \frac{d}{dz} \left( -\left(1 - z^2\right)^{-1/2} \right)
\]

\[
= -\left( -\frac{1}{2} \right) \left(1 - z^2\right)^{-3/2} (-2z) = -\frac{\cos \theta}{\sin^3 \theta}
\]

We also need expressions for the various derivatives wrt \( z \) in terms of \( \theta \)

\[
\frac{d}{dz} = \frac{d\theta}{dz} \frac{d}{d\theta} = \left( -\frac{1}{\sin \theta} \right) \frac{d}{d\theta}
\]

\[
\frac{d^2}{dz^2} = \left( \frac{d^2 \theta}{dz^2} \right) \frac{d}{d\theta} + \frac{d\theta}{dz} \frac{d}{dz} \frac{d}{d\theta} = \left( \frac{d^2 \theta}{dz^2} \right) \frac{d}{d\theta} + \left( \frac{1}{\sin \theta} \right)^2 \frac{d^2}{d\theta^2}
\]

\[
= -\frac{\cos \theta}{\sin^3 \theta} \frac{d}{d\theta} + \left( \frac{1}{\sin \theta} \right)^2 \frac{d^2}{d\theta^2}
\]
\[(1 - z^2) \frac{d^2 P^m_\ell}{dz^2} - 2z \frac{dP^m_\ell}{dz} + \left[ l(l + 1) - \frac{m^2}{1 - z^2} \right] P^m_\ell = 0 \]

becomes
\[(1 - \cos^2 \theta) \left[ -\frac{\cos \theta}{\sin^3 \theta} \frac{d}{d\theta} + \left( \frac{1}{\sin \theta} \right)^2 \frac{d^2}{d\theta^2} \right] P^m_\ell - 2 \cos \theta \left( -\frac{1}{\sin \theta} \right) \frac{dP^m_\ell}{d\theta} + \left[ l(l + 1) - \frac{m^2}{1 - \cos^2 \theta} \right] P^m_\ell = 0 \]

\[-\frac{\cos \theta}{\sin \theta} \frac{dP^m_\ell}{d\theta} + 2 \left( \frac{\cos \theta}{\sin \theta} \right) \frac{dP^m_\ell}{d\theta} + \frac{d^2 P^m_\ell}{d\theta^2} + \left[ l(l + 1) - \frac{m^2}{\sin^2 \theta} \right] P^m_\ell = 0 \]

\[\frac{d^2 P^m_\ell}{d\theta^2} + \left( \frac{\cos \theta}{\sin \theta} \right) \frac{dP^m_\ell}{d\theta} + \left[ l(l + 1) - \frac{m^2}{\sin^2 \theta} \right] P^m_\ell = 0 \]

This is equivalent to the associated Legendre's Equation but now it is written in polar coordinates.
Can we massage Schrödinger’s Eq. for $\Theta$ to match the associated Legendre Equation?

\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) \Theta(\theta) + \left[ \ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = 0
\]

\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ \ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0
\]

\[
\frac{1}{\sin \theta} \left( \cos \theta \frac{d\Theta}{d\theta} + \sin \theta \frac{d^2\Theta}{d\theta^2} \right) + \left[ \ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0
\]

\[
\frac{d^2\Theta}{d\theta^2} + \left( \frac{\cos \theta}{\sin \theta} \right) \frac{d\Theta}{d\theta} + \left[ \ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0
\]

Schrödinger’s $\Theta$ equation is equivalent to the associated Legendre’s Equation in polar coordinates. This means the solutions are given by

\[
\Theta(\theta) = P^m_\ell (\theta) = \Theta^m_\ell (\theta) \text{ or } \Theta^m_{\ell,m} (\theta)
\]
Math Note 2: Laguerre’s Equation

Laguerre polynomials were introduced by Laguerre in 1879. They were discovered when Laguerre was trying to solve the integral

\[ \int_{0}^{\infty} \frac{e^{-x}}{x} \, dx \]

using a continued fraction expansion. Laguerre’s Differential Equation can be written as

\[ x \frac{d^2 y(x)}{dx^2} + (1 - x) \frac{dy(x)}{dx} + n y(x) = 0 \]

IF \( n=0,1,2,3 \ldots \), the known solutions to Laguerre’s Differential Equation are given by the Laguerre polynomials \( L_n(x) \)

\[ y(x) = L_n(x) = e^x \frac{d^n}{dx^n} \left( x^n e^{-x} \right) \]
the first few Laguerre polynomials \( L_n(x) \) are plotted and listed below

Easy to check: choose a value for \( n \), find the corresponding \( L_n(x) \) and substitute into Laaguerre’s Differential Equation.

http://mathworld.wolfram.com/LaguerrePolynomial.html

<table>
<thead>
<tr>
<th>n</th>
<th>( L_n(x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>(-x + 1)</td>
</tr>
<tr>
<td>2</td>
<td>( x^2 - 4x + 2 )</td>
</tr>
<tr>
<td>3</td>
<td>(-x^3 + 9x^2 - 18x + 6)</td>
</tr>
</tbody>
</table>
Laguerre’s Equation is a special case of a differential equation known as the associated Laguerre’s differential equation which is written as

\[ x \frac{d^2 y(x)}{dx^2} + (m + 1 - x) \frac{dy(x)}{dx} + (n - m) y(x) = 0 \]

Note that when \( m = 0 \), we recover Laguerre’s Differential Equation.

Solutions to the associated equation for NON-NEGATIVE \( n \) and \( m \) are called the associated Laguerre polynomials. The solutions depend on BOTH \( n \) and \( m \). The solutions are often written as

\[ y(x) \equiv L_n^m(x) = \frac{d^m}{dx^m} L_n(x) \]
List of first few associated Laguerre polynomials are

<table>
<thead>
<tr>
<th>n</th>
<th>m</th>
<th>( L_n^m(x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>any n</td>
<td>0</td>
<td>( L_n(x) )</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>(-1)</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>(2x - 4)</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>(-3x^2 + 18x - 18)</td>
</tr>
</tbody>
</table>

Yet another equation related to Laguerre's associated differential equation can be written as

\[
\frac{d^2 y(x)}{dx^2} + \left[ -\frac{1}{4} + \left( \frac{2j+k+1}{2} \right) \frac{1}{x} - \frac{k^2-1}{4x^2} \right] y(x) = 0; \quad j = 0,1,2,3..... \quad k = 0,1,2,3.....
\]

This equation has known solutions given by the associated Laguerre functions given by

\[
y(x) \equiv y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x); \quad j = 0,1,2,3..... \quad k = 0,1,2,3.....
\]

where the \( L_j^k(x) \) are the associated Laguerre polynomials.
To understand why a discussion of Laguerre’s equations are relevant, we must massage Schrödinger’s radial wave equation for $R(r)$ to see if it can be made to match a differential equation with solutions related to the associated Laguerre polynomials.
Let's begin with Schrödinger's radial wave equation for $R(r)$. Three inspired substitutions are required to reach our goal.

\[
\frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{2m_e r^2}{\hbar^2} \left( \frac{1}{4\pi\varepsilon_o} \frac{e^2}{r} + E \right) = \ell (\ell + 1); \quad \ell = 0, 1, 2, 3... \\
\frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left( \frac{2m_e r^2}{\hbar^2} \frac{1}{4\pi\varepsilon_o} \frac{e^2}{r} + \frac{2m_e r^2}{\hbar^2} E - \ell (\ell + 1) \right) R(r) = 0
\]

**Step 1:** label solutions by $n, \ell$ and define $rR_{nl}(r) = P_{nl}(r)$

\[
\frac{d}{dr} \left( r^2 \frac{d}{dr} \right) R_{nl}(r) = \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \left[ r^{-1} P_{nl}(r) \right] = \frac{d}{dr} \left[ -r^{-2} P_{nl}(r) + r^{-1} \frac{dP_{nl}(r)}{dr} \right] = \frac{d}{dr} \left( -P_{nl}(r) + r \frac{dP_{nl}(r)}{dr} \right) = -\frac{dP_{nl}(r)}{dr} + \frac{dP_{nl}(r)}{dr} + r \frac{d^2 P_{nl}(r)}{dr^2} = r \frac{d^2 P_{nl}(r)}{dr^2}
\]

\[
\frac{r}{dr} \frac{d^2 P_{nl}(r)}{dr^2} = \left( \frac{2m_e r^2}{\hbar^2} \frac{1}{4\pi\varepsilon_o} \frac{e^2}{r} + \frac{2m_e r^2}{\hbar^2} E - \ell (\ell + 1) \right) \frac{P_{nl}(r)}{r} = 0
\]

\[
\frac{d^2 P_{nl}(r)}{dr^2} + \left( \frac{2m_e}{\hbar^2} \frac{1}{4\pi\varepsilon_o} \frac{e^2}{r} + \frac{2m_e}{\hbar^2} E - \frac{\ell (\ell + 1)}{r^2} \right) P_{nl}(r) = 0
\]
\[
\left[ \frac{d^2 P_{n\ell}(r)}{dr^2} \right] + \left( \frac{2m_e}{\hbar^2} \frac{1}{4\pi \varepsilon_o} \frac{e^2}{r} + \frac{2m_e}{\hbar^2} E - \frac{\ell(\ell + 1)}{r^2} \right) P_{n\ell}(r) = 0
\]

Step 2:

now let \( \left( \frac{\varepsilon}{2} \right)^2 = -\frac{2m_e}{\hbar^2}E \quad \Rightarrow \quad \varepsilon^2 = -\frac{8m_e}{\hbar^2}E \)

\[
\left[ \frac{d^2 P_{n\ell}(r)}{dr^2} \right] + \left( \frac{2m_e}{\hbar^2} \frac{1}{4\pi \varepsilon_o} \frac{e^2}{r} - \frac{\varepsilon^2}{4} - \frac{\ell(\ell + 1)}{r^2} \right) P_{n\ell}(r) = 0
\]

Step 3:

now let \( x = r\varepsilon \)

\[
\frac{dx}{\varepsilon} = \frac{dr}{\varepsilon} \quad \frac{d^2 P_{n\ell}(r)}{dr^2} = \frac{d}{dr} \frac{dP_{n\ell}(r)}{dr} = \varepsilon \frac{d}{dx} \frac{dP_{n\ell}(x)}{dx} = \varepsilon^2 \frac{d^2 P_{n\ell}(x)}{dx^2}
\]

\[
\varepsilon^2 \frac{d^2 P_{n\ell}(x)}{dx^2} + \left( \frac{2m_e}{\hbar^2} \frac{\varepsilon}{4\pi \varepsilon_o} \frac{e^2}{x} - \frac{\varepsilon^2}{4} - \frac{\ell(\ell + 1)}{x^2} \right) P_{n\ell}(x) = 0
\]

\[
\frac{d^2 P_{n\ell}(x)}{dx^2} + \left( \frac{2m_e}{\hbar^2} \frac{1}{4\pi \varepsilon_o} \varepsilon \right) \frac{1}{x} - \frac{1}{4} - \frac{\ell(\ell + 1)}{x^2} \right) P_{n\ell}(x) = 0 \quad (I)
\]

This equation is remarkably similar to the differential equation

\[
\frac{d^2 y_j^k(x)}{dx^2} + \left[ -\frac{1}{4} + \left( \frac{2j + k + 1}{2} \right) \frac{1}{x} - \frac{k^2 - 1}{4x^2} \right] y_j^k(x) = 0; \quad j = 0,1,2,3..... \quad k = 0,1,2,3..... \quad (II)
\]

which has known solutions given by

\[
y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x); \quad j = 0,1,2,3..... \quad k = 0,1,2,3.....
\]
The term $L^k_j(x)$ are the associated Laguerre polynomials and solve the associated Laguerre differential equation written in the form

$$x \frac{d^2 L^k_j(x)}{dx^2} + (1 - x + k) \frac{dL^k_j(x)}{dx} + jL^k_j(x) = 0; \quad j = 0, 1, 2, 3, \ldots \quad k = 0, 1, 2, 3, \ldots$$

We must now connect $j, k$ to $\ell$. Evidently, by comparing Eqs. I and II on previous slide, we must require

$$\ell(\ell + 1) = \frac{k^2 - 1}{4} \quad \Rightarrow \quad k = 2\ell + 1$$

and

$$\frac{2m_e}{\hbar^2} \frac{1}{4\pi\varepsilon_o} \frac{e^2}{\varepsilon} = \frac{2j + k + 1}{2} = \frac{2j + (2\ell + 1) + 1}{2} = j + \ell + 1$$

define $n = j + \ell + 1; \quad n = 1, 2, 3, \ldots$

then

$$\frac{2m_e}{\hbar^2} \frac{1}{4\pi\varepsilon_o} \frac{e^2}{\varepsilon} = n \quad \text{where} \quad \frac{\varepsilon^2}{4} = -\frac{2m_eE}{\hbar^2}$$

$$\left(\frac{2m_e}{\hbar^2}\right)^2 \left(\frac{1}{4\pi\varepsilon_o}\right)^2 \frac{e^4}{\varepsilon^2} = n^2 \quad \Rightarrow \quad \left(\frac{2m_e}{\hbar^2}\right)^2 \left(\frac{1}{4\pi\varepsilon_o}\right)^2 \frac{e^4}{n^2} = \varepsilon^2 = -\frac{8m_eE}{\hbar^2}$$

$$E_n = -\left(\frac{2m_e}{\hbar^2}\right)^2 \left(\frac{e^2}{4\pi\varepsilon_o}\right)^2 \frac{\hbar^2}{8m_e} \frac{1}{n^2} = -\frac{1}{2} m_e c^2 \alpha^2 \frac{1}{n^2} \quad \text{where} \quad \alpha \equiv \frac{e^2}{4\pi\varepsilon_o \hbar c}$$
How to index the eigenfunctions with respect to $n$ and $\ell$? We have

$$ y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x); \quad j = 0,1,2,3..... \quad k = 0,1,2,3..... $$

Since $k = 2\ell + 1$

$$ \frac{k+1}{2} = \left[ \frac{(2\ell+1)+1}{2} \right] = \ell + 1 $$

and

$$ j + \ell + 1 = n \quad \Rightarrow \quad j = n - \ell - 1 $$

These substitutions give

$$ y_j^k(x) \Rightarrow y_n^\ell(x) = e^{-x/2} x^{\ell+1} L_{j=n-\ell-1}^{k=2\ell+1}(x) $$

Next step, what’s $x$?

$$ \frac{\varepsilon^2}{4} = -\frac{2m_e E}{\hbar^2} = -\frac{2m_e}{\hbar^2} \left( -\frac{1}{2} m_e c^2 \alpha^2 \frac{1}{n^2} \right) = \frac{m_e^2 c^2 \alpha^2}{\hbar^2} \frac{1}{n^2} \quad \text{where} \quad \alpha \equiv \frac{e^2}{4\pi \varepsilon_o \hbar c} $$

define $a_o \equiv \frac{\hbar}{m_e c} \frac{1}{\alpha}$

$$ \frac{\varepsilon^2}{4} = \frac{1}{n^2 a_o^2} \quad \Rightarrow \quad \varepsilon = \frac{2}{na_o} \quad \Rightarrow \quad x \equiv r\varepsilon = \frac{2r}{na_o} $$
The eigenfunctions

\[ y_n^\ell (x) = e^{-x/2} x^{\ell+1} L_{j=n-\ell-1}^{k=2\ell+1}(x) \]
	now become

\[ y_n^\ell (r) = e^{-r/na_o} \left( \frac{2r}{na_o} \right)^{\ell+1} L_{n-\ell-1}^{2\ell+1}\left( \frac{2r}{na_o} \right) \]

To be complete, we also must find an expression for \( R_{n\ell}(r) \)

\[ y_n^\ell (r) = P_{n\ell} (r) = rR_{n\ell} (r) \]

This finally gives for \( R(r) \):

\[ R_{n\ell} (r) = \frac{P_{n\ell}(r)}{r} = A_{n\ell} e^{-r/na_o} \left( \frac{2r}{na_o} \right)^{\ell} L_{n-\ell-1}^{2\ell+1}\left( \frac{2r}{na_o} \right) \]

Note that a constant factor \( 2/na_o \) is often absorbed into the normalizing factor \( A_{n\ell} \) when \( P_{n\ell} \) is divided by \( r \).