# The Hydrogen Atom

**Introduction**

This section of the Study Guide is intended to supplement the study of the hydrogen atom in an introductory quantum mechanics class. At present, a non-spin treatment is provided, but it is intended that the spin, spin-orbit and spin-spin coupling will be included in future versions of this section. It is assumed that the subject will be covered in detail in class and a supporting text, and that this section of the Study Guide will provide some additional insight and problem-solving help for the student. The texts described in the References linked below were used by the author to provide different viewpoints and some variation in approach.

This section provides, in the Discussion below, consideration of the separation of variables approach in preparation to solution of the Schrodinger equation, some discussion of the solution of the angular portion of the equation, and supplemental insight into the detail behind the solution of the Radial equation. The Problem Solving Tips sections has a few math insights that might be of help to students, as well as listings of the first few spherical harmonics, Legendre polynomials, Laguerre polynomials, and associated Laguerre polynomials so that they will be readily available for practice using the solved wave function for the hydrogen atom. In the Worked Examples section there are some detailed sample problems that illustrate how the solved wave equation can be used to describe various states of the atom, given selected quantum numbers. Finally, in the References section are listings of both texts that may be useful to the student (as described above), and Weblinks that may provide additional understanding of this subject. Particularly useful in getting an intuitive understanding of the subject, may be the online sites of graphical applets listed in the Weblinks. These provide an interactive illustration of the changing probability densities of the described atomic system, as the viewer enters different quantum numbers. Again, it is anticipated that this section will be modified and amended on a continuing basis to provide student help with spin-related subjects and perhaps the Dirac equation for the hydrogen atom, as well as to keep current the Weblinks.

# Discussion

## I. The Schrodinger Equation for the Hydrogen Atom

The 3 dimensional Schrodinger equation for a single particle system with a non-time-dependent potential is written as follows: $\frac{-\hbar^2}{2m}\nabla^2\Psi + V\Psi = E\Psi$

The potential associated with the hydrogen atom can be viewed as one with a radial dependence only, in three dimensions, so that the equation is rewritten in spherical coordinates where,

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

resulting in the following form of the Schrodinger equation for the hydrogen atom:

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

with: $\Psi = \Psi(r,\theta,\phi)$, $\mu = \frac{m_e m_p}{m_e + m_p}$, $V(r) = \frac{-Ze^2}{r}$

The central potential used above for the hydrogen atom, is of the form of a Coulomb potential between the positively charged nucleus and the negatively charge electron, where Z is the atomic number of the atom. Also included above, is a term for the reduced mass, μ, which has been substituted for the single mass, m, since the hydrogen atom can be viewed as a two particle system, made of the electron and nuclear proton. When dealing with a system of more than one particle, as with the hydrogen atom, center of mass coordinates are used to represent the system. In this representation, the Hamiltonian of the system can be divided into 2 entirely independent portions, that of system as a "free particle" where the entire system is reduced to a single object at the center of the mass of the system, and a second portion that treats the system relative to the center of mass. The system as a free particle is a known solution, however the Hamiltonian of the system relative to the center of mass is the one used to solve the Radial equation, as described in subsection III below.

## II. Separation of Variables

Beginning with the 3 dimensional form of the Schrodinger equation in spherical coordinates:

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

we want to separate the equation into its radially-dependent portion and its angularly-dependent portion. We use a form of the wave function that assumes this separation: $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ and insert this into the above equation. When this is done the Y and R dependent portions of the wave function show up only in those portions of the equation when the relevant r, θ, and φ show up:

$$\frac{-\hbar^2}{2\mu}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right] + VRY = ERY$$

Notice that the partial derivatives associated with the R portions of the equation have been changed to ordinary derivatives by the separation. Those associated with the Y portions have not yet been changed to ordinary derivatives. Now, divide the entire equation by YR:

$$\frac{-\hbar^2}{2\mu}\left[\frac{1}{Rr^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{Yr^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Yr^2\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]+V=E$$

Multiply by $r^2$ and $\frac{-2\mu}{\hbar^2}$,

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Y\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]-\frac{2\mu}{\hbar^2}Vr^2=\frac{-2\mu}{\hbar^2}Er^2$$

The equation can now be separated into 2 portions, the radially-dependent portion and the angularly-dependent portion:

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2\mu r^2}{\hbar^2}(V-E)\right\}+\left\{\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Y\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right\}=0$$

The radial portion of the equation is set equal to a constant, $l(l+1)$, and the angularly dependent portion is set equal to the negative of that same constant,

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

$$\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Y\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)=-l(l+1)$$

The angularly-dependent equation can be further separated into its θ and ϕ portions. Begin by multiplying the angular equation by $Y\sin^2\theta$, resulting in,

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\left(\frac{\partial^2 Y}{\partial\phi^2}\right)=-l(l+1)Y\sin^2\theta$$

Then, redefine the angularly-dependent wave function to explicitly separate these two functions, $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$ and insert this new wave function into the angular equation,

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\frac{\partial^2\Phi}{\partial\phi^2}\right)=-l(l+1)\Theta\Phi\sin^2\theta$$

Divide by $\Theta\Phi$ and group into 2 portions, the θ-dependent and the ϕ-dependent,

$$\frac{1}{\Theta\Phi}\left[\sin\theta\frac{d}{d\theta}\left(\Phi\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\Theta\frac{d^2\Phi}{d\phi^2}\right)\right]=\frac{1}{\Theta\Phi}\left(-l(l+1)\Theta\Phi\sin^2\theta\right)$$

$$\left\{\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+l(l+1)\sin^2\theta\right\}+\left\{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}\right\}=0$$

Again, the partial derivatives of the equation become ordinary derivatives once separated. The θ-dependent portion is set equal to positive $m^2$ and the ϕ-dependent portion is set equal to negative $m^2$.

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

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

## III. Solving the Angular-dependent Portion of the Schrodinger Equation

First, we look at the solution to the ϕ-dependent equation (also known as the Azimuthal equation). Since this is a differential equation that we are familiar with, it is easy to see that the solution (actually 2 of them) to:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

is: $\Phi(\phi) = e^{im\phi}$, where $m = \pm m$

The possible values for m can be seen to be integers, based on the fact that when ϕ is allowed to cycle through 2π the function returns to the same position, so that:
$\Phi(\phi) = \Phi(\phi + 2\pi)$ and $e^{im(\phi)} = e^{im(\phi+2\pi)}$, so that $e^{im(2\pi)} = 1$. This requirement leads directly to the fact that *m* must be a range of integer values, otherwise the last equality could not true.

The solution to the θ-dependent equation (also known as the Colatitude equation),

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

or, rearranged slightly, $$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \Theta l(l+1)\sin^2\theta - \Theta m^2 = 0$$
is:

$$\Theta(\theta) = CP_l^m\cos\theta$$

where C is a constant and $P_l^m$, the associated Legendre function, is described by:

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

and $P_l(\alpha)$ is the *l*th Legendre polynomial, which can in turn, be defined as: $P_l(x) = \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l(x^2-1)^l$, which is known as the Rodrigues formula.
The Rodrigues formula requires that *l* always be a positive value; the formula does not make sense for negative values of *l*.
Combining the solutions to the Azimuthal and Colatitude equations, produces a solution to the non-radial portion of the Schrodinger equation for the hydrogen atom:
$Y_l^m(\theta,\phi) = Ce^{im\phi}P_l^m\cos\theta$
The constant C represents a normalization constant that is determined in the usual manner by integrating of the square of the wave function and setting the resulting value equal to one. The volume element in spherical coordinates, $r^2\sin\theta dr d\theta d\phi$, is used for this integration. (The radial and non-radial portions of the wave function may be normalized separately: $\int|\Psi|^2 r^2\sin\theta dr d\theta d\phi = \int|R|^2 r^2 dr\int|Y|^2\sin\theta d\theta d\phi = 1$. The radial portion of the wave function is normalized in the following subsection.) (The following normalization is taken from Mathematical Methods for Physicists, Fourth Edition, G. B. Arfken and H. J. Weber.)

$$C^2\int_0^{2\pi}\int_0^{\pi}|Y|^2\sin\theta d\theta d\phi = 1$$

$$C^2 \int_0^{2\pi} e^{im\phi} e^{-1m\phi} d\phi \int_0^{\pi} \left(P_l^m(\cos\theta)\right)^2 \sin\theta d\theta = 1$$

The $\phi$ dependent portion of the integral simply yields $2\pi$:

$$C'^2 2\pi \int_0^{\pi} \left(P_l^m(\cos\theta)\right)^2 \sin\theta d\theta = 1$$

Using the definition for the associated Legendre function:

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

together with Rodrigues' formula:

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

the θ dependent portion of the above integral can be rewritten, labeling the two Legendre functions with different subscripts (p and q) for the following normalization description:

$$C'^2 2\pi \int_{-1}^{1} P_p^m(x) P_q^m(x) dx = 1$$

, where $\cos\theta = x$ and $-\sin\theta d\theta = dx$

$$C'^2 2\pi \int_{-1}^{1} \left(1-x^2\right)^{m/2} \frac{d^m}{dx^m} P_p(x) \left(1-x^2\right)^{m/2} \frac{d^m}{dx^m} P_q(x) dx = 1$$

substituting in:

$$P_p(x) = \frac{1}{2^p p!}\left(\frac{d}{dx}\right)^p \left(x^2-1\right)^p, \quad P_q(x) = \frac{1}{2^q q!}\left(\frac{d}{dx}\right)^q \left(x^2-1\right)^q$$

$$C'^2 2\pi \int_{-1}^{1} \left(1-x^2\right)^m \frac{d^m}{dx^m}\left(\frac{1}{2^p p!}\left(\frac{d}{dx}\right)^p \left(x^2-1\right)^p\right) \frac{d^m}{dx^m}\left(\frac{1}{2^q q!}\left(\frac{d}{dx}\right)^q \left(x^2-1\right)^q\right) dx = 1$$

$$C'^2 2\pi \frac{1}{2^{p+q} p! q!} \int_{-1}^{1} \left(1-x^2\right)^m \frac{d^{m+p}}{dx^{m+p}} \left(x^2-1\right)^p \frac{d^{m+q}}{dx^{m+q}} \left(x^2-1\right)^q dx = 1$$

Set $\left(x^2-1\right) \equiv X$

$$C'^2 2\pi \frac{(-1)^m}{2^{p+q} p! q!} \int_{-1}^{1} X^m \frac{d^{m+p}}{dx^{m+p}} X^p \frac{d^{m+q}}{dx^{m+q}} X^q dx = 1$$

The integration is performed using integration by parts. After integrating *m*+*q* times you obtain:

$$C'^2 2\pi \frac{(-1)^m (-1)^{m+q}}{2^{p+q} p! q!} \int_{-1}^{1} \frac{d^{m+q}}{dx^{m+q}} \left(X^m \frac{d^{m+p}}{dx^{m+p}} X^p\right) X^q dx = 1$$

The term within the integral is expanded according to Leibniz's formula:

$$X^q \frac{d^{m+q}}{dx^{m+q}}\left(X^m \frac{d^{m+p}}{dx^{m+p}} X^p\right) = X^q \sum_{i=0}^{m+q} \frac{(m+q)!}{i!(m+q-i)!} \frac{d^{m+q-i}}{dx^{m+q-i}} X^m \frac{d^{m+p+i}}{dx^{m+p+i}} X^p$$

Because $X^m$ contains no power of *x* greater than $x^{2m}$, therefore $m+q-i \le 2m$, otherwise the derivative vanishes. The same thing applies for $X^p$, having no power of x greater than $x^{2p}$, so that $m+p+i \le 2p$. These are the two index conditions required for non-zero results: $i \le p-m$, $i \ge q-m$.

Given these two conditions, if $p < q$ or $q < p$ there is no solution and the integral vanishes. This leaves only one possible solution $q = p$, so that $i = q-m$. When the integral is rewritten incorporating these values:

$$\int_{-1}^{1} \left(P_q^m(x)\right)^2 dx = \frac{(-1)^{q+2m}(q+m)!}{2^{2q} q! q! (q-m)! (2m)!} \int_{-1}^{1} X^q \left(\frac{d^{2m}}{dx^{2m}} X^m\right)\left(\frac{d^{2q}}{dx^{2q}} X^q\right) dx$$

$$X^m = \left(x^2 - 1\right)^m = x^{2m} - m x^{2m-2} + \ldots, \quad \frac{d^{2m}}{dx^{2m}} X^m = (2m)!$$

$$\int_{-1}^{1} \left(P_q^m(x)\right)^2 dx = \frac{(-1)^{q+2m}(q+m)!(2q)!}{2^{2q} q! q! (q-m)!} \int_{-1}^{1} X^q dx$$

$$\int_{-1}^{1} \left(P_q^m(x)\right)^2 dx = \frac{(-1)^{q+2m}(q+m)!(2q)!}{2^{2q} q! q! (q-m)!} \int_{-1}^{1} X^q dx$$

The integral on the right can be represented as: (for odd n)

$$2(-1)^q \int_0^{\frac{\pi}{2}} \sin^n \theta d\theta = 2(-1)^q \frac{(n-1)!!}{n!!}$$

Substituting $n = 2q+1$:

$$\frac{(n-1)!!}{n!!} = \frac{(2q)!!}{(2q+1)!!} = \frac{2^q q! 2^q q!}{(2q+1)!} = \frac{2^{2q} q! q!}{(2q+1)!}$$

$$\int_{-1}^{1} \left(P_q^m(x)\right)^2 dx = \frac{(-1)^{q+2m}(q+m)!(2q)!}{2^{2q} q! q! (q-m)!} 2 \frac{(-1)^q 2^{2q} q! q!}{(2q+1)!}$$

$$\int_{-1}^{1} \left(P_q^m(x)\right)^2 dx = \frac{2(q+m)!}{(2q+1)(q-m)!}$$

Therefore, after substituting *l* for *q*, the normalization constant for the θ dependent portion of the integral is:

$$C' = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}$$

and when multiplied with the normalization constant from the ϕ dependent portion of the integral $\sqrt{\frac{1}{2\pi}}$ and combining that with the rest of the solution yields the following solution to the non-radial portion of the Schrodinger equation for the hydrogen atom.

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

$\alpha = (-1)^m$ for $m \geq 0$, and $\alpha = 1$ for $m \leq 0$

(The radial portion of the equation shall be solved in the next section and then combined with the non-radial solution to provide the full solution to the problem.)

## IV. **Solving the Radial Portion of the Schrodinger Equation**

What follows is a step-by-step approach to solving the radial portion of the Schrodinger equation for atoms that have a single electron in the outer shell. The negative eigenenergies of the Hamiltonian are sought as a solution, because these represent the bound states of the atom. We begin with the radial equation:

$$\frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}\left(rR(r)\right)+\frac{\hbar^2 l(l+1)}{2\mu r^2}R(r)-\frac{Ze^2}{r}R(r)+|E|R(r)=0$$

Step 1: You must first simplify the radial equation to make solving the differential equation easier. The following sub-steps use substitutions and cancellations to create a differential equation that will then be solvable.

First, substitute the variable u for rR(r),

$$\frac{\hbar^2}{2\mu r}\left[-\frac{d^2}{dr^2}u+\frac{l(l+1)}{r^2}u-\frac{2\mu Ze^2}{\hbar^2 r}u+\frac{2\mu|E|}{\hbar^2}u\right]=0$$

divide by $\frac{-\hbar^2}{2\mu r}$ and make the following substitutions:

$$\rho = 2\kappa r,\quad r^2=\frac{\rho^2}{4\kappa^2},\quad d\rho = 2\kappa dr,\quad dr^2=\frac{d\rho^2}{4\kappa^2}$$

so that the equation becomes:

$$\frac{-4\kappa^2 d^2}{d\rho^2}u+\frac{l(l+1)4\kappa^2}{\rho^2}u-\frac{4\kappa\mu Ze^2}{\hbar^2\rho}u+\frac{2\mu|E|}{\hbar^2}u=0$$

Substitute: $|E|=\frac{\hbar^2\kappa^2}{2\mu}$

$$\frac{-4\kappa^2 d^2}{d\rho^2}u+\frac{l(l+1)4\kappa^2}{\rho^2}u-\frac{4\kappa\mu Ze^2}{\hbar^2\rho}u+\kappa^2 u=0$$

Now, substitute: $a_0=\frac{\hbar^2}{\mu e^2}$, $\lambda=\frac{Z}{\kappa a_0}=\frac{Z\mu e^2}{\kappa\hbar^2}$

Yielding,

$$\frac{-4\kappa^2 d^2}{d\rho^2}u+\frac{l(l+1)4\kappa^2}{\rho^2}u-\frac{4\kappa^2\lambda}{\rho}u+\kappa^2 u=0$$

Finally, divide by $-4\kappa^2$, resulting in the equation in the final form, ready to begin solution:

$$\frac{d^2}{d\rho^2}u-\frac{l(l+1)}{\rho^2}u+\frac{\lambda}{\rho}u-\frac{1}{4}u=0$$

Step 2: Now that the equation is in the proper form for solution, the next step is to identify the singular points. The form of the full solution to the differential equation will be that of a wave function multiplied by a polynomial, P(r):

R(r) = ($\varphi_{\text{singular pts}}$)(P(r))

Changing the variables R to u and r to ρ, yields

$u(\rho) = (\varphi_{\text{singular pts}})(P(\rho))$.

In this step, we will work with the wave function portion of the full solution form above, and in the next step we will work with the polynomial portion of the solution. Singular points exist where the wave function must go to zero. In this case, the wave function must disappear in the center of the atom, at r (radius of the atom) equal to zero, and at a relatively large distance from the atom, taken as r equal to infinity. Each singular point must be considered individually and the behavior of the wave function approximated at that point.

As the distance ( r) from the atom goes to infinity (and, hence as ρ goes to infinity), the $-\frac{l(l+1)}{\rho^2}u$ and $\frac{\lambda}{\rho}u$ terms go to zero and are, therefore, unimportant to this portion of the solution. Because of this, the differential equation to solve, under the infinite distance condition, becomes:

$$\frac{d^2u}{d\rho^2} - \frac{u}{4} = 0, \text{ or } \frac{d^2u}{d\rho^2} = \frac{1}{4}u$$

Not knowing the exact solution at this point, an appropriate guess of the solution is:

$$u = e^{\pm\frac{\rho}{2}}, \text{ yielding, } \frac{du}{d\rho} = \pm\frac{1}{2}e^{\pm\frac{\rho}{2}}, \quad \frac{d^2u}{d\rho^2} = \frac{1}{4}e^{\pm\frac{\rho}{2}}$$

It can be readily seen that as ρ goes to infinity the positive solution to u, $e^{+\frac{\rho}{2}}$, does <u>not</u> go to zero as required by observation, instead blowing up and, therefore, is not a solution at the infinite singular point. On the other hand, the negative solution to u at infinity, $e^{-\frac{\rho}{2}}$, <u>does</u> go to zero as required and is the solution at the infinite singular point:

$$u = e^{-\frac{\rho}{2}} \text{ as } \rho \to \infty, \ (r \to \infty).$$

At the second singular point identified, where r equals zero (at the center of the atom), the $\frac{d^2u}{d\rho^2}$ and $-\frac{l(l+1)}{\rho^2}u$ terms are the most important terms in the differential equation, while the other two terms are of relative unimportance and dropped when considering a solution at the zero singular point. Therefore, the equation to solve becomes:

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

Again, an appropriate guess of a solution that goes to zero as ρ goes to zero is $u = \rho^{l+1}$, yielding $\frac{du}{d\rho} = (l+1)\rho^l$, and $\frac{d^2u}{d\rho^2} = l(l+1)\rho^{l-1}$ which gives the same solution when $u = \rho^{l+1}$ is substituted into the original differential equation:

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

Therefore, at this second singular point, where r equals zero, the solution to the differential equation is:

$u = \rho^{l+1}$ as $\rho \to 0$ $(r \to 0)$

These two solutions (for the two singular points) are combined to create an exact solution for wave function portion of the full solution:

$$u(\rho) = e^{-\frac{\rho}{2}} \rho^{l+1} P(\rho)$$, where P(ρ) is of the form: $\sum_n a_n \rho^n$

<u>Step 3</u>: Having created a solution for the wave function portion of the full solution (a solution for the differential equation taken from the radial equation for a hydrogenic atom), we now must find an equation for the polynomial portion of that full solution. First substitute the solution found thus far, $u(\rho) = e^{-\frac{\rho}{2}} \rho^{l+1} P(\rho)$, into the differential equation $\frac{d^2}{d\rho^2}u - \frac{l(l+1)}{\rho^2}u + \frac{\lambda}{\rho}u - \frac{1}{4}u = 0$, the new form of the equation is:

$$\frac{d^2\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right)}{d\rho^2} - \frac{l(l+1)}{\rho^2}\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right) + \frac{\lambda}{\rho}\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right) - \frac{1}{4}\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right) = 0 \quad \textbf{(A)}$$

Solving for the first term on the LHS, performing first order differentiation using the chain rule: (resulting in three terms)

$$\frac{d\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right)}{d\rho} = \left(-\frac{1}{2}e^{-\frac{\rho}{2}}\rho^{l+1}P\right) + \left(e^{-\frac{\rho}{2}}(l+1)\rho^{l}P\right) + \left(e^{-\frac{\rho}{2}}\rho^{l+1}P'\right)$$

and then differentiating again using the chain rule: (resulting in nine terms)

$$\begin{aligned}\frac{d^2\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right)}{d\rho^2} = &\left(\frac{1}{4}e^{-\frac{\rho}{2}}\rho^{l+1}P\right) + \left(-\frac{1}{2}e^{-\frac{\rho}{2}}(l+1)\rho^{l}P\right) + \left(-\frac{1}{2}e^{-\frac{\rho}{2}}\rho^{l+1}P'\right)\\ &+\left(-\frac{1}{2}e^{-\frac{\rho}{2}}(l+1)\rho^{l}P\right) + \left(e^{-\frac{\rho}{2}}l(l+1)\rho^{l-1}P\right) + \left(e^{-\frac{\rho}{2}}(l+1)\rho^{l}P'\right)\\ &+\left(-\frac{1}{2}e^{-\frac{\rho}{2}}\rho^{l+1}P'\right) + \left(e^{-\frac{\rho}{2}}(l+1)\rho^{l}P'\right) + \left(e^{-\frac{\rho}{2}}\rho^{l+1}P''\right)\end{aligned}$$

Insert this term into equation **(A)**, cancel and combine like terms.

Canceling :

$\left(-\frac{1}{4}e^{-\frac{\rho}{2}}\rho^{l+1}P\right)$ with the 4th term of **(A)**, $-\frac{1}{4}\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right)$, and

$\left(e^{-\frac{\rho}{2}}l(l+1)\rho^{l-1}P\right)$ with the 2nd term of (A), $-\frac{l(l+1)}{\rho^2}\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right)$

Combining:

$\left(-\frac{1}{2}e^{-\frac{\rho}{2}}(l+1)\rho^{l}P\right)$ with $\left(-\frac{1}{2}e^{-\frac{\rho}{2}}(l+1)\rho^{l}P\right)$ and $\frac{\lambda}{\rho}\left(e^{-\frac{\rho}{2}}\rho^{l+1}P\right)$

gives: $e^{-\frac{\rho}{2}}\rho^l(\lambda-l-1)P$

These operations result in the following equation:

$$(e^{-\frac{\rho}{2}}\rho^{l+1}P'')-(e^{-\frac{\rho}{2}}\rho^{l+1}P')+(2e^{-\frac{\rho}{2}}(l+1)\rho^l P')+(e^{-\frac{\rho}{2}}\rho^l(\lambda-l-1)P)=0$$

Dividing by $e^{-\frac{\rho}{2}}$, gives:

$$(\rho^{l+1}P'')-(\rho^{l+1}P')+(2(l+1)\rho^l P')+(\rho^l(\lambda-l-1)P)=0$$

And, further diving by $\rho^l$, results in the final form of the polynomial:

$$\rho P''+(2l+2-\rho)P'+(\lambda-l-1)P=0$$

We are not done with the polynomial yet, as we must determine the recursion relationship for the coefficients of the polynomial. We need to determine this relationship not only to know how the polynomial will be generated, but also to use in determining the limits of the summations within the polynomial, as we shall see in Step 4 that follows.

To establish the recursion relationship between successive coefficients of the polynomial, begin by substituting the summation forms of the polynomial for the each differential level of P:

$$P=\sum_i a_i\rho^i \quad ; \quad P'=\sum_i (i)a_i\rho^{i-1} \quad ; \quad P''=\sum_i (i)(i-1)a_i\rho^{i-2}$$

and inserting these into the final form of the polynomial:

$$\rho\sum_i (i)(i-1)a_i\rho^{i-2}+(2l-2-\rho)\sum_i (i)a_i\rho^{i-1}+(\lambda-l-1)\sum_i a_i\rho^i=0$$
$$=\sum_i (i)(i-1)a_i\rho^{i-1}-\rho\sum_i (i)a_i\rho^{i-1}+2(l+1)\sum_i (i)a_i\rho^{i-1}+(\lambda-l-1)\sum_i a_i\rho^i=0$$
$$=\sum_i (i)(i-1)a_i\rho^{i-1}-\sum_i (i)a_i\rho^i+2(l+1)\sum_i (i)a_i\rho^{i-1}+(\lambda-l-1)\sum_i a_i\rho^i=0$$
$$\sum_i [(i)(i-1)+(2l+2)(i)]a_i\rho^{i-1}+\sum_i [(-i)a+(\lambda-l-1)a_i]_i\rho^i=0$$

Substitute: $i'=i-1$, in the left-most term,

$$=\sum_{i'} [(i'+1)(i')+(2l+2)(i'+1)]a_{i'+1}\rho^{i'}+\sum_i [(-i)a+(\lambda-l-1)a_i]_i\rho^i=0$$

Now, substitute *i* for *i*′, in the same term,

$$=\sum_i [(i+1)(i+2l+2)]a_{i+1}\rho^i+\sum_i [(-i)a+(\lambda-l-1)a_i]_i\rho^i=0$$

Divide by $\rho^i$, and solve for $a_{i+1}$:

$$a_{i+1}=\frac{a_i(i-\lambda+l+1)}{(i+1)(i+2l+2)}$$

This is the recursion relationship for the coefficients in the polynomial.

Step 4: In this last step in solving the radial equation, we examine the polynomial to determine if it is finite and if not, to determine what condition is necessary to make it finite. This condition of finiteness produces a quantum that characterizes the state of the system and serves to quantize the bound state energies of the atom.

The polynomial P(ρ) must go to zero, so the behavior of the polynomial must be examined when $i$ goes to infinity:

$$P(\rho) \stackrel{?}{=} \sum_i a_i p^i \rightarrow 0, \text{ as } i \rightarrow \infty$$

In order to determine whether the polynomial converges, first examine the ratio of the coefficients in the limit where $i$ goes to infinity,

$$\frac{a_{i+1}}{a_i}_{\, i \rightarrow \infty} \cong \frac{i}{i^2} \cong \frac{1}{i}$$

This ratio of coefficients is the same as that of the power series for $e^x$:

$$e^x = \sum b_i x^i = \sum \frac{x^i}{i!}$$

$$\lim_{i \rightarrow \infty} \frac{b_{i+1}}{b_i} = \frac{i!}{(i+1)!} \cong \frac{(i)(i-1)(....)}{(i+1)(i)(i-1)(....)} \cong \frac{1}{i}$$

So, as $i$ goes to infinity, the polynomial P(ρ) behaves like the series $e^\rho$. When $e^\rho$ is substituted for P(ρ) into the solution for u:

$$u_{\rho \rightarrow \infty} = e^{\frac{-\rho}{2}} \rho^{l+1} P \cong e^{\frac{-\rho}{2}} \rho^{l+1} e^\rho = e^\rho \rho^{l+1}$$

This representation for the solution of u blows up when ρ is very large; exhibiting behavior that is not acceptable (not observed to be true for the atom) in our solution. Therefore, the summation must be terminated at a particular number, in order to force the polynomial into the correct behavior. In order to determine the value for the needed termination number, we set the coefficient of the polynomial P(ρ) equal to zero at a maximum number, forcing the termination of the solution at large distances from the atom:

For $a_{i+1} = 0$, at $a_{i\max}$:

$$a_{i+1} = \frac{a_i(i - \lambda + l + 1)}{(i+1)(i+2l+2)} = 0;$$

therefore, $i - \lambda + l + 1 = 0$, $i_{\max} = l + 1 - \lambda$

And the summation is terminated at $i_{\max}$ equal to $l$+1-λ.

Since $\lambda = i_{\max} + l + 1$, and both l and $i_{\max}$ are integers then λ is also an integer and is represented by the quantum number n. Using this relationship for n, and the fact that the smallest value for $l$ is zero, the smallest value of n can be determined:

$n = i_{\max} + l + 1$, $n \geq l + 1$

Therefore, if $l$ is zero (the lowest value possible), then the minimal value for n must be 1, showing how there is no zero energy level for the bound energy states for the atom:

$$E_n = \frac{Z^2(-13.6eV)}{n^2}$$

In conclusion, our total solution for the radial portion of the Schrodinger equation for the relative Hamiltonian of a hydrogenic atom, is

$$u_{nl}(\rho) = e^{\frac{-\rho}{2}} \rho^{l+1} A_{nl} \sum_{i=0}^{n-l-1} a_i \rho^i$$ (where $A_{nl}$ is a normalization constant)

The polynomial term, $\sum_{i=0}^{n-l-1} a_i \rho^i$, describes a family of polynomials known as the associated Laguerre polynomials. They are usually represented as $F_{nl}(\rho)$ or $L_{n-l-1}^{2l+1}(\rho)$, and the recursion relationship for $a_i$ (the means to generate the coefficients of the summation) is:

$$a_{i+1} = \frac{a_i(i-n+l+1)}{(i+1)(i+2l+2)}$$

The normalization constant $A_{nl}$, is determined according to the following relationship:

$$A_{nl} = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

The hydrogenic atom is normalized using this constant and the term for $a_0$, the first coefficient in the summation $\sum_{i=0}^{n-l-1} a_i \rho^i$. This initial coefficient is determined as follows:

$$u_{nl}(\rho) = rR_{nl}$$

$$R_{nl}(r) = \frac{1}{r} u_{nl}(\rho) = \frac{1}{r} e^{\frac{-\rho}{2}} \rho^{l+1} \sum_{i=0}^{n-l-1} a_i \rho^i$$

With $l = 0$ and $n = 1$, and with $k = \frac{2Z}{a_0}$,

$$R_{nl}(r) = \frac{1}{r} e^{\frac{-kr}{2}} kra_0 = e^{\frac{-kr}{2}} ka_0,$$

as the recursion formula yields zero for the coefficients beyond $a_{i=0}$. To normalize this equation and complete the solution for $a_{i=0}$, we square the equation, integrate between zero and infinity, and set it equal to one:

$$\int_0^\infty |R_{nl}|^2 r^2 dr = k^2 a_{i=0}^2 \int_0^\infty e^{-kr} r^2 dr = 1$$

$$k^2 a_{i=0}^2 2k^{-3} = 1, \quad a_{i=0}^2 = \frac{k}{2}, \quad a_{i=0} = \sqrt{\frac{k}{2}}$$

Substituting this value back into the general solution to the radial equation for the ground state of a hydrogenic atom yields:

$$R_{nl}(r) = e^{\frac{-kr}{2}} k\sqrt{\frac{k}{2}} = e^{\frac{-2Z}{2a_0}} \sqrt{\frac{1}{2}} \left(\frac{2Z}{a_0}\right)^{\frac{3}{2}}$$

The normalized radial portion of the eigenfunctions of hydrogenic atoms is:

$$R_{nl}(r) = \left(\frac{2Z}{na_0}\right)^{\frac{3}{2}} \left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{\frac{1}{2}} e^{\frac{-Zr}{na_0}} \left(\frac{2Zr}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

The associated Laguerre polynomials (the last term in the above equation) are usually represented as $F_{nl}(\rho)$ or $L_{n-l-1}^{2l+1}(\rho)$ and are constructed according to the following formula:

$$L_{n-l-1}^{2l+1}(\rho)=\sum_{i=0}^{n-l-1}\frac{(-1)^i[(n+l)!]^2\rho^i}{i!(n-l-1-i)!(2l+1+i)!}$$

where $\rho = 2\kappa r$ and $\kappa_n = \frac{Z}{a_0 n}$, as indicated at the beginning of this solution.
The associated Laguerre polynomials may also be determined using the following definitions:

$$L_p^q(\rho)=\frac{d^q}{d\rho^q}L_p(\rho), \quad L_p(\rho)=e^{\rho}\frac{d^p}{d\rho^p}\left(\rho^p e^{-\rho}\right)$$

The full wave function for the hydrogenic atom is created by combining the radial solution with the theta and phi-dependent portion solution:

$$\varphi_{nlm}(r,\theta,\phi)=\left(\frac{2Z}{na_0}\right)^{\frac{3}{2}}\left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{\frac{1}{2}}e^{\frac{-Zr}{na_0}}\left(\frac{2Zr}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)Y_l^m(\theta,\phi)$$

# Problem Solving Tips

General:

- Remember that the normalization value for the radial equation is adjusted for each new value of the quantum numbers *n* and *l*.
- 0! = 1

A few Laguerre polynomials:

$$L_0 = 1$$
$$L_1 = 1 - x$$
$$L_2 = 2 - 4x + x^2$$
$$L_3 = 6 - 18x + 9x^2 - x^3$$
$$L_4 = 24 - 96x + 72x^2 - 16x^3 + x^4$$

A few associated Laguerre polynomials:

$$L_0^0 = 1$$
$$L_1^0 = 1 - x$$
$$L_0^1 = 1$$
$$L_1^1 = 4 - 2x$$
$$L_2^0 = 2 - 4x + x^2$$
$$L_2^1 = 18 - 18x + 3x^2$$
$$L_0^2 = 2$$
$$L_1^2 = 18 - 6x$$
$$L_2^2 = 144 - 96x + 12x^2$$

A few associated Legendre functions:

$$P_0 = 1$$
$$P_1^0 = \cos\theta$$
$$P_1^1 = -\sin\theta$$
$$P_1^{-1} = \frac{1}{2}\sin\theta$$
$$P_2^0 = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$
$$P_2^1 = -3\sin\theta\cos\theta$$
$$P_2^{-1} = \frac{1}{2}\sin\theta\cos\theta$$

A few Spherical Harmonics:

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$
$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} e^{i\phi} \sin\theta$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} e^{-i\phi} \sin\theta$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}} \left(3\cos^2\theta - 1\right)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}} e^{i\phi} \sin\theta \cos\theta$$

$$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} e^{-i\phi} \sin\theta \cos\theta$$

# Worked Examples

**Eigenfunction solutions for the hydrogen atom**:

Using the general formula,

$$\varphi_{nlm}(r,\theta,\phi)=\left(\frac{2Z}{na_0}\right)^{\frac{3}{2}}\left(\frac{(n-l-1)!}{2n[(n+l)!]^3}\right)^{\frac{1}{2}} e^{\frac{-Zr}{na_0}}\left(\frac{2Zr}{na_0}\right)^{l} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right)Y_l^m(\theta,\phi)$$

1) For $n$ = 1, $l$ = 0, and $m$ = 0, substitute these values into the general equation,

$$\varphi_{100}(r,\theta,\phi)=\left(\frac{2Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{1}{2}\right)^{\frac{1}{2}} e^{\frac{-Zr}{a_0}} L_0^1\left(\frac{2Zr}{a_0}\right)Y_0^0(\theta,\phi)$$

Solving the associated Laguerre polynomial:

□

$$L_{n-l-1}^{2l+1}(\rho)=\sum_{i=0}^{n-l-1}\frac{(-1)^i[(n+l)!]^2\rho^i}{i!(n-l-1-i)!(2l+1+i)!}$$

$$L_0^1(\rho)=\sum_{i=0}^{0}\frac{(-1)^i[(1)!]^2\rho^i}{i!(0-i)!(1+i)!}$$

$$L_0^1(\rho)=\frac{(1)(1)(1)}{(1)(1)(1)}=1$$

With, Z = 1 (for hydrogen), $L_0^1(\rho)=1$ and $Y_0^0=\sqrt{\frac{1}{4\pi}}$, the wave equation is:

$$\varphi_{100}(r,\theta,\phi)=\sqrt{\frac{1}{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{\frac{-r}{a_0}}$$

2) For $n$ = 2, $l$ = 0, and $m$ = 0, substitute these values into the general equation,

$$\varphi_{200}(r,\theta,\phi)=\left(\frac{2Z}{(2)a_0}\right)^{\frac{3}{2}}\left(\frac{(2-0-1)!}{2(2)[(2+0)!]^3}\right)^{\frac{1}{2}} e^{\frac{-Zr}{(2)a_0}}\left(\frac{2Zr}{(2)a_0}\right)^{0} L_{2-0-1}^{2(0)+1}\left(\frac{2Zr}{(2)a_0}\right)Y_0^0(\theta,\phi)$$

$$\varphi_{200}(r,\theta,\phi)=\left(\frac{2Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{1}{32}\right)^{\frac{1}{2}} e^{\frac{-Zr}{2a_0}} L_1^1\left(\frac{2Zr}{2a_0}\right)Y_0^0(\theta,\phi)$$

Solving the associated Laguerre polynomial:

□

$$L_{n-l-1}^{2l+1}(\rho)=\sum_{i=0}^{n-l-1}\frac{(-1)^i[(n+l)!]^2\rho^i}{i!(n-l-1-i)!(2l+1+i)!}$$

$$L_1^1(\rho)=\sum_{i=0}^{1}\frac{(-1)^i[(2)!]^2\rho^i}{i!(1-i)!(1+i)!}$$

$$L_0^1(\rho)=\frac{(1)(4)(1)}{(1)(1)(1)}+\frac{(-1)(4)(\rho)}{(1)(1)(2)}$$

$$L_0^1(\rho)=4-2\rho$$

With, Z = 1 (for hydrogen), $L_1^1(\rho)=4-2\rho$ , $Y_0^0=\sqrt{\frac{1}{4\pi}}$ , the wave equation is:

$$\varphi_{200}(r,\theta,\phi)=\sqrt{\frac{1}{4\pi}}\left(\frac{1}{2a_0}\right)^{\frac{3}{2}}\left(\frac{1}{2}\right)e^{\frac{-r}{2a_0}}(4-2\rho)$$

$$\varphi_{200}(r,\theta,\phi)=\sqrt{\frac{1}{4\pi}}\left(\frac{1}{2a_0}\right)^{\frac{3}{2}}e^{\frac{-r}{2a_0}}\left(2-\frac{r}{a_0}\right)$$

# References

**Weblinks**: These are just a few of the many links available on line for this subject.

These links provide background on the hydrogen atom and solution of equations.

http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/hydsch.html
http://scienceworld.wolfram.com/physics/HydrogenAtom.html
http://xbeams.chem.yale.edu/~batista/vvv/node21.html (some graphics here)
http://astro.temple.edu/~meziani/lecture_hydrogen.pdf
http://en.wikipedia.org/wiki/Hydrogen_atom (some graphics here, too)
http://tesla.phys.unm.edu/phy537/1/node2.html

These links are to interactive graphics depicting the effects of various quantum numbers on probability distributions for the hydrogen atom.

http://webphysics.davidson.edu/physletprob/ch10_modern/radial.html
http://www.phy.davidson.edu/StuHome/cabell_f/Radial.html
http://physics.usc.edu/~pilch/Classes/163/math/H/

**Texts**: Again, these are only a few of the many available books with information and insight into this subject.

These texts provide different viewpoints and treatments of the hydrogen atom, at the introductory level and with significant discussion and explanation of the subject and solution approach.

Introductory Quantum Mechanics, by R. L. Liboff

Introduction to Quantum Mechanics, by D. J. Griffiths

Modern Quantum Mechanics (Revised Edition), by J.J. Sakurai

Quantum Mechanics, a Modern Introduction, by Ashok Das & A. C. Melissinos

The following texts provide background and explanation of the Laguerre and Legendre polynomials.

Mathematical Methods for Physicists, by G. B. Arfken & H. J. Weber

Mathematical Physics, by Sadri Hassani (w/ an example using the hydrogen atom)