

Chapter 10 The Hydrogen Atom

There are many good reasons to address the hydrogen atom beyond its historical significance. Though hydrogen spectra motivated much of the early quantum theory, research involving the hydrogen remains at the cutting edge of science and technology. For instance, transitions in hydrogen are being used in 1997 and 1998 to examine the constancy of the fine structure constant over a cosmological time scale². From the view point of pedagogy, the hydrogen atom merges many of the concepts and techniques previously developed into one package. It is a particle in a box with spherical, soft walls. Finally, the hydrogen atom is one of the precious few realistic systems which can actually be solved analytically.

The Schrodinger Equation in Spherical Coordinates

In chapter 5, we separated time and position to arrive at the time independent Schrodinger equation which is

$$\mathcal{H}|E_i\rangle = E_i|E_i\rangle, \quad (10-1)$$

where E_i are eigenvalues and $|E_i\rangle$ are energy eigenstates. Also in chapter 5, we developed a one dimensional position space representation of the time independent Schrodinger equation, changing the notation such that $E_i \rightarrow E$, and $|E_i\rangle \rightarrow \psi$. In three dimensions the Schrodinger equation generalizes to

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi,$$

where ∇^2 is the Laplacian operator. Using the Laplacian in spherical coordinates, the Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi + V(r)\psi = E\psi. \quad (10-2)$$

In spherical coordinates, $\psi = \psi(r, \theta, \phi)$, and the plan is to look for a variables separable solution such that $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$. We will in fact find such solutions where $Y(\theta, \phi)$ are the spherical harmonic functions and $R(r)$ is expressible in terms of associated Laguerre functions. Before we do that, interfacing with the previous chapter and arguments of linear algebra may partially explain why we are proceeding in this direction.

Complete Set of Commuting Observables for Hydrogen

Though we will return to equation (10-2), the Laplacian can be expressed

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \quad (10-3)$$

Compare the terms in parenthesis to equation 11-33. The terms in parenthesis are equal to $-\mathcal{L}^2/\hbar^2$, so assuming spherical symmetry, the Laplacian can be written

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2},$$

² Schwarzschild. "Optical Frequency Measurement is Getting a Lot More Precise," Physics Today 50(10) 19-21 (1997).

and the Schrodinger equation becomes

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2 \hbar^2} \right) + V(r) \right] \psi = E\psi. \quad (10-4)$$

Assuming spherical symmetry, which we will have because a Coulomb potential will be used for $V(r)$, we have complicated the system of chapter 11 by adding a radial variable. Without the radial variable, we have a complete set of commuting observables for the angular momentum operators in \mathcal{L}^2 and \mathcal{L}_z . Including the radial variable, we need a minimum of one more operator, if that operator commutes with both \mathcal{L}^2 and \mathcal{L}_z . The total energy operator, the Hamiltonian, may be a reasonable candidate. What is the Hamiltonian here? It is the group of terms within the square brackets. Compare equations (10-1) and (10-4) if you have difficulty visualizing that. In fact,

$$[\mathcal{H}, \mathcal{L}^2] = 0, \quad \text{and} \quad [\mathcal{H}, \mathcal{L}_z] = 0,$$

so the Hamiltonian is a suitable choice. The complete set of commuting observables for the hydrogen atom is \mathcal{H} , \mathcal{L}^2 , and \mathcal{L}_z . We have all the eigenvalue/eigenvector equations, because the time independent Schrodinger equation is the eigenvalue/eigenvector equation for the Hamiltonian operator, *i.e.*, the the eigenvalue/eigenvector equations are

$$\begin{aligned} \mathcal{H}|\psi\rangle &= E_n|\psi\rangle, \\ \mathcal{L}^2|\psi\rangle &= l(l+1)\hbar^2|\psi\rangle, \\ \mathcal{L}_z|\psi\rangle &= m\hbar|\psi\rangle, \end{aligned}$$

where we subscripted the energy eigenvalue with an n because that is the symbol conventionally used for the energy quantum number (per the particle in a box and SHO). Then the solution to the problem is the eigenstate which satisfies all three, denoted $|n, l, m\rangle$ in abstract Hilbert space. The representation in position space in spherical coordinates is

$$\langle r, \theta, \phi | n, l, m \rangle = \psi_{nlm}(r, \theta, \phi).$$

Example 10-1: Starting with the Laplacian included in equation (10-2), show the Laplacian can be express as equation (10-3).

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{1}{r^2} \left(2r \frac{\partial}{\partial r} + r^2 \frac{\partial^2}{\partial r^2} \right) + \frac{1}{r^2 \sin \theta} \left(\cos \theta \frac{\partial}{\partial \theta} + \sin \theta \frac{\partial^2}{\partial \theta^2} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \end{aligned}$$

which is the form of equation (10-3).

Example 10-2: Show $[\mathcal{H}, \mathcal{L}^2] = 0$.

$$[\mathcal{H}, \mathcal{L}^2] = \mathcal{H}\mathcal{L}^2 - \mathcal{L}^2\mathcal{H}$$

$$\begin{aligned}
&= \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2 \hbar^2} \right) + V(r) \right] \mathcal{L}^2 - \mathcal{L}^2 \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2 \hbar^2} \right) + V(r) \right] \\
&= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \mathcal{L}^2 - \frac{\hbar^2}{2m} \frac{2}{r} \frac{\partial}{\partial r} \mathcal{L}^2 + \frac{\hbar^2}{2m} \frac{\mathcal{L}^4}{r^2 \hbar^2} + \frac{\hbar^2}{2m} V(r) \mathcal{L}^2 \\
&\quad + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \frac{\mathcal{L}^4}{r^2 \hbar^2} - \frac{\hbar^2}{2m} \mathcal{L}^2 V(r) \\
&= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \mathcal{L}^2 - \frac{\hbar^2}{2m} \frac{2}{r} \frac{\partial}{\partial r} \mathcal{L}^2 + \frac{\hbar^2}{2m} V(r) \mathcal{L}^2 + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \mathcal{L}^2 V(r)
\end{aligned}$$

where the third and seventh terms in \mathcal{L}^4 sum to zero. The spherical coordinate representation of \mathcal{L}^2 is

$$\mathcal{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

and has angular dependence only. The partial derivatives with respect to the radial variable act only on terms without radial dependence. Partial derivatives with respect to angular variables do not affect the potential which is a function only of the radial variable. Therefore, the order of the operator products is interchangeable, and

$$[\mathcal{H}, \mathcal{L}^2] = -\frac{\hbar^2}{2m} \mathcal{L}^2 \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{2}{r} \frac{\partial}{\partial r} + \frac{\hbar^2}{2m} \mathcal{L}^2 V(r) + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \mathcal{L}^2 V(r) = 0.$$

Instead of the verbal argument, we could substitute the angular representation of \mathcal{L}^2 , form the 18 resultant terms, explicitly interchange nine of them, and get the same result.

Example 10-3: Show $[\mathcal{H}, \mathcal{L}_z] = 0$.

$$\begin{aligned}
[\mathcal{H}, \mathcal{L}_z] &= \mathcal{H} \mathcal{L}_z - \mathcal{L}_z \mathcal{H} \\
&= \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2 \hbar^2} \right) + V(r) \right] \mathcal{L}_z - \mathcal{L}_z \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2 \hbar^2} \right) + V(r) \right] \\
&= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \mathcal{L}_z - \frac{\hbar^2}{2m} \frac{2}{r} \frac{\partial}{\partial r} \mathcal{L}_z + \frac{\hbar^2}{2m} \frac{\mathcal{L}^2 \mathcal{L}_z}{r^2 \hbar^2} + \frac{\hbar^2}{2m} V(r) \mathcal{L}_z \\
&\quad + \frac{\hbar^2}{2m} \mathcal{L}_z \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}_z \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \frac{\mathcal{L}_z \mathcal{L}^2}{r^2 \hbar^2} - \frac{\hbar^2}{2m} \mathcal{L}_z V(r) \\
&= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \mathcal{L}_z - \frac{\hbar^2}{2m} \frac{2}{r} \frac{\partial}{\partial r} \mathcal{L}_z + \frac{\hbar^2}{2m} V(r) \mathcal{L}_z + \frac{\hbar^2}{2m} \mathcal{L}_z \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}_z \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \mathcal{L}_z V(r)
\end{aligned}$$

where the third and seventh terms in $\mathcal{L}^2 \mathcal{L}_z$ sum to zero because we already know those two operators commute. The spherical coordinate representation of \mathcal{L}_z is

$$\mathcal{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

and has angular dependence only. Again there are no partial derivatives which affect any term of the other operator, or the potential $V(r)$, in any of the operator products. Therefore, the order of the operator products is interchangeable, and

$$[\mathcal{H}, \mathcal{L}_z] = -\frac{\hbar^2}{2m} \mathcal{L}_z \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2m} \mathcal{L}_z \frac{2}{r} \frac{\partial}{\partial r} + \frac{\hbar^2}{2m} \mathcal{L}_z V(r) + \frac{\hbar^2}{2m} \mathcal{L}_z \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}_z \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \mathcal{L}_z V(r) = 0.$$

Separating Radial and Angular Dependence

In this and the following three sections, we illustrate how the angular momentum and magnetic moment quantum numbers enter the symbology from a calculus based argument. In writing equation (10-2), we have used a representation, so are no longer in abstract Hilbert space. One of the consequences of the process of representation is the topological arguments of linear algebra are obscured. They are still there, simply obscured because the special functions we use are orthogonal, so can be made orthonormal, and complete, just as bras and kets in a dual space are orthonormal and complete. The primary reason to proceed in terms of a position space representation is to attain a position space description. One of the by-products of this chapter may be to convince you that working in the generality of Hilbert space in Dirac notation can be considerably more efficient. Since we used topological arguments to develop angular momentum in the last chapter, and arrive at identical results to those of chapter 11, we rely on connections between the two to establish the meanings of l and m . They have the same meanings within these calculus based discussions.

As noted, we assume a variables separable solution to equation (10-2) of the form

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi). \quad (10-5)$$

An often asked question is “How do you know you can assume that?” You do not know. You assume it, and if it works, you have found a solution. If it does not work, you need to attempt other methods or techniques. Here, it will work. Using equation (10-5), equation (10-2) can be written

$$\begin{aligned} & \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) Y(\theta, \phi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) R(r) Y(\theta, \phi) \\ & + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} R(r) Y(\theta, \phi) - \frac{2m}{\hbar^2} [V(r) - E] R(r) Y(\theta, \phi) = 0 \\ \Rightarrow & Y(\theta, \phi) \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) + R(r) \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) \\ & + R(r) \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) - \frac{2m}{\hbar^2} [V(r) - E] R(r) Y(\theta, \phi) = 0. \end{aligned}$$

Dividing the equation by $R(r) Y(\theta, \phi)$, multiplying by r^2 , and rearranging terms, this becomes

$$\begin{aligned} & \left\{ \frac{1}{R(r)} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} \\ & + \left[\frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) + \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) \right] = 0. \end{aligned}$$

The two terms in the curly braces depend only on r , and the two terms in the square brackets depend only upon angles. With the exception of a trivial solution, the only way the sum of the groups can be zero is if each group is equal to the same constant. The constant chosen is known as the **separation constant**. Normally, an arbitrary separation constant, like K , is selected and then you solve for K later. In this example, we are instead going to stand on the shoulders of

some of the physicists and mathematicians of the previous 300 years, and make the enlightened choice of $l(l+1)$ as the separation constant. It should become clear l is the angular momentum quantum number introduced in chapter 11. Then

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{2mr^2}{\hbar^2} [V(r) - E] = l(l+1) \quad (10-6)$$

which we call the **radial equation**, and

$$\frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) + \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) = -l(l+1), \quad (10-7)$$

which we call the **angular equation**. Notice the signs on the right side are opposite so they do, in fact, sum to zero.

The Angular Equation

The solutions to equation (10-7) are the spherical harmonic functions, and the l used in the separation constant is, in fact, the same used as the index l in the spherical harmonics $Y_{l,m}(\theta, \phi)$. In fact, it is the angular momentum quantum number. But where is the index m ? How is the magnetic moment quantum number introduced? To answer these questions, remember the spherical harmonics are also separable, *i.e.*, $Y_{l,m}(\theta, \phi) = f_{l,m}(\theta) g_m(\phi)$. We will use such a solution in the angular equation, without the indices until we see where they originate. Using the solution $Y(\theta, \phi) = f(\theta) g(\phi)$ in equation (10-7),

$$\begin{aligned} \frac{1}{f(\theta) g(\phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) f(\theta) g(\phi) + \frac{1}{f(\theta) g(\phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} f(\theta) g(\phi) &= -l(l+1) \\ \Rightarrow \frac{1}{f(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) f(\theta) + \frac{1}{g(\phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} g(\phi) &= -l(l+1). \end{aligned}$$

Multiplying the equation by $\sin^2 \theta$ and rearranging,

$$\frac{\sin \theta}{f(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) f(\theta) + l(l+1) \sin^2 \theta + \frac{1}{g(\phi)} \frac{\partial^2}{\partial \phi^2} g(\phi) = 0.$$

The first two terms depend only on θ , and the last term depends only on ϕ . Again, the only non-trivial solution such that the sum is zero is if the groups of terms each dependent on a single variable is equal to the same constant. Again using an enlightened choice, we pick $-m^2$ as the separation constant, so

$$\frac{\sin \theta}{f(\theta)} \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) f(\theta) + l(l+1) \sin^2 \theta = m^2, \quad (10-8)$$

$$\frac{1}{g(\phi)} \frac{d^2}{d\phi^2} g(\phi) = -m^2, \quad (10-9)$$

and that is how the magnetic moment quantum number is introduced. Again, (10-8) and (10-9) need to sum to zero so the separation constant has opposite signs on the right side in the two equations.

The Azimuthal Angle Equation

The solution to the azimuthal angle equation, equation (10-9), is

$$g(\phi) = e^{im\phi} \Rightarrow g_m(\phi) = e^{im\phi}, \quad (10-10)$$

where the subscript m is added to $g(\phi)$ because it is now clear there are as many solutions as there are allowed values of m .

Example 10-4: Show $g_m(\phi) = e^{im\phi}$ is a solution to equation (10-9).

$$\frac{d^2}{d\phi^2} g_m(\phi) = \frac{d^2}{d\phi^2} e^{im\phi} = \frac{d}{d\phi} (im) e^{im\phi} = (im)^2 e^{im\phi} = -m^2 g_m(\phi).$$

Using this in equation (10-9),

$$\frac{1}{g(\phi)} \frac{d^2}{d\phi^2} g(\phi) = -m^2 \Rightarrow \frac{1}{g(\phi)} \left(-m^2 g_m(\phi) \right) = -m^2 \Rightarrow -m^2 = -m^2,$$

therefore $g_m(\phi) = e^{im\phi}$ is a solution to equation (10-9).

The Polar Angle Equation

This section is a little more substantial than the last. Equation (10-8) can be written

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) f(\theta) + l(l+1) \sin^2 \theta f(\theta) - m^2 f(\theta) = 0.$$

Evaluating the first term,

$$\begin{aligned} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d}{d\theta} \right) f(\theta) &= \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{df(\theta)}{d\theta} \right) \\ &= \sin \theta \left(\cos \theta \frac{df(\theta)}{d\theta} + \sin \theta \frac{d^2 f(\theta)}{d\theta^2} \right) \\ &= \sin^2 \theta \frac{d^2 f(\theta)}{d\theta^2} + \sin \theta \cos \theta \frac{df(\theta)}{d\theta}. \end{aligned}$$

Using this, equation (10-8) becomes

$$\sin^2 \theta \frac{d^2 f(\theta)}{d\theta^2} + \sin \theta \cos \theta \frac{df(\theta)}{d\theta} + l(l+1) \sin^2 \theta f(\theta) - m^2 f(\theta) = 0. \quad (10-11)$$

We are going to change variables using $x = \cos \theta$, and will comment on this substitution later. We then need the derivatives with respect to x vice θ , so

$$\frac{df(\theta)}{d\theta} = \frac{df(x)}{dx} \frac{dx}{d\theta} = \frac{df(x)}{dx} (-\sin \theta) = -\sin \theta \frac{df(x)}{dx},$$

and

$$\begin{aligned}
\frac{d^2 f(\theta)}{d\theta^2} &= \frac{d}{d\theta} \left(-\sin \theta \frac{df(x)}{dx} \right) = -\cos \theta \frac{df(x)}{dx} - \sin \theta \frac{d}{d\theta} \frac{df(x)}{dx} \\
&= -\cos \theta \frac{df(x)}{dx} - \sin \theta \frac{d}{dx} \frac{dx}{d\theta} \frac{df(x)}{dx} = -\cos \theta \frac{df(x)}{dx} - \sin \theta \frac{d}{dx} \left(-\sin \theta \right) \frac{df(x)}{dx} \\
&= -\cos \theta \frac{df(x)}{dx} + \sin^2 \theta \frac{d^2 f(x)}{dx^2}.
\end{aligned}$$

Substituting just the derivatives in the equation (10–11),

$$\sin^2 \theta \left(\sin^2 \theta \frac{d^2 f(x)}{dx^2} - \cos \theta \frac{df(x)}{dx} \right) + \sin \theta \cos \theta \left(-\sin \theta \frac{df(x)}{dx} \right) + l(l+1) \sin^2 \theta f(x) - m^2 f(x) = 0,$$

which gives us an equation in both θ and x , which is not formally appropriate. This is, however, an informal text, and it becomes difficult to keep track of the terms if all the substitutions and reductions are done at once. Dividing by $\sin^2 \theta$, we get

$$\sin^2 \theta \frac{d^2 f(x)}{dx^2} - \cos \theta \frac{df(x)}{dx} - \cos \theta \frac{df(x)}{dx} + l(l+1) f(x) - \frac{m^2}{\sin^2 \theta} f(x) = 0.$$

The change of variables is complete upon summing the two first derivatives, using $\cos \theta = x$, and $\sin^2 \theta = 1 - \cos^2 \theta = 1 - x^2$, which is

$$(1 - x^2) \frac{d^2 f(x)}{dx^2} - 2x \frac{df(x)}{dx} + l(l+1) f(x) - \frac{m^2}{1 - x^2} f(x) = 0.$$

This is the **associated Legendre equation**, which reduces to **Legendre equation** when $m = 0$. The function has a single argument so there is no confusion if the derivatives are indicated with primes, and the associated Legendre equation is often written

$$(1 - x^2) f''(x) - 2x f'(x) + l(l+1) f(x) - \frac{m^2}{1 - x^2} f(x) = 0,$$

and becomes the Legendre equation,

$$(1 - x^2) f''(x) - 2x f'(x) + l(l+1) f(x) = 0,$$

when $m = 0$. The solutions to the associated Legendre equation are the associated Legendre polynomials discussed briefly in the last section of chapter 11. To review that in the current context, associated Legendre polynomials can be generated from Legendre polynomials using

$$P_{l,m}(x) = (-1)^m \sqrt{(1 - x^2)^m} \frac{d^m}{dx^m} P_l(x),$$

where the $P_l(x)$ are Legendre polynomials. Legendre polynomials can be generated using

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

The use of these generating functions was illustrated in example 11–26 as intermediate results in calculating spherical harmonics.

The first few Legendre polynomials are listed in table 10–1. Our interest in those is to generate associated Legendre functions. The first few associated Legendre polynomials are listed in table 10–2.

$$\begin{array}{ll} P_0(x) = 1 & P_3(x) = \frac{1}{2}(5x^3 - 3x) \\ P_1(x) = x & P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3) \\ P_2(x) = \frac{1}{2}(3x^2 - 1) & P_5(x) = \frac{1}{8}(63x^5 - 70x^3 + 15x) \end{array}$$

Table 10 – 1. The First Six Legendre Polynomials.

$$\begin{array}{ll} P_{0,0}(x) = 1 & P_{2,0}(x) = \frac{1}{2}(3x^2 - 1) \\ P_{1,1}(x) = -\sqrt{1-x^2} & P_{3,3}(x) = -15(\sqrt{1-x^2})^3 \\ P_{1,0}(x) = x & P_{3,2}(x) = 15x(1-x^2) \\ P_{2,2}(x) = 3(1-x^2) & P_{3,1}(x) = -\frac{3}{2}(5x^2 - 1)\sqrt{1-x^2} \\ P_{2,1}(x) = -3x\sqrt{1-x^2} & P_{3,0}(x) = \frac{1}{2}(5x^3 - 3x) \end{array}$$

Table 10 – 2. The First Few Associated Legendre Polynomials.

Two comment concerning the tables are appropriate. First, notice $P_l = P_{l,0}$. That makes sense. If the Legendre equation is the same as the associated Legendre equation with $m = 0$, the solutions to the two equations must be the same when $m = 0$. Also, many authors will use a positive sign for all associated Legendre polynomials. This is a different choice of phase. We addressed that following table 11–1 in comments on spherical harmonics. We choose to include a factor of $(-1)^m$ with the associated Legendre polynomials, and the sign of all spherical harmonics will be positive as a result.

Finally, remember the change of variables $x = \cos \theta$. That was done to put the differential equation in a more elementary form. In fact, a dominant use of associated Legendre polynomials is in applications where the argument is $\cos \theta$. One example is the generating function for spherical harmonic functions,

$$Y_{l,m}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{l,m}(\cos \theta) e^{im\phi} \quad m \geq 0, \quad (10-10)$$

and

$$Y_{l,-m}(\theta, \phi) = Y_{l,m}^*(\theta, \phi), \quad m < 0,$$

where the $P_{l,m}(\cos \theta)$ are associated Legendre polynomials. If we need a spherical harmonic with $m < 0$, we will calculate the spherical harmonic with $m = |m|$, and then calculate the adjoint.

To summarize the last three sections, we separated the angular equation into an azimuthal and a polar portion. The solutions to the azimuthal angle equation are exponentials including the magnetic moment quantum number in the argument. The solutions to the polar angle equation are the associated Legendre polynomials, which are different for each choice of orbital angular momentum and magnetic moment quantum number. Both quantum numbers are introduced into

the respective differential equations as separation constants. Since we assumed a product of the two functions to get solutions to the azimuthal and polar parts, the solutions to the original angular equation (10–7) are the products of the two solutions $P_{l,m}(\cos \theta) e^{im\phi}$. These factors are included in equation (10–10). All other factors in equation (10–12) are simply normalization constants. The products $P_{l,m}(\cos \theta) e^{im\phi}$ are the spherical harmonic functions, the alternating sign and radical just make the orthogonal set orthonormal.

Associated Laguerre Polynomials and Functions

The azimuthal equation was easy, the polar angle equation a little more substantial, but you will likely perceive the solution to the radial equation as plain, old heavy! There is no easy way to do this. Our approach will be to relate the radial equation to the associated Laguerre equation, for which the associated Laguerre functions are solutions. A popular option to solve the radial equation is a power series solution, for which we will refer you to Griffiths³, or Cohen–Tannoudji⁴.

Laguerre polynomials are solutions to the Laguerre equation

$$x L_j''(x) + (1 - x) L_j'(x) + j L_j(x) = 0.$$

The first few Laguerre polynomials are listed in table 10–3.

$$\begin{aligned} L_0(x) &= 1 \\ L_1(x) &= -x + 1 \\ L_2(x) &= x^2 - 4x + 2 \\ L_3(x) &= -x^3 + 9x^2 - 18x + 6 \\ L_4(x) &= x^4 - 16x^3 + 72x^2 - 96x + 24 \\ L_5(x) &= -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120 \\ L_6(x) &= x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720 \end{aligned}$$

Table 10 – 3. The First Seven Laguerre Polynomials.

Laguerre polynomials of any order can be calculated using the generating function

$$L_j(x) = e^x \frac{d^j}{dx^j} e^{-x} x^j.$$

The Laguerre polynomials do not form an orthogonal set. The related set of **Laguerre functions**,

$$\phi_j(x) = e^{-x/2} L_j(x) \tag{10 – 13}$$

is orthonormal on the interval $0 \leq x < \infty$. The Laguerre functions are not solutions to the Laguerre equation, but are solutions to an equation which is related.

Just as the Legendre equation becomes the associated Legendre equation by adding an appropriate term containing a second index, the associated Laguerre equation is

$$x L_j^{k''}(x) + (1 - x + k) L_j^{k'}(x) + j L_j^k(x) = 0, \tag{10 – 14}$$

³ Griffiths, *Introduction to Quantum Mechanics* (Prentice Hall, Englewood Cliffs, New Jersey, 1995), pp. 134–141.

⁴ Cohen–Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 794–797.

which reduces to the Laguerre equation when $k = 0$. The first few associated Laguerre polynomials are

$L_0^0(x) = L_0(x)$	$L_0^2(x) = 2$
$L_1^0(x) = L_1(x)$	$L_3^0(x) = L_3(x)$
$L_1^1(x) = -2x + 4$	$L_3^1(x) = -4x^3 + 48x^2 - 144x + 96$
$L_0^1(x) = 1$	$L_2^3(x) = 60x^2 - 600x + 1200$
$L_2^0(x) = L_2(x)$	$L_3^3(x) = -120x^3 + 2160x^2 - 10800x + 14400$
$L_2^1(x) = 3x^2 - 18x + 18$	$L_3^2(x) = -20x^3 + 300x^2 - 1200x + 1200$
$L_2^2(x) = 12x^2 - 96x + 144$	$L_1^3(x) = -24x + 96$
$L_1^2(x) = -6x + 18$	$L_0^3(x) = 6$

Table 10 – 4. Some Associated Laguerre Polynomials.

Notice $L_j^0 = L_j$. Also notice the indices are all non-negative, and either index may assume any integral value. We will be interested only in those associated Laguerre polynomials where $k < j$ for hydrogen atom wave functions.

Associated Laguerre polynomials can be calculated from Laguerre polynomials using the generating function

$$L_j^k(x) = (-1)^k \frac{d^k}{dx^k} L_{j+k}(x).$$

Example 10–5: Calculate $L_3^1(x)$ starting with the generating function.

We first need to calculate $L_4(x)$, because

$$L_j^k(x) = (-1)^k \frac{d^k}{dx^k} L_{j+k}(x) \Rightarrow L_3^1(x) = (-1)^1 \frac{d^1}{dx^1} L_{3+1}(x) = -\frac{d}{dx} L_4(x).$$

Similarly, if you want to calculate L_3^2 , you need to start with L_5 , and to calculate L_4^3 , you need to start with L_7 . So using the generating function,

$$\begin{aligned}
 L_4(x) &= e^x \frac{d^4}{dx^4} e^{-x} x^4 \\
 &= e^x \frac{d^3}{dx^3} \left(-e^{-x} x^4 + e^{-x} 4x^3 \right) \\
 &= e^x \frac{d^2}{dx^2} \left(e^{-x} x^4 - e^{-x} 4x^3 - e^{-x} 4x^3 + e^{-x} 12x^2 \right) = e^x \frac{d^2}{dx^2} \left(e^{-x} x^4 - e^{-x} 8x^3 + e^{-x} 12x^2 \right) \\
 &= e^x \frac{d}{dx} \left(-e^{-x} x^4 + e^{-x} 4x^3 + e^{-x} 8x^3 - e^{-x} 24x^2 - e^{-x} 12x^2 + e^{-x} 24x \right) \\
 &= e^x \frac{d}{dx} \left(-e^{-x} x^4 + e^{-x} 12x^3 - e^{-x} 36x^2 + e^{-x} 24x \right) \\
 &= e^x \left(e^{-x} x^4 - e^{-x} 4x^3 - e^{-x} 12x^3 + e^{-x} 36x^2 + e^{-x} 36x^2 - e^{-x} 72x - e^{-x} 24x + e^{-x} 24 \right) \\
 &= e^x e^{-x} \left(x^4 - 16x^3 + 72x^2 - 96x + 24 \right) \\
 &= x^4 - 16x^3 + 72x^2 - 96x + 24,
 \end{aligned}$$

per table 10–4. Then to get $L_3^1(x)$,

$$\begin{aligned} L_3^1 &= -\frac{d}{dx} L_4(x) \\ &= -\frac{d}{dx} (x^4 - 16x^3 + 72x^2 - 96x + 24) \\ &= -(4x^3 - 48x^2 + 144x - 96) \\ &= -4x^3 + 48x^2 - 144x + 96, \end{aligned}$$

per table 10–3.

Associated Laguerre polynomials are not orthogonal but **associated Laguerre functions** of the type

$$\Phi_j^k(x) = e^{-x/2} x^{k/2} L_j^k(x)$$

are orthogonal on the interval $0 \leq x < \infty$, so can be made an orthonormal set. Again, the $\Phi_j^k(x)$ are not solutions to the associated Laguerre equation but are solutions to a related equation.

We are specifically interested in a slightly different associated Laguerre function than the usual first choice indicated above, *i.e.*, we are interested in

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x). \quad (10-15)$$

These are also not solutions to the associated Laguerre equation, but they are solutions to

$$y_j^{k''}(x) + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2} \right) y_j^k(x) = 0. \quad (10-16)$$

The reason for our interest in (10–16) and its solutions (10–15), is that equation (10–16) is a form of the radial equation, so the radial functions $R(r)$ we seek are $R_{n,l}(r) = A y_n^l(r)$, where A is simply a normalization constant.

Example 10–6: Show equation (10–15) satisfies equation (10–16).

Unlike some of the toy problems given as examples, this example is a critical connection...unless you take our word for it, and then you should skip this. We are going to use the result of this example as a direct link to the solution of the radial equation. We are going to simplify the notation to minimize clutter, and will explain as we go.

To attain the second derivative, we need the first derivative, and use the notation

$$y = e^{-x/2} x^{(k+1)/2} v,$$

for equation (10–15) where $v = L_j^k(x)$, because the indices do not change and only serve to add clutter, and we can remember the independent variable is x . The first derivative is

$$\begin{aligned} y' &= -\frac{1}{2} e^{-x/2} x^{(k+1)/2} v + e^{-x/2} \left(\frac{k+1}{2} \right) x^{(k-1)/2} v + e^{-x/2} x^{(k+1)/2} v' \\ &= \left[-\frac{1}{2} v + \left(\frac{k+1}{2x} \right) v + v' \right] e^{-x/2} x^{(k+1)/2} \\ \Rightarrow \quad \left(e^{x/2} x^{-(k+1)/2} \right) y' &= -\frac{1}{2} v + \frac{k+1}{2x} v + v'. \end{aligned}$$

Notice we adjusted the second term on the right to do the factoring. Using the same adjustment technique, will factor these terms out of the second derivative as we go. These are also factors common to equation (10–15). Since the right side of equation (10–16) is zero, after we substitute the second derivative and the function into (10–16), we will simplify the equation by dividing the equation by common factors, therefore, none of the common factors will enter into the final solution. The exponentials and powers still need to be considered in differentiation, but their inverses will appear on the left and only the terms which have impact will appear on the right. Proceeding....

$$\left(e^{x/2}x^{-(k+1)/2}\right)y'' = \frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \frac{k+1}{2x}\frac{k-1}{2x}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v' + v''.$$

Substituting the second derivative and the function into equation (10–16),

$$y'' + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right)y = 0,$$

and dividing by the common factor of $e^{-x/2}x^{(k+1)/2}$, the remaining terms are

$$\begin{aligned} & \left(\frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \frac{k+1}{2x}\frac{k-1}{2x}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v' + v''\right) \\ & \quad + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right)v = 0 \\ \Rightarrow & \quad v'' + \cancel{\frac{1}{4}}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \cancel{\frac{k^2-1}{4x^2}}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v' \\ & \quad - \cancel{\frac{1}{4}}v + \frac{2j+k+1}{2x}v - \cancel{\frac{k^2-1}{4x^2}}v = 0 \\ \Rightarrow & \quad v'' - \cancel{\frac{k+1}{2x}}v - \frac{1}{2}v' - \cancel{\frac{k+1}{2x}}v + \frac{k+1}{x}v' - \frac{1}{2}v' + \frac{j}{x}v + \cancel{\frac{k+1}{2x}}v = 0 \\ \Rightarrow & \quad v'' - v' + \frac{k+1}{x}v' + \frac{j}{x}v = 0 \\ \Rightarrow & \quad xv'' - xv' + (k+1)v' + jv = 0 \\ \Rightarrow & \quad xv'' + (1-x+k)v' + jv = 0 \end{aligned} \tag{10-17}$$

which is the associated Laguerre equation. Since $v = L_j^k(x)$, and the $L_j^k(x)$ are solutions to the associated Laguerre equation, equation (10–17) is equivalent to

$$xL_j^{k''}(x) + (1-x+k)L_j^{k'}(x) + jL_j^k(x) = 0,$$

which is the associated Laguerre, which we know to be a true statement, so

$$\begin{aligned} y &= e^{-x/2}x^{(k+1)/2}v \\ &= e^{-x/2}x^{(k+1)/2}L_j^k(x) \end{aligned}$$

are solutions to equation (10–16).

The Reduced Mass

Equation (10-2) describes a single particle in a central potential. The hydrogen atom is a two body problem, and the potential is not central but is dependent upon the distance between the nucleus and the electron. Were we able to anchor the nucleus to a stationary location we could designate an origin, equation (10-2) would be an accurate description. This is not possible, but we can reach a similar end by picturing the center of mass being anchored to a fixed location. If we use the **reduced mass** in place of the electron mass,

$$\mu = \frac{m_p m_e}{m_p + m_e},$$

the radial coordinate r accurately describes the distance between the nucleus and the electron. The effect in equation (10-2) is cosmetic; where there was an m representing m_e , it is replaced by μ . Because the proton is about 1836 times more massive than the electron, the reduced mass is nearly identically the electron mass. Many authors simply retain the electron mass. Since the center of mass is not actually anchored, a second set of coordinates is required to track the center of mass using this scheme. This consideration and other details of reducing a two particle problem to a one particle problem are adequately covered in numerous texts, including Chohen-Tannoudji⁵, Levine⁶, and many classical mechanics texts.

Solution of the Radial Equation

The radial equation (10-6) using the reduced mass and the Coulomb potential, $V(r) = -e^2/r$, is

$$\begin{aligned} & \frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{2\mu r^2}{\hbar^2} \left[-\frac{e^2}{r} - E \right] - l(l+1) = 0 \\ \Rightarrow & \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{2\mu r^2}{\hbar^2} \left[-\frac{e^2}{r} - E \right] R(r) - l(l+1) R(r) = 0 \\ \Rightarrow & \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) + \left[\frac{2\mu r^2}{\hbar^2} \frac{e^2}{r} + \frac{2\mu r^2}{\hbar^2} E - l(l+1) \right] R(r) = 0. \end{aligned} \quad (10-18)$$

The plan is to get (10-18) into a form comparable to equation (10-16), and we already know the solutions are equation (10-15). We will be able to glean additional information by comparing the equations term by term. The energy levels of the hydrogen atom and the meaning of the indices of the associated Laguerre polynomials, which will be quantum numbers for the hydrogen atom, will come from the comparison of individual terms.

We will make three substitutions to get the last equation into the form of equation (10-16). The first is

$$y(r) = r R(r) \quad \Rightarrow \quad R(r) = \frac{y(r)}{r}. \quad (10-19)$$

⁵ Cohen-Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 784-788.

⁶ Levine, *Quantum Chemistry* (Allyn and Bacon, Inc., Boston, Massachusetts, 1983), pp. 101-106.

Making this substitution in the first term and evaluating the derivatives

$$\begin{aligned}
\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) &= \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) (r^{-1}) y(r) \\
&= \frac{d}{dr} r^2 \left[(-r^{-2}) y(r) + (r^{-1}) \frac{dy(r)}{dr} \right] \\
&= \frac{d}{dr} \left[-y(r) + r \frac{dy(r)}{dr} \right] \\
&= -\frac{dy(r)}{dr} + \frac{dy(r)}{dr} + r \frac{d^2 y(r)}{dr^2} \\
&= r \frac{d^2 y(r)}{dr^2}.
\end{aligned}$$

The substitution serves to eliminate the first derivative. We would have both a first and second derivative if we had evaluated the first term using $R(r)$. With this and the substitution of equation (10-19), equation (10-18) becomes

$$\begin{aligned}
r \frac{d^2 y(r)}{dr^2} + \left[\frac{2\mu r e^2}{\hbar^2} + \frac{2\mu r^2}{\hbar^2} E - l(l+1) \right] \frac{y(r)}{r} &= 0 \\
\Rightarrow \frac{d^2 y(r)}{dr^2} + \left[\frac{2\mu e^2}{r \hbar^2} + \frac{2\mu E}{\hbar^2} - \frac{l(l+1)}{r^2} \right] y(r) &= 0.
\end{aligned}$$

The second substitution is essentially to simplify the notation, and is

$$\left(\frac{\epsilon}{2} \right)^2 = -\frac{2\mu E}{\hbar^2} \quad (10-20)$$

where the negative sign on the right indicates we are looking for bound states, states such that $E < 0$, so including the negative sign here lets us have an ϵ which is real. The last equation becomes

$$\frac{d^2 y(r)}{dr^2} + \left[\frac{2\mu e^2}{r \hbar^2} - \frac{\epsilon^2}{4} - \frac{l(l+1)}{r^2} \right] y(r) = 0.$$

The third substitution is a change of variables, and notice it relates radial distance and energy through equation (10-20),

$$x = r\epsilon \Rightarrow r = \frac{x}{\epsilon}, \quad (10-21)$$

$$\Rightarrow dr = \frac{dx}{\epsilon} \Rightarrow \frac{d^2 y(r)}{dr^2} = \frac{d}{dr} \frac{dy(r)}{dr} = \epsilon \frac{d}{dx} \epsilon \frac{dy(x)}{dx} = \epsilon^2 \frac{d^2 y(x)}{dx^2},$$

so our radial equation becomes

$$\begin{aligned}
\epsilon^2 \frac{d^2 y(x)}{dx^2} + \left[\frac{2\mu e^2 \epsilon}{x \hbar^2} - \frac{\epsilon^2}{4} - \epsilon^2 \frac{l(l+1)}{x^2} \right] y(x) &= 0 \\
\Rightarrow \frac{d^2 y(x)}{dx^2} + \left[-\frac{1}{4} + \frac{2\mu e^2}{\hbar^2 \epsilon x} - \frac{l(l+1)}{x^2} \right] y(x) &= 0,
\end{aligned} \quad (10-22)$$

and equation (10-22) is equation (10-16) where

$$l(l+1) = \frac{k^2 - 1}{4}, \quad (10-23)$$

and

$$\frac{2\mu e^2}{\hbar^2 \epsilon} = \frac{2j + k + 1}{2}, \quad (10-24)$$

Per example 10-6, the solutions are equation (10-15),

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x).$$

Eigenenergies from the Solution of the Radial Equation

Equation (10-23) tells us $k = 2l + 1$.

Example 10-7: Show $k = 2l + 1$.

Equation (10-23) is

$$\begin{aligned} \frac{k^2 - 1}{4} &= l(l + 1) \\ \Rightarrow k^2 &= 4l(l + 1) + 1 \\ &= 4l^2 + 4l + 1 \\ &= (2l + 1)^2 \\ \Rightarrow k &= 2l + 1. \end{aligned}$$

We are going to take what appears to be a slight diversion to evaluate a particular set of factors in equation (10-24), $\hbar^2/\mu e^2$, which recurs repeatedly. Going back to the old quantum theory, this is called the Bohr radius, that is

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.529 \text{ \AA}. \quad (10-25)$$

We want to express lengths in terms of the Bohr radius because it is a natural length for the hydrogen atom.

Example 10-8: Show $a_0 = 0.529 \text{ \AA}$, using both the electron mass and the reduced mass.

This example is intended to illustrate three simple things. First, $a_0 = 0.529 \text{ \AA}$, second is to work out the CGS units for e^2 , and then to show the electron mass is a very good approximation to the reduced mass in hydrogen. The electrostatic force in MKS and CGS systems is defined

$$\begin{aligned} \frac{1}{4\pi\epsilon_0} \frac{e_{\text{MKS}}^2}{r^2} &= F = \frac{e_{\text{CGS}}^2}{r^2} \\ \Rightarrow e_{\text{CGS}}^2 &= \frac{e_{\text{MKS}}^2}{4\pi\epsilon_0} = (1.602 \times 10^{-19} \text{ C})^2 (8.988 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2) \\ &= 2.307 \times 10^{-28} \text{ N} \cdot \text{m}^2 = 2.307 \times 10^{-19} \text{ dyne} \cdot \text{cm}^2 \\ &= 2.307 \times 10^{-19} \text{ erg} \cdot \text{cm} = 14.42 \text{ eV} \cdot \text{\AA}. \end{aligned}$$

So

$$a_0 = \frac{\hbar^2}{m_e e^2} = \frac{1}{4\pi^2} \frac{(hc)^2}{m_e c^2 e^2} = \frac{1}{4\pi^2} \frac{(1.240 \times 10^4 \text{ eV} \cdot \text{\AA})^2}{(0.5110 \times 10^6 \text{ eV})(14.42 \text{ eV} \cdot \text{\AA})} = 0.5286 \text{ \AA}.$$

The reduced mass is

$$\mu = \frac{m_p m_e}{m_p + m_e} = \frac{1.673 \times 10^{-24}}{1.673 \times 10^{-24} + 9.110 \times 10^{-28}} m_e = 0.9995 m_e,$$

$$\Rightarrow \frac{\hbar^2}{\mu e^2} = \frac{\hbar^2}{0.9995 m_e e^2} = \frac{0.5286 \text{ \AA}}{0.9995} = 0.5288 \text{ \AA}.$$

There is 0.03% difference between the electron mass and reduced mass values. Many authors simply use the electron mass and it yields a good approximation. The CGS value of e^2 can be mysterious for those who have worked primarily in MKS units. By the way, the square root $e = 3.797 (eV \cdot \text{\AA})^{1/2}$ can be a convenient way to express the charge on the electron in CGS units.

Equation (10–24) gives us the eigenenergies of the hydrogen atom, but requires some development. Since $k = 2l + 1$,

$$\frac{2j + k + 1}{2} = \frac{2j + (2l + 1) + 1}{2} = j + l + 1.$$

From the discussion on associated Laguerre polynomials, the indices j and k are non-negative. The sum $j + l + 1$ can, therefore, assume any integer values of 1 or greater. We are going to rename it n , or

$$n = j + l + 1. \quad (10 - 26)$$

The new integer index n is known as the **principal quantum number**. Using the principal quantum number, it follows that the eigenenergies of the hydrogen atom are

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{13.6 \text{ eV}}{n^2}, \quad (10 - 27)$$

where the quantity 13.6 eV is called the Rydberg, usually denoted R or Ry . The ground state energy is $E_0 = -13.6 \text{ eV}$ when $n = 1$. It is often convenient to express excited state energies in terms of the ground state energy.

Example 10–9: Show equation (10–27) follows from equation (10–24).

$$\frac{2\mu e^2}{\hbar^2 \epsilon} = \frac{2j + k + 1}{2}$$

$$\Rightarrow j + l + 1 = n = \frac{2\mu e^2}{\hbar^2 \epsilon}$$

$$\Rightarrow \epsilon = \frac{2\mu e^2}{\hbar^2 n}$$

$$\Rightarrow \epsilon^2 = \frac{4\mu^2 e^4}{\hbar^4 n^2}.$$

Substituting equation (10–20) to eliminate ϵ and insert energy,

$$-4 \frac{2\mu E}{\hbar^2} = \frac{4\mu^2 e^4}{\hbar^4 n^2}$$

$$\begin{aligned}\Rightarrow E &= -\frac{\mu^2 e^4 \hbar^2}{2\mu \hbar^4 n^2} = -\left(\frac{\mu e^2}{\hbar^2}\right)^2 \frac{\hbar^2}{2\mu n^2} \\ \Rightarrow E_n &= -\frac{\hbar^2}{2\mu a_0^2 n^2}.\end{aligned}$$

Inserting numerical values,

$$\begin{aligned}E_n &= -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{1}{4\pi^2} \frac{(hc)^2}{2(\mu c^2) a_0^2 n^2} \\ &= -\frac{1}{4\pi^2} \frac{(1.24 \times 10^4 \text{ eV} \cdot \text{\AA})^2}{2(0.511 \times 10^6 \text{ eV})(0.529 \text{ \AA})^2 n^2} = -\frac{13.6 \text{ eV}}{n^2},\end{aligned}$$

so eigenenergies do follow from the solution of the radial equation.
