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 scale[2]. 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

$$\mathcal{H}\big|E_i> = E_i\big|E_i>, \tag{10-1}$$

where E_i are eigenvalues and $\big|E_i>$ 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 $\big|E_i> \rightarrow \psi$. 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

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

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

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

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

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

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

and the Schrodinger equation becomes

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

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,

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

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

$$\mathcal{H}\,|\psi> = E_n|\psi>,$$
$$\mathcal{L}^2|\psi> = l(l+1)\hbar^2|\psi>,$$
$$\mathcal{L}_z|\psi> = m\hbar|\psi>,$$

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 $|n,l,m>$ in abstract Hilbert space. The representation in position space in spherical coordinates is

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

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 $\left[\mathcal{H}, \mathcal{L}^2 \right] = 0$.

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

$$= \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2}\right) + V(r)\right]\mathcal{L}^2 - \mathcal{L}^2\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2}\right) + V(r)\right]$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}^2 - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}^2 + \frac{\hbar^2}{2m}\frac{\mathcal{L}^4}{r^2\hbar^2} + \frac{\hbar^2}{2m}V(r)\mathcal{L}^2$$

$$+ \frac{\hbar^2}{2m}\mathcal{L}^2\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\frac{\mathcal{L}^4}{r^2\hbar^2} - \frac{\hbar^2}{2m}\mathcal{L}^2 V(r)$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}^2 - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}^2 + \frac{\hbar^2}{2m}V(r)\mathcal{L}^2 + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\mathcal{L}^2 V(r)$$

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

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

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 $\left[\mathcal{H},\,\mathcal{L}_z\right] = 0$.

$$\left[\mathcal{H},\,\mathcal{L}_z\right] = \mathcal{H}\mathcal{L}_z - \mathcal{L}_z\mathcal{H}$$

$$= \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2}\right) + V(r)\right]\mathcal{L}_z - \mathcal{L}_z\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2}\right) + V(r)\right]$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}_z - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}_z + \frac{\hbar^2}{2m}\frac{\mathcal{L}^2\mathcal{L}_z}{r^2\hbar^2} + \frac{\hbar^2}{2m}V(r)\mathcal{L}_z$$

$$+ \frac{\hbar^2}{2m}\mathcal{L}_z\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\frac{\mathcal{L}_z\mathcal{L}^2}{r^2\hbar^2} - \frac{\hbar^2}{2m}\mathcal{L}_z V(r)$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}_z - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}_z + \frac{\hbar^2}{2m}V(r)\mathcal{L}_z + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\mathcal{L}_z V(r)$$

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

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

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 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

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

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

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r)\,Y(\theta, \phi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)R(r)\,Y(\theta, \phi)$$

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}R(r)\,Y(\theta, \phi) - \frac{2m}{\hbar^2}\Big[V(r) - E\Big]R(r)\,Y(\theta, \phi) = 0$$

$$\Rightarrow\quad Y(\theta, \phi)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) + R(r)\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta, \phi)$$

$$+R(r)\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta, \phi) - \frac{2m}{\hbar^2}\Big[V(r) - E\Big]R(r)\,Y(\theta, \phi) = 0.$$

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

$$\left\{\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) - \frac{2mr^2}{\hbar^2}\Big[V(r) - E\Big]\right\}$$

$$+\left[\frac{1}{Y(\theta, \phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta, \phi) + \frac{1}{Y(\theta, \phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta, \phi)\right] = 0.$$

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

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

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

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

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),

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

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

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

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

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

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.

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The Azimuthal Angle Equation

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

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

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),

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

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,

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d}{d\theta}\right) f(\theta) = \sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d f(\theta)}{d\theta}\right)$$

$$= \sin\theta \left(\cos\theta \frac{d f(\theta)}{d\theta} + \sin\theta \frac{d^2 f(\theta)}{d\theta^2}\right)$$

$$= \sin^2\theta \frac{d^2 f(\theta)}{d\theta^2} + \sin\theta \, \cos\theta \frac{d f(\theta)}{d\theta}.$$

Using this, equation (10–8) becomes

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

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

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

and

$$\frac{d^2 f(\theta)}{d\theta^2} = \frac{d}{d\theta}\left(-\sin\theta\,\frac{d\,f(x)}{dx}\right) = -\cos\theta\,\frac{d\,f(x)}{dx} - \sin\theta\,\frac{d}{d\theta}\frac{d\,f(x)}{dx}$$

$$= -\cos\theta\,\frac{d\,f(x)}{dx} - \sin\theta\,\frac{d}{dx}\frac{dx}{d\theta}\frac{d\,f(x)}{dx} = -\cos\theta\,\frac{d\,f(x)}{dx} - \sin\theta\,\frac{d}{dx}\left(-\sin\theta\right)\frac{d\,f(x)}{dx}$$

$$= -\cos\theta\,\frac{d\,f(x)}{dx} + \sin^2\theta\,\frac{d^2\,f(x)}{dx^2}.$$

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

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

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

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

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

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

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

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

and becomes the Legendre equation,

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

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

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

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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.

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

Table $10 - 1$. The First Six Legendre Polynomials.

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

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,

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

and

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

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 percieve 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 Griffiths[3], or Cohen–Tannoudji[4].

Laguerre polynomials are solutions to the Laguerre equation

$$x\,L_j^{''}(x) + \left(1 - x\right)L_j^{'}(x) + j\,L_j(x) = 0.$$

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

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

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**,

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

is orthonormal on the interval $0 \le x < \infty$. 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

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

[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

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

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

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

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

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

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

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,

$$L_4(x) = e^x \frac{d^4}{dx^4} e^{-x} x^4$$

$$= e^x \frac{d^3}{dx^3} \Big(- e^{-x} x^4 + e^{-x} 4x^3 \Big)$$

$$= e^x \frac{d^2}{dx^2} \Big(e^{-x} x^4 - e^{-x} 4x^3 - e^{-x} 4x^3 + e^{-x} 12x^2 \Big) = e^x \frac{d^2}{dx^2} \Big(e^{-x} x^4 - e^{-x} 8x^3 + e^{-x} 12x^2 \Big)$$

$$= e^x \frac{d}{dx} \Big(- e^{-x} x^4 + e^{-x} 4x^3 + e^{-x} 8x^3 - e^{-x} 24x^2 - e^{-x} 12x^2 + e^{-x} 24x \Big)$$

$$= e^x \frac{d}{dx} \Big(- e^{-x} x^4 + e^{-x} 12x^3 - e^{-x} 36x^2 + e^{-x} 24x \Big)$$

$$= e^x \Big(e^{-x} x^4 - e^{-x} 4x^3 - e^{-x} 12x^3 + e^{-x} 36x^2 + e^{-x} 36x^2 - e^{-x} 72x - e^{-x} 24x + e^{-x} 24 \Big)$$

$$= e^x e^{-x} \Big(x^4 - 16x^3 + 72x^2 - 96x + 24 \Big)$$

$$= x^4 - 16x^3 + 72x^2 - 96x + 24,$$

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

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

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

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

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

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

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

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

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

$$\left(\frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \frac{k+1}{2x}\frac{k-1}{2x}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v' + v''\right)$$

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

$$\Rightarrow \quad v'' + \frac{1}{\cancel{4}}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \frac{k^2\cancel{-1}}{\cancel{4}x^2}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v'$$

$$-\frac{1}{\cancel{4}}v + \frac{2j+k+1}{2x}v - \frac{k^2\cancel{-1}}{\cancel{4}x^2}v = 0$$

$$\Rightarrow \quad v'' - \frac{k\cancel{+1}}{\cancel{4}x}v - \frac{1}{2}v' - \frac{k\cancel{+1}}{\cancel{4}x}v + \frac{k+1}{x}v' - \frac{1}{2}v' + \frac{j}{x}v + \frac{k\cancel{+1}}{\cancel{2}x}v = 0$$

$$\Rightarrow \quad v'' - v' + \frac{k+1}{x}v' + \frac{j}{x} = 0$$
$$\Rightarrow \quad xv'' - xv' + (k+1)v' + jv = 0$$
$$\Rightarrow \quad xv'' + (1 - x + k)v' + jv = 0 \qquad\qquad (10-17)$$

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

$$x\,L_j^{k''}(x) + \left(1 - x + k\right)L_j^{k'}(x) + j\,L_j^k(x) = 0,$$

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

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

are solutions to equation (10–16).

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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–Tannoudji[5], Levine[6], 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

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

$$\Rightarrow \quad \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{2\mu r^2}{\hbar^2} \left[-\frac{e^2}{r} - E \right] R(r) - l(l+1) \, R(r) = 0$$

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

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

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

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[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

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) = \frac{d}{dr}\left(r^2\frac{d}{dr}\right)\left(r^{-1}\right)y(r)$$

$$= \frac{d}{dr}\,r^2\left[\left(-r^{-2}\right)y(r) + \left(r^{-1}\right)\frac{d\,y(r)}{dr}\right]$$

$$= \frac{d}{dr}\left[-y(r) + r\frac{d\,y(r)}{dr}\right]$$

$$= -\frac{d\,y(r)}{dr} + \frac{d\,y(r)}{dr} + r\frac{d^2\,y(r)}{dr^2}$$

$$= r\frac{d^2\,y(r)}{dr^2}.$$

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

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

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

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

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

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),

$$x = r\epsilon \quad \Rightarrow \quad r = \frac{x}{\epsilon}, \tag{10 – 21}$$

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

so our radial equation becomes

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

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

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

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

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and

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

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

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

$$\Rightarrow \quad k^2 = 4l(l+1) + 1$$

$$= 4l^2 + 4l + 1$$

$$= (2l + 1)^2$$

$$\Rightarrow \quad k = 2l + 1.$$

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

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.529 \, \text{Å}. \tag{10-25}$$

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 $a_0 = 0.529 \, \text{Å}$, using both the electron mass and the reduced mass.

This example is intended to illustrate three simple things. First, $a_0 = 0.529 \, \text{Å}$, 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

$$\frac{1}{4\pi\epsilon_0} \frac{e^2_{\text{MKS}}}{r^2} = F = \frac{e^2_{\text{CGS}}}{r^2}$$

$$\Rightarrow \quad e^2_{\text{CGS}} = \frac{e^2_{\text{MKS}}}{4\pi\epsilon_0} = \left(1.602 \times 10^{-19} \, C\right)^2 \left(8.988 \times 10^9 \, N \cdot m^2/C^2\right)$$

$$= 2.307 \times 10^{-28} \, N \cdot m^2 = 2.307 \times 10^{-19} \, dyne \cdot cm^2$$

$$= 2.307 \times 10^{-19} \, erg \cdot cm = 14.42 \, eV \cdot \text{Å}.$$

So

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

The reduced mass is

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

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

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 $e = 3.797\,(eV \cdot \text{Å})^{1/2}$ 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

$$n = j + l + 1. \tag{10 - 26}$$

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

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{13.6\,eV}{n^2}, \tag{10 - 27}$$

where the quantity $13.6\,eV$ is called the Rydberg, usually denoted R or Ry. The ground state energy is $E_0 = -13.6\,eV$ 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).

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

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

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

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

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

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

$$\Rightarrow \quad E = -\frac{\mu^2 e^4 \hbar^2}{2\mu\hbar^4 n^2} = -\left(\frac{\mu e^2}{\hbar^2}\right)^2 \frac{\hbar^2}{2\mu n^2}$$

$$\Rightarrow \quad E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2}.$$

Inserting numerical values,

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{1}{4\pi^2} \frac{(hc)^2}{2(\mu c^2) a_0^2 n^2}$$

$$= -\frac{1}{4\pi^2} \frac{(1.24 \times 10^4 \, eV \cdot \text{Å})^2}{2(0.511 \times 10^6 \, eV)(0.529 \, \text{Å})^2 n^2} = -\frac{13.6 \, eV}{n^2},$$

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

Radial Wave Functions from the Solution of the Radial Equation

Again per example 10–6, the solutions of the radial equation are equation (10–15),

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

Since

$$k = 2l + 1, \ (k+1)/2 = ((2l+1)+1)/2 = l+1, \ \text{and} \ j + l + 1 = n \ \Rightarrow \ j = n - l - 1,$$

we can now express the indices in terms of the quantum numbers n and l, meaning

$$y_n^l(x) = e^{-x/2} x^{l+1} L_{n-l-1}^{2l+1}(x),$$

so the solution starts to assume some of the traits of the hydrogen atom. The independent variable is still $x = \epsilon r$. We need an independent variable r, or at least in terms of r, to be consistent with the spherical coordinate system. Using (10–20) and (10–27), we can solve for ϵ in terms of the Bohr radius and the principal quantum number,

$$\left(\frac{\epsilon}{2}\right)^2 = -\frac{2\mu E}{\hbar^2} = -\frac{2\mu}{\hbar^2}\left(-\frac{\hbar^2}{2\mu a_0^2 n^2}\right) = \frac{1}{a_0^2 n^2}$$

$$\Rightarrow \ \epsilon^2 = \frac{4}{a_0^2 n^2} \ \Rightarrow \ \epsilon = \frac{2}{a_0 n},$$

$$\Rightarrow \ x = \frac{2r}{na_0},$$

and this is in terms of the desired independent variable, or

$$y_n^l(r) = e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{l+1} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right).$$

Finally we can relate the associated Laguerre function to the radial function we set out to find through equation (10–19). Remember $y(r) = r R(r)$, so

$$r R_{n,l}(r) = e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{l+1} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$\Rightarrow \ R_{n,l}(r) = A e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{l} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right),$$

where we have added a normalization constant which has absorbed the factor $2/na_0$ from the power term when we cancel the factor of r. This still needs to be normalized. We want the radial functions to be individually normalized so the product of the radial wave functions and spherical harmonics, the hydrogen wave function, is normalized. The normalized radial wave functions are

$$R_{n,l}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{l} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right). \qquad (10-28)$$

The first few normalized radial wave functions are listed in table 10–5.

$$R_{1,0}(r) = 2a_0^{-3/2} e^{-r/a_0}$$

$$R_{2,0}(r) = \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

$$R_{2,1}(r) = \frac{1}{\sqrt{24}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0}$$

$$R_{3,0}(r) = \frac{2}{\sqrt{27}} a_0^{-3/2} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$$

$$R_{3,1}(r) = \frac{8}{27\sqrt{6}} a_0^{-3/2} \left(1 - \frac{r}{6a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$$

$$R_{3,2}(r) = \frac{4}{81\sqrt{30}} a_0^{-3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}$$

Table $10-5$. The First Six Radial Wave Functions for Hydrogen.

Example 10–10: Show equation (10–28) is properly normalized.

We want to normalize

$$R_{n,l}(r) = A\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right).$$

The normalization condition for a function of the radial variable in spherical coordinates is

$$<\psi(r)|\psi(r)> = 1 = \int_0^\infty \Big(R_{n,l}(r)\Big)^* R_{n,l}(r)\, r^2\, dr$$

where the factor of r^2 is the radial portion of the volume element in spherical coordinates. Using the radial wave functions, this is

$$1 = \int_0^\infty \left(A\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)\right)^* A\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) r^2\, dr$$

$$= \int_0^\infty A^* A\,, e^{-2r/na_0} \left(\frac{2r}{na_0}\right)^{2l} (r^2) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) dr$$

$$= |A|^2 \left(\frac{na_0}{2}\right)^3 \int_0^\infty e^{-2r/na_0} \left(\frac{2r}{na_0}\right)^{2l+2} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) d\left(\frac{2r}{na_0}\right) \quad (10-29)$$

where the cubic factor preceding the integral comes from the fact we have grouped the factor of r^2 with the other powers of r, and also have expressed the differential in terms of the argument of the associated Laguerre polynomial. We are going to borrow two relations from Morse and Feshbach[7], the first of which is

$$\int_0^\infty z^a\, e^{-z}\, L_b^a(z)\, L_b^a(z)\, dz = \delta_{b,c} \frac{[\Gamma(a+b+1)]^3}{\Gamma(b+1)}. \qquad (10-30)$$

---

[7] Morse and Feshbach, *Methods of Theoretical Physics* (McGraw–Hill, New York, 1953), pp. 784–785

There are some things to notice about equation (10–30). The Kronecker delta $\delta_{b,c}$ reflects the orthogonality of the associated Laguerre polynomials. The integral is zero unless the lower indices of the two associated Laguerre polynomials are identical. Also, we expect all indices to be integers, so expect the gamma functions to become factorials. Comparing (10–29) and (10–30), the argument of the associated Laguerre polynomial, the base of the power term, and the differential are all the same in both equations. The upper index of the associated Laguerre polynomials and the power term are the same in (10–30), but differ in (10–29). We can adjust (10-29) using a recursion relation from Morse and Feshbach,

$$z\,L_b^a(z) = \left(a + 2b + 1\right)L_b^a(z) - \frac{b+1}{a+b+1}\,L_{b+1}^a(z) - \left(a+b\right)^2 L_{b-1}^a(z).$$

If we take one factor of the power term and group it with the first associated Laguerre polynomial, we get

$$1 = \left|A\right|^2 \left(\frac{na_0}{2}\right)^3 \int_0^\infty e^{-2r/na_0} \left(\frac{2r}{na_0}\right)^{2l+1} \left\{ \left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \right\} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) d\left(\frac{2r}{na_0}\right),$$

which makes the exponent of the power term match the upper index of the associated Laguerre polynomial, and we can evaluate the term in braces using the recursion relation. For $a = 2l + 1$ and $b = c = n - l - 1$, this is

$$\left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) = \left(2l + 1 + 2n - 2l - 2 + 1\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$- \frac{n-l-1+1}{2l+1+n-l-1+1} L_{n-l}^{2l+1}\left(\frac{2r}{na_0}\right) - \left(2l+1+n-l-1\right)^2 L_{n-l-2}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$= 2n\,L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) - \frac{n-l}{n+l+1} L_{n-l}^{2l+1}\left(\frac{2r}{na_0}\right) - \left(n+l\right)^2 L_{n-l-2}^{2l+1}\left(\frac{2r}{na_0}\right).$$

We are going to ignore all but the first term. We could substitute all three terms into the integral, distribute other factors, break the integral into three integrals, and evaluate each one using equation (10–30). But the Kronecker delta tells us integrals with unequal lower associated Laguerre polynomial indices will be zero. The only non–vanishing integral will come from the first term, so

$$1 = \left|A\right|^2 \left(\frac{na_0}{2}\right)^3 \int_0^\infty e^{-2r/na_0} \left(\frac{2r}{na_0}\right)^{2l+1} \left\{ 2n\,L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \right\} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) d\left(\frac{2r}{na_0}\right),$$

$$= \left|A\right|^2 2n \left(\frac{na_0}{2}\right)^3 \int_0^\infty e^{-2r/na_0} \left(\frac{2r}{na_0}\right)^{2l+1} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) d\left(\frac{2r}{na_0}\right),$$

and we are ready to evaluate this integral using equation (10–30) where

$$z \;\rightarrow\; \left(\frac{2r}{na_0}\right), \qquad a \;\rightarrow\; 2l + 1, \qquad b = c \;\rightarrow\; n - l - 1,$$

and for integers $\Gamma(j) = (j - 1)!$. Then

$$1 = \left|A\right|^2 2n \left(\frac{na_0}{2}\right)^3 \frac{\left[\Gamma\left(2l + 1 + n - l - 1 + 1\right)\right]^3}{\Gamma(n - l - 1 + 1)}$$

$$= \left|A\right|^2 2n \left(\frac{na_0}{2}\right)^3 \frac{\left[\Gamma\left(n + l + 1\right)\right]^3}{\Gamma(n - l)}$$

$$= \left|A\right|^2 2n \left(\frac{na_0}{2}\right)^3 \frac{\left[(n + l)!\right]^3}{(n - l - 1)!}$$

$$\Rightarrow \quad A = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\big[(n+l)!\big]^3}}$$

$$\Rightarrow \quad R_{n,l}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\big[(n+l)!\big]^3}}\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right).$$

Example 10–11: Calculate $R_{3,1}(r)$ from equation (10–29).

For $n = 3,\ l = 1,$

$$R_{3,1}(r) = \sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-1-1)!}{2(3)\big[(3+1)!\big]^3}}\, e^{-r/3a_0} \left(\frac{2r}{3a_0}\right)^1 L_{3-1-1}^{2(1)+1}\left(\frac{2r}{3a_0}\right)$$

$$= \frac{2}{3}\sqrt{\left(\frac{2^3}{3^3 a_0^3}\right)\frac{1}{2\cdot 3\big[(4\cdot 3\cdot 2)\big]^3}}\, e^{-r/3a_0}\left(\frac{r}{a_0}\right) L_1^3\left(\frac{2r}{3a_0}\right)$$

$$= \frac{2}{3}\sqrt{\frac{2^2}{3^4\big[2^6\cdot 3^3\cdot 2^3\big]}}\, a_0^{-3/2} e^{-r/3a_0}\left(\frac{r}{a_0}\right)\left(-24\left(\frac{2r}{3a_0}\right)+96\right)$$

$$= 96\frac{2}{3}\sqrt{\frac{2^2}{2^9\cdot 3^7}}\, a_0^{-3/2}\left(-\left(\frac{r}{6a_0}\right)+1\right)\frac{r}{a_0}\, e^{-r/3a_0},$$

and because $96 = 2^5 \cdot 3,$

$$R_{3,1}(r) = \frac{2^6}{2^3\cdot 3^3}\sqrt{\frac{1}{2\cdot 3}}\, a_0^{-3/2}\left(1-\frac{r}{6a_0}\right)\frac{r}{a_0}\, e^{-r/3a_0}$$

$$= \frac{8}{27\sqrt{6}}\, a_0^{-3/2}\left(1-\frac{r}{6a_0}\right)\frac{r}{a_0}\, e^{-r/3a_0},$$

in agreement with table 10–5.

Graphs of Radial Wave Functions

The radial wave functions listed in table 10–5 are plotted in figure 10–1. The radial wave functions are all individually normalized, so the probability associated with radial wave functions is

$$<\psi(r)\big|\psi(r)> = <R_{n,l}(r)\big|R_{n,l}(r)> = \int_0^\infty R_{n,l}^*(r)\,R_{n,l}(r)\,r^2\,dr = \int_0^\infty R_{n,l}^2(r)\,r^2\,dr,$$

where the factor of r^2 in the integrals is from the volume element in spherical coordinates. The functions $R_{n,l}^2(r)\,r^2$ are the radial probability densities for the hydrogen atom. The radial probability densities are plotted abreast their corresponding radial wave function in figure 10–2.
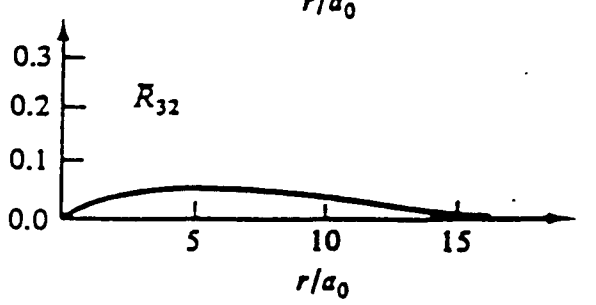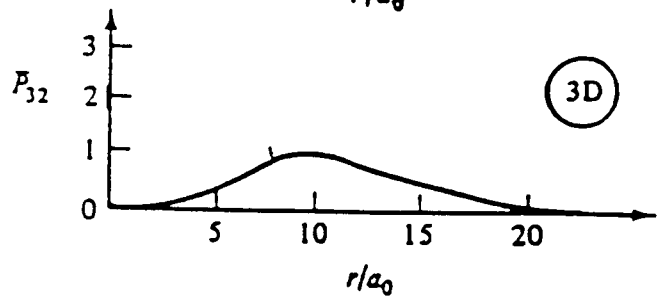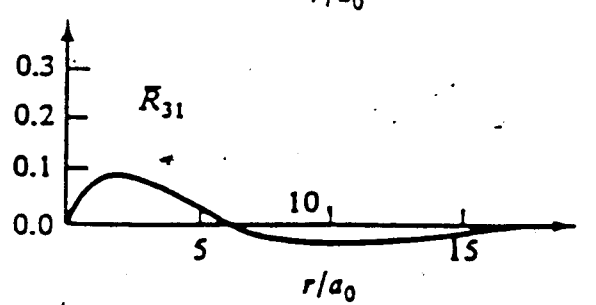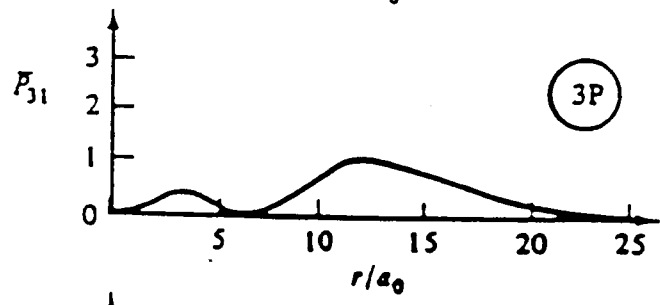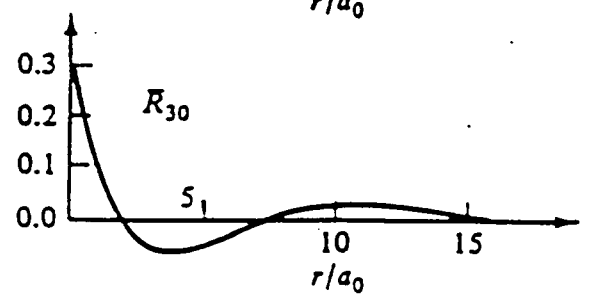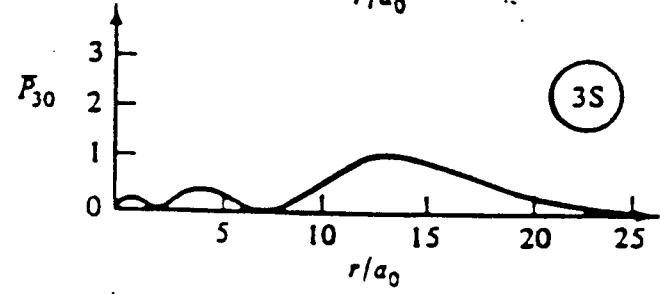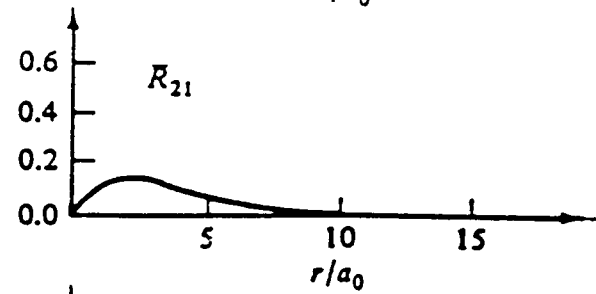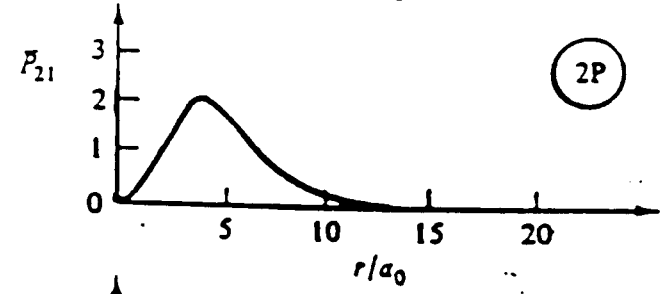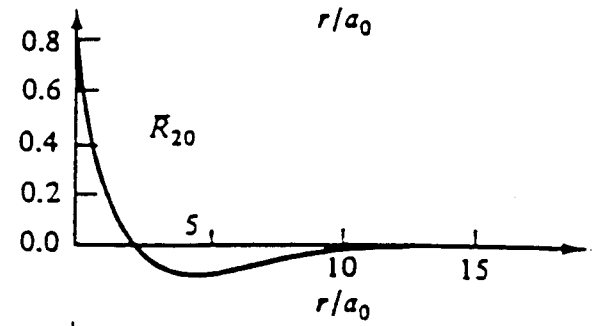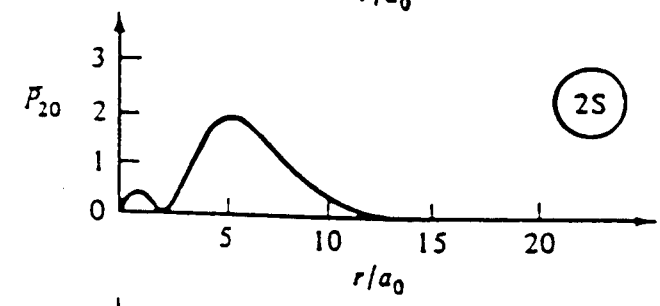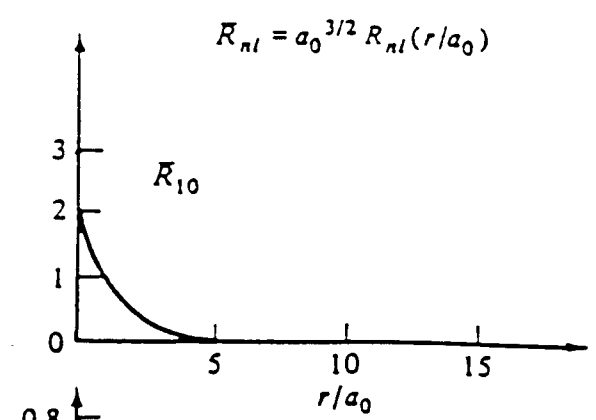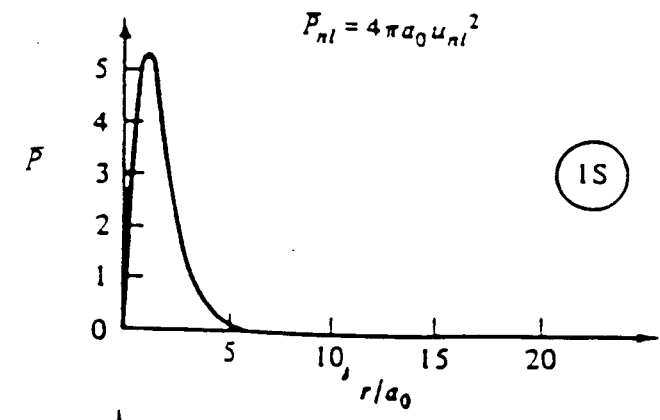
$P_{nl} = 4\pi a_0 u_{nl}^2$

$\bar{R}_{nl} = a_0^{3/2} R_{nl}(r/a_0)$

FIGURE 12-5.

FIG. 12-4

Hydrogen Wave Functions

We have all three parts. The product of the azimuthal, polar, and radial wave functions are the hydrogen wave functions. The product of the azimuthal and polar wave functions are the spherical harmonics, so the hydrogen wave functions are the product of the radial wave functions and spherical harmonics,

$$\psi_{nlm}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m}(\theta,\phi).$$

You can construct the desired hydrogen wave function by selecting the appropriate radial wave function from table 10–5, or calculating it from equation 10–28, and multiplying it by the appropriate spherical harmonic from table 11–1, or calculating it from equation 10–10, *i.e.*,

$$\psi_{nlm}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m}(\theta,\phi).$$

The equation

$$<r,\theta,\phi|n,l,m> = R_{n,l}(r)Y_{l,m}(\theta,\phi)$$

denotes representation from Hilbert space.

Example 10–10:   What is $\psi_{3,1,-1}(r,\theta,\phi)$?

From tables 10–5 and 11–1,

$$R_{3,1}(r) = \frac{8}{27\sqrt{6}}a_0^{-3/2}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}, \qquad Y_{1,-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta\,e^{-i\phi},$$

so

$$\psi_{3,1,-1}(r,\theta,\phi) = R_{3,1}(r)\,Y_{1,-1}(\theta,\phi)$$

$$= \frac{8}{27\sqrt{6}}a_0^{-3/2}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\sqrt{\frac{3}{8\pi}}\sin\theta\,e^{-i\phi}$$

$$= \frac{8\sqrt{3}}{27\sqrt{6}\sqrt{8\pi}}a_0^{-3/2}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\sin\theta\,e^{-i\phi}$$

$$= \frac{2}{27\sqrt{\pi}}a_0^{-3/2}\left(1 - \frac{r}{6a_0}\right)\frac{r}{a_0}\sin\theta\,e^{-r/3a_0-i\phi}.$$

Graphics of Hydrogen Wave Functions

The probability of finding the electron in a hydrogen atom in a specific volume is

$$\int_{\Delta V}\left|\psi_{nlm}(r,\theta,\phi)\right|^2 dV = \int_{r_1}^{r_2}\int_{\theta_1}^{\theta_2}\int_{\phi_1}^{\phi_2}\left|\psi_{nlm}(r,\theta,\phi)\right|^2 r^2\sin\theta\,dr\,d\theta\,d\phi.$$

The probability of finding the electron of the hydrogen atom anywhere in space is non–zero, however, the probability is vanishingly small for most locations. The locations where the probability densities are highest are depicted in figure 10–3.

$n = 1, l = m_l = 0$

$n = 2, l = m_l = 0$

$n = 2, l = 1, m_l = \pm 1$

$n = 2, l = 1, m_l = 0$

$n = 3, l = 2, m_l = \pm 2$

$n = 3, l = 1, m_l = \pm 1$

$n = 3, l = m_l = 0$

$n = 3, l = 2, m_l = \pm 1$
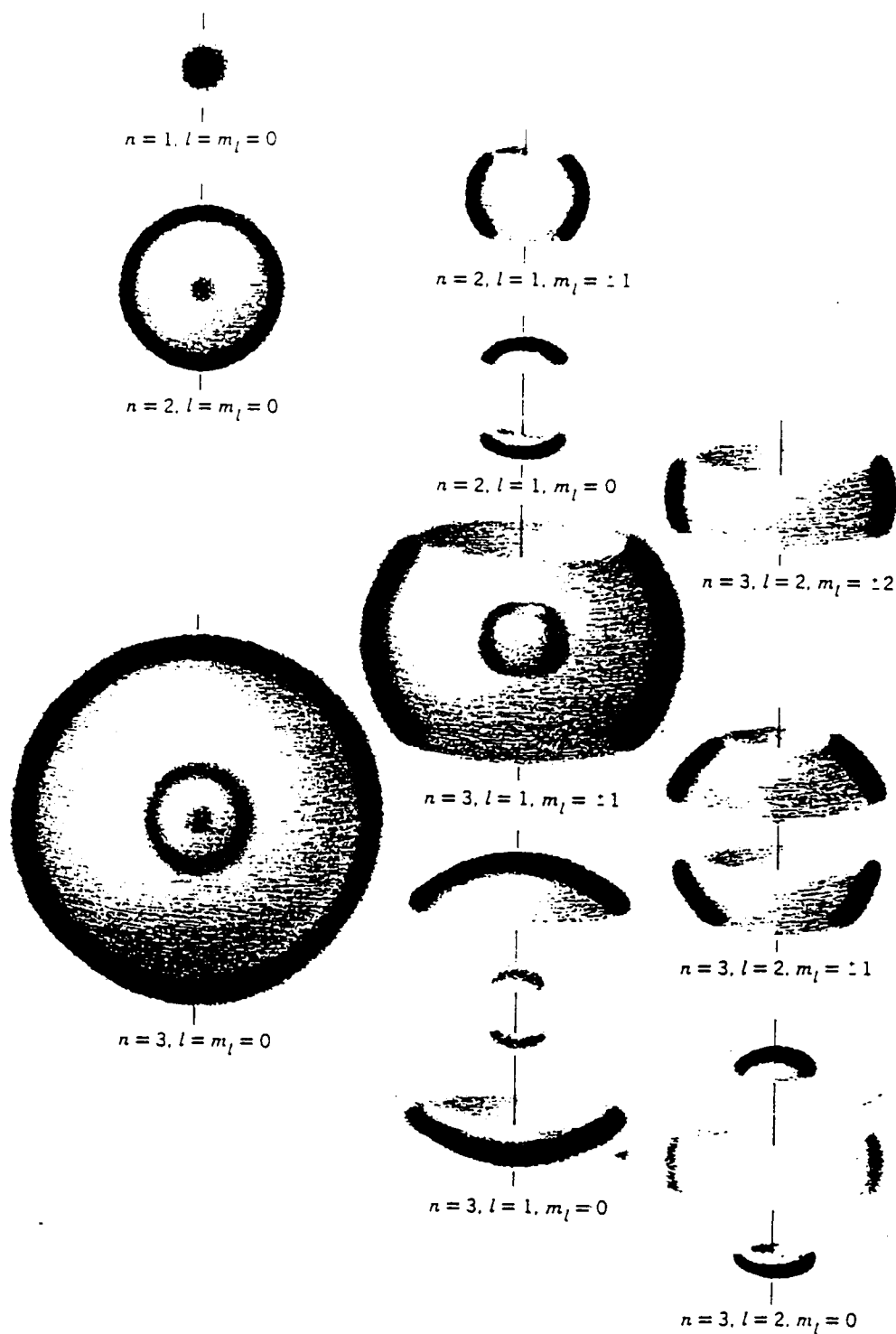
$n = 3, l = 1, m_l = 0$

$n = 3, l = 2, m_l = 0$

FIGURE 7-10

An artist's conception of the three-dimensional appearance of several one-electron atom probability density functions. For each of the drawings a line represents the z axis. If all the probability densities for a given n and l are combined, the result is spherically symmetrical.

The graphics of figure 10–3 are illustrative and are a culmination of the calculations of this chapter. Additional calculations demonstrate the similarity of simpler systems to this realistic system. In many regards, the techniques developed earlier with simpler systems were examined so we could arrive at the hydrogen atom and figure 10–3.

Quantum Numbers and Chemistry Terminology

Another depiction explains common chemistry terminology in terms of quantum numbers. The ground state of hydrogen is $n = 1$, $l = 0$ and $m = 0$. Common chemistry designations for the ground state are the K–shell and the $1s$ subshell. Remember the K–shell may house two electrons in many electron atoms. This means the one electron in the hydrogen atom can exist in one of two possible states, though there is only one possible combination of the three quantum numbers n, l, and m. There is, however, a fourth quantum number associated with spin. For each set of the three quantum numbers n, l, m, there is a possibility of spin up or spin down, and thus two possible states associated with the quantum numbers $n = 1$, $l = 0$, and $m = 0$, therefore two states associated with the K–shell. We will examine spin in the next chapter. The point of the moment is the desigation K–shell and quantum number $n = 1$ have the same meaning. The quantum number $n = 2$ is the same as the chemical designation of L–shell. The L–shell has subshells $2s$ and $2p$, where s corresponds to $l = 0$ and p corresponds to $l = 1$, which are possible quantum numbers for $n = 2$. For $l = 1$, $m = -1, 0$, or 1 so there are three states possible in the p subshell. Each of the four L–shell states may have spin up or spin down, so there are eight possible eigenstates in the L–shell. The M–shell corresponds to $n = 3$, the N–shell corresponds to $n = 4$, and the O–shell corresponds to $n = 5$. As the quantum number n becomes larger, the quantum number l can take on a greater range of values. The quantum number $l = 0$ corresponds to the s–subshell, the quantum number $l = 1$ corresponds to the p–subshell, the quantum number $l = 2$ corresponds to the d–subshell, the quantum number $l = 3$ corresponds to the f–subshell, and the quantum number $l = 4$ corresponds to the g–subshell. Each subshell has $2l + 1$ states. The total states in each shell is n^2. Figure 10–4 summarizes the commentary in this discussion.

	shell							total n^2
	O	$n=5$	$\underline{5s}_{\,1}$	$\underline{5p}_{\,3}$	$\underline{5d}_{\,5}$	$\underline{5f}_{\,7}$	$\underline{5g}_{\,9}$	25
	N	$n=4$	$\underline{4s}_{\,1}$	$\underline{4p}_{\,3}$	$\underline{4d}_{\,5}$	$\underline{4f}_{\,7}$		16
↑	M	$n=3$	$\underline{3s}_{\,1}$	$\underline{3p}_{\,3}$	$\underline{3d}_{\,5}$			9
E	L	$n=2$	$\underline{2s}_{\,1}$	$\underline{2p}_{\,3}$				4
	K	$n=1$	$\underline{1s}_{\,1}$					1
				$l=1$	$l=2$	$l=3$	$l=4$	$l=5$

Figure 10 − 4. Quantum Number, Chemical Designation Correspondence.

The subscripts on the underbars of the subshells indicate the number of states $2l + 1$ in that subshell.

One final comment. Since the energy, to this point, depends only on n, the quantum numbers l and m having no effect on energy, we have an n^2–fold degeneracy in energy using this picture.

A magnetic field removes this degeneracy...the same magnetic field that will define the z-axis and provide orientation to the scheme, will remove this degeneracy. This was explored by Pieter Zeeman, so is known as the Zeeman effect. Pragmatically, a field is necessary if the orientation is to make sense.

Possibilities and Probabilities

In addition to being of intrinsic interest because it is a real system, the electron in a hydrogen atom is a particle in a fancy box. Comparable to a particle in the infinite square well or harmonic oscillator, the electron is confined. Also comparable to other systems, the state vector describing the electron in a hydrogen atom is a linear combination of eigenstates. We assume a limited linear combination to provide some sample calculations which should be reminiscent of calculations for other systems. The examples in that follow all refer to the $t = 0$ state vector

$$\Psi(r, \theta, \phi) = 2\psi_{1,0,0} + \psi_{2,1,0} \qquad (10-31)$$

Example 10–13: Normalize equation (10–31).

The state function is composed of 2 parts ground state and 1 part of the given excited state, so we can write

$$\Psi(r, \theta, \phi) = 2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 2 \\ 1 \end{pmatrix},$$

so the normalization condition can be written

$$1 = A^*(2, \ 1) \, A \begin{pmatrix} 2 \\ 1 \end{pmatrix} = |A|^2 (4 + 1)$$

$$\Rightarrow \quad A = \frac{1}{\sqrt{5}}$$

$$\Rightarrow \quad \Psi(r, \theta, \phi) = \frac{2}{\sqrt{5}} \psi_{1,0,0} + \frac{1}{\sqrt{5}} \psi_{2,1,0}$$

is the properly normalized wave function or state vector.

Example 10–14: Normalize equation (10–31) using the orthonormality of the spherical harmonics.

This example demonstrates a useful technique using spherical harmonics as well as the reason the radial wave functions are individually normalized.

$$\Psi(r, \theta, \phi) = 2\psi_{1,0,0} + \psi_{2,1,0}$$
$$= 2\, R_{1,0} Y_{0,0} + R_{2,1} Y_{1,0},$$

and the normalization condition is

$$1 = \int_V A^* \left(2\, R_{1,0} Y_{0,0} + R_{2,1} Y_{1,0} \right) A \left(2\, R_{1,0} Y_{0,0} + R_{2,1} Y_{1,0} \right) dV$$

$$= |A|^2 \int_V \left(4\, R_{1,0}^2 Y_{0,0}^2 + 4 R_{2,1} R_{1,0} Y_{1,0} R_{1,0} Y_{0,0} + R_{2,1}^2 Y_{1,0}^2 \right) dV$$

$$= |A|^2 \left(\int_V 4\, R_{1,0}^2 Y_{0,0}^2 \, dV + \int_V 4 R_{2,1} R_{1,0} Y_{1,0} Y_{0,0} \, dV + \int_V R_{2,1}^2 Y_{1,0}^2 \, dV \right)$$

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$$= |A|^2 \left(4 \int_0^\infty R_{1,0}^2 r^2 \, dr \int_\Omega Y_{0,0}^2 \, d\Omega + 4 \int_0^\infty R_{2,1} R_{1,0} r^2 \, dr \int_\Omega Y_{1,0} Y_{0,0} \, d\Omega + \int_0^\infty R_{2,1}^2 r^2 \, dr \int_\Omega Y_{1,0}^2 \, d\Omega \right)$$

$$= |A|^2 \left(4(1)(1) + 4 \int_0^\infty R_{2,1} R_{1,0} r^2 \, dr \, (0) + (1)(1) \right) \qquad (10-32)$$

where $\int Y_{1,0} Y_{0,0} \, d\Omega$ is zero because the spherical harmonics are orthonormal, so

$$1 = |A|^2 (4 + 0 + 1) \quad \Rightarrow \quad A = \frac{1}{\sqrt{5}}$$

$$\Rightarrow \quad \Psi(r, \theta, \phi) = \frac{2}{\sqrt{5}} \psi_{1,0,0} + \frac{1}{\sqrt{5}} \psi_{2,1,0}.$$

The orthonormality of spherical harmonics means

$$\int Y_{i,j} Y_{k,l} \, d\Omega = \delta_{i,k} \delta_{j,l},$$

We have previously done this calculation using $<i|j> = \delta_{i,j}$, which is the same statement for systems in a Hilbert space. If integrated over solid angle, the indices must be identical or the integral is zero, as illustrated in equation (10–32). The radial wave functions are not orthonormal, but they are normalized. This means

$$\int_0^\infty R_{i,j} R_{i,j} r^2 \, dr = 1.$$

Note the matching indices. If the indices match, the integral of their product and r^2 over all possible values of radius is 1. If the indices do not match, you will often have the good fortune of a multiplication by zero by virtue of the integral of the spherical harmonics as in equation (10–32). In the circumstance the spherical harmonics are the same, the integral of radial functions will vanish. The bottom line is the hydrogen wave functions are orthonormal. The radial wave functions themselves, however, are normalized but they are not orthonormal.

A third method to calculate the normalization constant is to use the representations of the hydrogen wave functions and do the integrations explicitly. That method is much longer and more difficult than either of the previous two examples, and will yield the same result.

Example 10–15: What are the possible results of individual measurements of energy, angular momentum, and the z–component of angular momentum?

The possible results are the eigenvalues. For

$$\Psi(r, \theta, \phi) = \frac{2}{\sqrt{5}} \psi_{1,0,0} + \frac{1}{\sqrt{5}} \psi_{2,1,0}$$

we could measure a state with a principal quantum number of $n = 1$ or $n = 2$. The corresponding eigenenergies are

$$E_n = -\frac{13.6 \, eV}{n^2} \quad \Rightarrow \quad E_1 = -13.6 \, eV, \quad \text{or} \quad -\frac{13.6 \, eV}{4} = -3.4 \, eV$$

so are the possible results of a measurement of energy. For a measurement of angular momentum, we could measure a state with orbital angular momentum quantum number of $l = 0$ or $l = 1$, so anticipate a measurement of

$$\sqrt{0(0+1)}\hbar = 0 \ \text{ or } \ \sqrt{1(1+1)}\hbar = \sqrt{2}\hbar$$

because the eigenvalues of the square of angular momentum, $\mathcal{L}^2$, are $l(l+1)\hbar$. The eigenvalues of the z–component of angular momentum are $m\hbar$, and both eigenstates of the state vector have $m = 0$, so the only possibility of a measurement of the z–component of angular momentum is $0\,\hbar = 0$.

Example 10–16: What are the probabilites of the possible results of individual measurements of energy, angular momentum, and the z–component of angular momentum?

The probabilites are $\big| <\psi|\Psi> \big|^2$, so the probability of measuring $E_0 = -13.6\,eV$, corresponding to measuring the eigenstate with $n = 1$, and the probability of measuring orbital angular momentum of 0, corresponding to measuring the eigenstate with $l = 0$, is

$$
\begin{aligned}
P\big(E = -13.6\,eV\big) = P\big(\sqrt{\mathcal{L}^2} = 0\big) &= \left| <\psi_{1,0,0}\bigg| \frac{2}{\sqrt{5}}\psi_{1,0,0} + \frac{1}{\sqrt{5}}\psi_{2,1,0}> \right|^2 \\
&= \left| \frac{2}{\sqrt{5}} <\psi_{1,0,0}|\psi_{1,0,0}> + \frac{1}{\sqrt{5}} <\psi_{1,0,0}|\psi_{2,1,0}> \right|^2 \\
&= \left| \frac{2}{\sqrt{5}}(1) + 0 \right|^2 = \frac{4}{5}
\end{aligned}
$$

where we have used the orthonorality of eigenstates, regardless of whether we represent the eigenstates as functions of position and use the orthonormality of the spherical harmonics, or use a more general argument like $<i|j> = \delta_{ij}$. Similarly, the probability of measuring $E_1 = -3.4\,eV$, corresponding to measurement of the eigenstate with $n = 2$, and the probability of measuring orbital angular momentum of $\sqrt{2}\hbar$, corresponding to measuring the eigenstate with $l = 1$, is

$$
\begin{aligned}
P\big(E = -3.4\,eV\big) = P\big(\sqrt{\mathcal{L}^2} = \sqrt{2}\hbar\big) &= \left| <\psi_{2,1,0}\bigg| \frac{2}{\sqrt{5}}\psi_{1,0,0} + \frac{1}{\sqrt{5}}\psi_{2,1,0}> \right|^2 \\
&= \left| \frac{2}{\sqrt{5}} <\psi_{2,1,0}|\psi_{1,0,0}> + \frac{1}{\sqrt{5}} <\psi_{2,1,0}|\psi_{2,1,0}> \right|^2 \\
&= \left| 0 + \frac{1}{\sqrt{5}}(1) \right|^2 = \frac{1}{5}.
\end{aligned}
$$

Notice the sum of the probabilities is 1, $P\big(E = -13.6\,eV\big) + P\big(E = -3.4\,eV\big) = 4/5 + 1/5 = 1$, for example. Notice also, we use the normalized state vector, and the bra of the eigenstate serves only to identify the eigenstate is being used for the calculation.

Lastly, there is but one possibility for z–component of angular momentum, corresponding to $m = 0$ in both eigenstates, so we can conclude

$$P\big(\mathcal{L}_z = 0\big) = 1,$$

without further calculation. Just to illustrate a calculation for which two eigenstates have the same eigenvalue,

$$P\big(\mathcal{L}_z = 0\big) = \left| <\psi_{1,0,0}\Big| \frac{2}{\sqrt{5}}\psi_{1,0,0} + \frac{1}{\sqrt{5}}\psi_{2,1,0}> \right|^2 + \left| <\psi_{2,1,0}\Big| \frac{2}{\sqrt{5}}\psi_{1,0,0} + \frac{1}{\sqrt{5}}\psi_{2,1,0}> \right|^2$$

$$= \left| \frac{2}{\sqrt{5}} <\psi_{1,0,0}|\psi_{1,0,0}> \right|^2 + \left| \frac{1}{\sqrt{5}} <\psi_{2,1,0}|\psi_{2,1,0}> \right|^2$$

$$= \left| \frac{2}{\sqrt{5}}(1) \right|^2 + \left| \frac{1}{\sqrt{5}}(1) \right|^2$$

$$= \frac{4}{5} + \frac{1}{5} = 1.$$

There are two additional teaching points in exercise 10–16. If we have a more general linear combination of eigenstates, say

$$\Psi = \sum_i c_i\,\psi_i = c_1\,\psi_1 + c_2\,\psi_2 + c_3\,\psi_3 + \cdots$$

where the sum may terminate at some value n or be an infinite sum as indicated above. The c_i are **expansion coefficients** or more simply, the c_i are individual normalization constants for individual eigenstates. Generalizing from a two eigenstate system to a many eigenstate system, the probability of measuring a property associated with one specific eigenstate, say eigenstate ψ_j, is

$$P = \big| <\psi_j|\Psi> \big|^2 = \big| <\psi_j|c_1\,\psi_1 + c_2\,\psi_2 + c_3\,\psi_3 + \cdots> \big|^2 = \big| c_j <\psi_j|\psi_j> \big|^2 = \big| c_j \big|^2,$$

where the orthonormality condition $<i|j> = \delta_{ij}$ tells us $<\psi_j|\psi_j> = 1$, and cross terms with unlike indices are zero. Knowing this, the calculation for any property associated with $\psi_{1,0,0}$ for instance is

$$P\big(\psi_{1,0,0}\big) = \left| \frac{2}{\sqrt{5}} \right|^2 = \frac{4}{5}$$

and the remainder of the symbology in the calculation is unnecessary.

The second teaching point concerns the calculation of $P\big(\mathcal{L}_z = 0\big)$. Why do we use

$$P\big(\mathcal{L}_z = 0\big) = \left| <\psi_{1,0,0}\Big| \frac{2}{\sqrt{5}}\psi_{1,0,0} + \frac{1}{\sqrt{5}}\psi_{2,1,0}> \right|^2 + \left| <\psi_{2,1,0}\Big| \frac{2}{\sqrt{5}}\psi_{1,0,0} + \frac{1}{\sqrt{5}}\psi_{2,1,0}> \right|^2,$$

and not

$$\left| <\psi_{1,0,0} + \psi_{2,1,0}\Big| \frac{2}{\sqrt{5}}\psi_{1,0,0} + \frac{1}{\sqrt{5}}\psi_{2,1,0}> \right|^2 ?$$

The answer, referring to equations (1–2) and (1–3), is a measurement will place a linear combination into one specific eigenstate. We have a final state which is distinctly one of two eigenstates, and we can ascertain from the measurement which one. That tells us $\big|\psi\big|^2 = \big|\psi_a\big|^2 + \big|\psi_b\big|^2$. If we could not uniquely distinguish a final state, a situation we will encounter in the circumstance of degeneracy, $\big|\psi\big|^2 = \big|\psi_a + \psi_b\big|^2$. One reason a complete set of commuting observables is important is to provide a capability to uniquely distinguish final states, thus avoiding the indeterminacy associated with

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$|\psi|^2 = |\psi_a + \psi_b|^2$, where we do not know what portion of the probability originates with which eigenstate.

Expectation Value, Uncertainty and Time Dependence

Example 10–17:   What are the expectation values of energy, orbital angular momentum, and the z–component of angular momentum?

$$<E> = \sum_i P(E_i)E_i = \frac{4}{5}\big(-13.6\,eV\big) + \frac{1}{5}\big(-3.4\,eV\big) = -10.88\,eV - 0.68\,eV = -11.56\,eV.$$

$$<\sqrt{\mathcal{L}^2}> = \sum_i P(\alpha_i)\alpha_i = \frac{4}{5}(0) + \frac{1}{5}\big(\sqrt{2}\hbar\big) = \frac{\sqrt{2}\hbar}{5}.$$

The expectation value of the z–component of angular momentum is 0, since that is the only possibility.

Example 10–18:   What are the uncertainties of energy, orbital angular momentum, and the z–component of angular momentum?

$$\Delta E = \sqrt{\sum_i P(E_i)\big(E_i - <E>\big)^2}$$

$$= \left[\frac{4}{5}\big(-13.6\,eV - -11.56\,eV\big)^2 + \frac{1}{5}\big(-3.4\,eV - -11.56\,eV\big)^2\right]^{1/2}$$

$$= \left[\frac{4}{5}\big(-2.04\big)^2 + \frac{1}{5}\big(8.16\big)^2\right]^{1/2} eV = \left[\frac{4}{5}\big(4.16\big) + \frac{1}{5}\big(66.59\big)\right]^{1/2} eV$$

$$= [3.33 + 13.32]^{1/2}\,eV = [16.65]^{1/2}\,eV$$

$$= 4.08\,eV.$$

$$\Delta\sqrt{\mathcal{L}^2} = \left[\frac{4}{5}\left(0 - \frac{\sqrt{2}\hbar}{5}\right)^2 + \frac{1}{5}\left(\sqrt{2}\hbar - \frac{\sqrt{2}\hbar}{5}\right)^2\right]^{1/2} = \left[\frac{4}{5}\left(-\frac{\sqrt{2}}{5}\right)^2 + \frac{1}{5}\left(\frac{4\sqrt{2}}{5}\right)^2\right]^{1/2}\hbar$$

$$= \left[\frac{4}{5}\left(\frac{2}{5^2}\right) + \frac{1}{5}\left(\frac{16\cdot 2}{5^2}\right)\right]^{1/2}\hbar = \left[\frac{8}{5^3} + \frac{32}{5^3}\right]^{1/2}\hbar = \left[\frac{40}{5^3}\right]^{1/2}\hbar$$

$$= \frac{2\sqrt{2}}{5}\hbar.$$

The uncertainty in the z–component of angular momentum is 0, since there is only one possibility.

Example 10–19:   What is the time dependent state vector?

$$\big|\Psi(t)\big> = \sum |j><j|\psi(0)>\,e^{-iE_jt/\hbar}$$

$$= \begin{pmatrix}1\\0\end{pmatrix}(1,\,0)\frac{1}{\sqrt{5}}\begin{pmatrix}2\\1\end{pmatrix}e^{-iE_1t/\hbar} + \begin{pmatrix}0\\1\end{pmatrix}(0,\,1)\frac{1}{\sqrt{5}}\begin{pmatrix}2\\1\end{pmatrix}e^{-iE_2t/\hbar}$$

$$= \begin{pmatrix}1\\0\end{pmatrix}\frac{1}{\sqrt{5}}(2)e^{-iE_1t/\hbar} + \begin{pmatrix}0\\1\end{pmatrix}\frac{1}{\sqrt{5}}(1)e^{-iE_2t/\hbar}$$

$$= \frac{2}{\sqrt{5}}\begin{pmatrix}1\\0\end{pmatrix}e^{-iE_1t/\hbar} + \frac{1}{\sqrt{5}}\begin{pmatrix}0\\1\end{pmatrix}e^{-iE_2t/\hbar},$$

and using eigenenergies in terms of fundamental constants, *i.e.,*

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2},$$

this becomes

$$\left|\Psi(t)\right> = \frac{2}{\sqrt{5}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} e^{it\hbar/2\mu a_0^2} + \frac{1}{\sqrt{5}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} e^{it\hbar/8\mu a_0^2}.$$