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

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

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,

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

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

$$\Rightarrow \quad x = \frac{2r}{n a_0},$$

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

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

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

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

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

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

$$
\begin{aligned}
R_{1,0}(r) &= 2a_0^{-3/2} e^{-r/a_0} \\
R_{2,0}(r) &= \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \\
R_{2,1}(r) &= \frac{1}{\sqrt{24}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0} \\
R_{3,0}(r) &= \frac{2}{\sqrt{27}} a_0^{-3/2} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0} \\
R_{3,1}(r) &= \frac{8}{27\sqrt{6}} a_0^{-3/2} \left(1 - \frac{r}{6a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \\
R_{3,2}(r) &= \frac{4}{81\sqrt{30}} a_0^{-3/2} \frac{r^2}{a_0^2} e^{-r/3a_0}
\end{aligned}
$$

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

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

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

$$
\begin{aligned}
1 &= \int_0^\infty \left(A\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)\right)^* A\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) r^2\, dr \\
&= \int_0^\infty A^* A\,, e^{-2r/na_0} \left(\frac{2r}{na_0}\right)^{2l} (r^2) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) dr \\
&= \big|\, A \,\big|^2 \left(\frac{na_0}{2}\right)^3 \int_0^\infty e^{-2r/na_0} \left(\frac{2r}{na_0}\right)^{2l+2} L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) d\left(\frac{2r}{na_0}\right) \qquad (10-29)
\end{aligned}
$$

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,

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

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

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

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

$$\begin{aligned}
\left(\frac{2r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) &= \big(2l+1+2n-2l-2+1\big) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \\
&\quad - \frac{n-l-1+1}{2l+1+n-l-1+1} L_{n-l}^{2l+1}\left(\frac{2r}{na_0}\right) - \big(2l+1+n-l-1\big)^2 L_{n-l-2}^{2l+1}\left(\frac{2r}{na_0}\right) \\
&= 2n\, L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) - \frac{n-l}{n+l+1} L_{n-l}^{2l+1}\left(\frac{2r}{na_0}\right) - \big(n+l\big)^2 L_{n-l-2}^{2l+1}\left(\frac{2r}{na_0}\right).
\end{aligned}$$

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

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

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

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

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

$$\begin{aligned}
1 &= \big|\, A \,\big|^2 2n \left(\frac{na_0}{2}\right)^3 \frac{\left[\Gamma\left(2l+1+n-l-1+1\right)\right]^3}{\Gamma(n-l-1+1)} \\
&= \big|\, A \,\big|^2 2n \left(\frac{na_0}{2}\right)^3 \frac{\left[\Gamma\left(n+l+1\right)\right]^3}{\Gamma(n-l)} \\
&= \big|\, A \,\big|^2 2n \left(\frac{na_0}{2}\right)^3 \frac{\left[(n+l)!\right]^3}{(n-l-1)!}
\end{aligned}$$

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

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

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

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

$$\begin{aligned}
R_{3,1}(r) &= \sqrt{\left(\frac{2}{3a_0}\right)^3 \frac{(3-1-1)!}{2(3)\big[(3+1)!\big]^3}} e^{-r/3a_0} \left(\frac{2r}{3a_0}\right)^1 L_{3-1-1}^{2(1)+1}\left(\frac{2r}{3a_0}\right) \\
&= \frac{2}{3}\sqrt{\left(\frac{2^3}{3^3 a_0^3}\right) \frac{1}{2\cdot 3\big[(4\cdot 3\cdot 2)\big]^3}} e^{-r/3a_0} \left(\frac{r}{a_0}\right) L_1^3\left(\frac{2r}{3a_0}\right) \\
&= \frac{2}{3}\sqrt{\frac{2^2}{3^4\big[2^6\cdot 3^3\cdot 2^3\big]}} a_0^{-3/2} e^{-r/3a_0} \left(\frac{r}{a_0}\right)\left(-24\left(\frac{2r}{3a_0}\right)+96\right) \\
&= 96\frac{2}{3}\sqrt{\frac{2^2}{2^9\cdot 3^7}} a_0^{-3/2}\left(-\left(\frac{r}{6a_0}\right)+1\right)\frac{r}{a_0}\, e^{-r/3a_0},
\end{aligned}$$

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

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

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.

Figure 10 − 1. Radial Wave Functions. Figure 10 − 2. Radial Probability Densities.

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

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

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

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

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.

Figure $10-3$. Graphics for Significant Probability Densities by Quantum Number.

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
$\uparrow$	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

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

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

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

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

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

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.

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

and the normalization condition is

$$\begin{aligned} 1 &= \int_V A^*\big(2\, R_{1,0}Y_{0,0} + R_{2,1}Y_{1,0}\big)\, A\, \big(2\, R_{1,0}Y_{0,0} + R_{2,1}Y_{1,0}\big)\, dV \\ &= \big|A\big|^2 \int_V \big(4\, R_{1,0}^2 Y_{0,0}^2 + 4R_{2,1}R_{1,0}Y_{1,0}R_{1,0}Y_{0,0} + R_{2,1}^2 Y_{1,0}^2\big)\, dV \\ &= \big|A\big|^2 \left(\int_V 4\, R_{1,0}^2 Y_{0,0}^2\, dV + \int_V 4R_{2,1}R_{1,0}Y_{1,0}Y_{0,0}\, dV + \int_V R_{2,1}^2 Y_{1,0}^2\, dV\right) \end{aligned}$$

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

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

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

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

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 $\left| <\psi|\Psi> \right|^2$, 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

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

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

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

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,

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

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

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

and not

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

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

$\left|\psi\right|^2 = \left|\psi_a + \psi_b\right|^2$, 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?

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

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

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?

$$\begin{aligned}
\Delta E &= \sqrt{\sum_i P(E_i)\big(E_i - <E>\big)^2} \\
&= \left[\frac{4}{5}\big(-13.6\,eV - -11.56\,eV\big)^2 + \frac{1}{5}\big(-3.4\,eV - -11.56\,eV\big)^2\right]^{1/2} \\
&= \left[\frac{4}{5}\big(-2.04\big)^2 + \frac{1}{5}\big(8.16\big)^2\right]^{1/2} eV = \left[\frac{4}{5}\big(4.16\big) + \frac{1}{5}\big(66.59\big)\right]^{1/2} eV \\
&= [3.33 + 13.32]^{1/2}\,eV = [16.65]^{1/2}\,eV \\
&= 4.08\,eV.
\end{aligned}$$

$$\begin{aligned}
\Delta\sqrt{\mathcal{L}^2} &= \left[\frac{4}{5}\left(0 - \frac{\sqrt{2}\hbar}{5}\right)^2 + \frac{1}{5}\left(\sqrt{2}\hbar - \frac{\sqrt{2}\hbar}{5}\right)^2\right]^{1/2} = \left[\frac{4}{5}\left(-\frac{\sqrt{2}}{5}\right)^2 + \frac{1}{5}\left(\frac{4\sqrt{2}}{5}\right)^2\right]^{1/2}\hbar \\
&= \left[\frac{4}{5}\left(\frac{2}{5^2}\right) + \frac{1}{5}\left(\frac{16\cdot 2}{5^2}\right)\right]^{1/2}\hbar = \left[\frac{8}{5^3} + \frac{32}{5^3}\right]^{1/2}\hbar = \left[\frac{40}{5^3}\right]^{1/2}\hbar \\
&= \frac{2\sqrt{2}}{5}\hbar.
\end{aligned}$$

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?

$$\begin{aligned}
\left|\Psi(t)\right> &= \sum |j><j|\psi(0)>\, e^{-iE_j t/\hbar} \\
&= \begin{pmatrix}1\\0\end{pmatrix}(1,\ 0)\frac{1}{\sqrt{5}}\begin{pmatrix}2\\1\end{pmatrix}e^{-iE_1 t/\hbar} + \begin{pmatrix}0\\1\end{pmatrix}(0,\ 1)\frac{1}{\sqrt{5}}\begin{pmatrix}2\\1\end{pmatrix}e^{-iE_2 t/\hbar} \\
&= \begin{pmatrix}1\\0\end{pmatrix}\frac{1}{\sqrt{5}}(2)e^{-iE_1 t/\hbar} + \begin{pmatrix}0\\1\end{pmatrix}\frac{1}{\sqrt{5}}(1)e^{-iE_2 t/\hbar} \\
&= \frac{2}{\sqrt{5}}\begin{pmatrix}1\\0\end{pmatrix}e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{5}}\begin{pmatrix}0\\1\end{pmatrix}e^{-iE_2 t/\hbar},
\end{aligned}$$

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

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

this becomes

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