

# **Physics 4617/5617: Quantum Physics Course Lecture Notes**

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## **Abstract**

These class notes are designed for use of the instructor and students of the course **Physics 4617/5617: Quantum Physics**.

## V. Quantum Mechanics in Three Dimensions

### A. Schrödinger Equation in Spherical Coordinates.

1. In three dimensions, we can write the Hamiltonian operator (note that I'll leave the “hats” off of the operators in this section, but they are there “virtually”) as

$$H = \frac{1}{2}mv^2 + V = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V , \quad (\text{V-1})$$

where

$$p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} , \quad p_y \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial y} , \quad p_z \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial z} , \quad (\text{V-2})$$

or

$$\boxed{\mathbf{p} \rightarrow \frac{\hbar}{i} \nabla ,} \quad (\text{V-3})$$

for short.

2. Using this notation in the Schrödinger equation gives

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi ,} \quad (\text{V-4})$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (\text{V-5})$$

is the **Laplacian** in Cartesian coordinates.

3. The potential energy  $V$  and the wave function  $\Psi$  are now functions of  $\mathbf{r} = (x, y, z)$  and  $t$ .
4. The probability of finding the particle in the infinitesimal volume  $d^3\mathbf{r} = dx dy dz$  is  $|\Psi(\mathbf{r}, t)|^2 d^3\mathbf{r}$ , and the normalization condition reads

$$\int |\Psi|^2 d^3\mathbf{r} = 1 , \quad (\text{V-6})$$

with the integral taken over all space.

5. If the potential is independent of time, there will be a complete set of stationary states,

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-iE_n/\hbar}, \quad (\text{V-7})$$

where the spatial wave function  $\psi_n$  satisfies the time-*independent* Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n = E_n \psi_n. \quad (\text{V-8})$$

6. The general solution to the (time-*dependent*) Schrödinger equation is

$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n/\hbar}, \quad (\text{V-9})$$

with the constants  $c_n$  determined by the initial wave function,  $\Psi(\mathbf{r}, 0)$ , in the usual way. (If the potential admits continuum states, then the sum in Eq. (V-9) becomes an integral.)

## 7. Separation of Variables.

- a) Typically, the potential is a function only of the distance from the origin. In that case it is natural to adopt **spherical coordinates**,  $(r, \theta, \phi)$ . In spherical coordinates, the Laplacian takes the form

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

- b) In spherical coordinates, then, the time-independent Schrödinger equation reads

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V \psi = E \psi. \quad (\text{V-11})$$

- c) To solve this equation, we will assume that the solution can be represented as the product of separable terms composed of a radial part ( $R$ ) and an angular part ( $Y$ ):

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) . \quad (\text{V-12})$$

- d) Putting this into Eq. (V-11) we get

$$\begin{aligned} -\frac{\hbar^2}{2m} \left[ \frac{Y}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \left( \frac{\partial^2 Y}{\partial \phi^2} \right) \right] \\ + VRY = ERY . \end{aligned} \quad (\text{V-13})$$

- e) Dividing by  $RY$  and multiplying by  $-2mr^2/\hbar^2$  we get

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

- f) The term in the first curly (“woob-woob-woob”) bracket depends only upon  $r$ , whereas the remainder depends only on  $\theta$  and  $\phi$ ; accordingly, each must be constant. We will write this separation constant as  $\ell(\ell + 1)$  (the reason for choosing this form of the constant will become apparent in §VI of the notes), as such

$$\frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] = \ell(\ell + 1) ; \quad (\text{V-14})$$

$$\frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2 Y}{\partial \phi^2} \right) \right\} = -\ell(\ell + 1) . \quad (\text{V-15})$$

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**Example V–1.** Use separation of variables in Cartesian coordinates to solve the infinite cubical well (or “particle in a box”):

$$V(x, y, z) = \begin{cases} 0, & \text{if } x, y, \text{ and } z \text{ are all between } 0 \text{ and } a; \\ \infty, & \text{otherwise.} \end{cases}$$

(a) Find the stationary state wave functions and the corresponding energies.

**Solution (a):**

In the box, we can write the TISE (Eq. V-8) as

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi.$$

The separable solution is:  $\psi(x, y, z) = X(x)Y(y)Z(z)$ . Put this in the above equation and divide by  $XYZ$ :

$$\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} = -\frac{2m}{\hbar^2} E = -(k_x^2 + k_y^2 + k_z^2),$$

where

$$E \equiv \frac{(k_x^2 + k_y^2 + k_z^2)\hbar^2}{2m},$$

and  $k_x$ ,  $k_y$ , and  $k_z$  are three constants. The three terms on the left of this equation are functions of  $x$ ,  $y$ , and  $z$ , respectively, so each must be a constant, where  $k_x^2$ ,  $k_y^2$ , and  $k_z^2$  are the three separation constants.

This leads to three separate differential equations:

$$\frac{d^2 X}{dx^2} = -k_x^2 X; \quad \frac{d^2 Y}{dy^2} = -k_y^2 Y; \quad \frac{d^2 Z}{dz^2} = -k_z^2 Z.$$

The solution to these three equations are

$$\begin{aligned} X(x) &= A_x \sin k_x x + B_x \cos k_x x; \\ Y(y) &= A_y \sin k_y y + B_y \cos k_y y; \\ Z(z) &= A_z \sin k_z z + B_z \cos k_z z. \end{aligned}$$

But  $X(0) = 0$ , so  $B_x = 0$ ;  $Y(0) = 0$ , so  $B_y = 0$ ;  $Z(0) = 0$ , so  $B_z = 0$ . Likewise,  $X(a) = 0 \Rightarrow \sin(k_x a) = 0 \Rightarrow k_x = n_x \pi/a$ , ( $n_x = 1, 2, 3, \dots$ ) (note that negative values of  $k$  are redundant

with the positive values and  $n_x \neq 0$  since this would give us no wave function). Likewise,  $k_y = n_y\pi/a$  and  $k_z = n_z\pi/a$ . So

$$E = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} (n_x^2 + n_y^2 + n_z^2),$$

and

$$\psi(x, y, z) = A_x A_y A_z \sin\left(\frac{n_x\pi}{a}x\right) \sin\left(\frac{n_y\pi}{a}y\right) \sin\left(\frac{n_z\pi}{a}z\right).$$

We can normalize the three independent solutions separately (which was done in Eq. III-32), giving  $A_x = A_y = A_z = \sqrt{2/a}$ . So the final solution is

$$\psi(x, y, z) = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{n_x\pi}{a}x\right) \sin\left(\frac{n_y\pi}{a}y\right) \sin\left(\frac{n_z\pi}{a}z\right);$$

$$E = \frac{\pi^2\hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2);$$

$$n_x, n_y, n_z = 1, 2, 3, \dots$$

(b) Call the distinct energies  $E_1, E_2, E_3, \dots$ , in order of increasing energy. Find  $E_1, E_2, E_3, E_4, E_5$ , and  $E_6$ . Determine the *degeneracy* of each of these energies (that is, the number of different states that share the same energy). Note that degenerate bound states do not occur in *one* dimension, but they are common in three dimensions.

**Solution (b):**

Set up the following data table:

$\underline{n_x}$	$\underline{n_y}$	$\underline{n_z}$	$\underline{(n_x^2 + n_y^2 + n_z^2)}$
1	1	1	3
1	1	2	6
1	2	1	
2	1	1	
1	2	2	9
2	1	2	
2	2	1	
1	1	3	11
1	3	1	
3	1	1	
$\underline{n_x}$	$\underline{n_y}$	$\underline{n_z}$	$\underline{(n_x^2 + n_y^2 + n_z^2)}$
2	2	2	12
1	2	3	14
1	3	2	
2	1	3	
2	3	1	
3	1	2	
3	2	1	

The number of degenerate levels is given by the number of rows available for each energy (*i.e.*,  $n_x^2 + n_y^2 + n_z^2$ ). As such, the first 6



energy levels are

$$E_1 = 3 \frac{\pi^2 \hbar^2}{2ma^2}; \quad \text{degeneracy } (d) = 1.$$

$$E_2 = 6 \frac{\pi^2 \hbar^2}{2ma^2}; \quad d = 3.$$

$$E_3 = 9 \frac{\pi^2 \hbar^2}{2ma^2}; \quad d = 3.$$

$$E_4 = 11 \frac{\pi^2 \hbar^2}{2ma^2}; \quad d = 3.$$

$$E_5 = 12 \frac{\pi^2 \hbar^2}{2ma^2}; \quad d = 1.$$

$$E_6 = 14 \frac{\pi^2 \hbar^2}{2ma^2}; \quad d = 6.$$

## 8. The Angular Equation.

a) Taking Eq. (V-15) and multiplying by  $Y \sin^2 \theta$  gives

$$\sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -\ell(\ell + 1)Y \sin^2 \theta . \quad (\text{V-16})$$

b) Once again, use separation of variables:

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) . \quad (\text{V-17})$$

Plugging this into Eq. (V-16) and dividing by  $\Theta\Phi$  gives

$$\begin{aligned} \sin \theta \frac{\partial}{\partial \theta} \left[ \sin \theta \frac{\partial}{\partial \theta} (\Theta\Phi) \right] + \frac{\partial^2}{\partial \phi^2} (\Theta\Phi) &= -\ell(\ell + 1)\Theta\Phi \sin^2 \theta \\ \Phi \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \Theta \frac{\partial^2 \Phi}{\partial \phi^2} &= -\ell(\ell + 1)\Theta\Phi \sin^2 \theta \\ \frac{1}{\Theta} \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} &= -\ell(\ell + 1) \sin^2 \theta , \end{aligned}$$

or

$$\left\{ \frac{1}{\Theta} \left[ \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \right] + \ell(\ell + 1) \sin^2 \theta \right\} + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0 . \quad (\text{V-18})$$

- c) The first term of Eq. (V-18) is a function only of  $\theta$ , and the second is a function only of  $\phi$ , so each must be constant. Let's choose the separation constant  $m^2$  ( $m$  will later be called the **magnetic quantum number**), then

$$\frac{1}{\Theta} \left[ \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) \right] + \ell(\ell + 1) \sin^2 \theta = m^2, \quad (\text{V-19})$$

and

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2. \quad (\text{V-20})$$

- d) The equation for  $\phi$  is easy with the solution

$$\Phi(\phi) = e^{im\phi} \quad (\text{V-21})$$

(actually, there are two solutions:  $e^{im\phi}$  and  $e^{-im\phi}$ , but we will fold the negative exponents into the positive solution by letting  $m$  be negative as well as positive). We also will fold the integration constant into the solution for  $\Theta$ .

- e) Since Eq. (V-21) is nothing more than trigonometric functions in complex space, note that

$$\Phi(\phi + 2\pi) = \Phi(\phi) . \quad (\text{V-22})$$

In other words,  $\mathbf{exp}[im(\phi+2\pi)] = \mathbf{exp}(im\phi)$ , or  $\mathbf{exp}(2\pi im) = 1$ . From this it follows that  $m$  must be an integer:

$$m = 0, \pm 1, \pm 2, \dots \quad (\text{V-23})$$

- f) The equation for  $\theta$  becomes

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + [\ell(\ell + 1) \sin^2 \theta - m^2] \Theta = 0 . \quad (\text{V-24})$$

The solution to this differential equation is not trivial. It is

$$\Theta(\theta) = A P_\ell^m(\cos \theta) , \quad (\text{V-25})$$

where  $P_\ell^m$  is the **associated Legendre function**, defined by

$$P_\ell^m(x) \equiv (1 - x^2)^{|m|/2} \left( \frac{d}{dx} \right)^{|m|} P_\ell(x) , \quad (\text{V-26})$$

and  $P_\ell(x)$  is the  $\ell$ -th Legendre polynomial.

**g)** Legendre polynomials are determined with the **Rodrigues formula**:

$$P_\ell(x) \equiv \frac{1}{2^\ell \ell!} \left( \frac{d}{dx} \right)^\ell (x^2 - 1)^\ell. \quad (\text{V-27})$$

For example,

$$P_0(x) = 1, \quad P_1(x) = \frac{1}{2} \frac{d}{dx} (x^2 - 1) = x ,$$

$$P_2(x) = \frac{1}{4 \cdot 2} \left( \frac{d}{dx} \right)^2 (x^2 - 1)^2 = \frac{1}{2} (3x^2 - 1) ,$$

and so on.

**h)**  $P_\ell(x)$  is a polynomial (of degree  $\ell$ ) in  $x$ , and is even or odd according to the parity of  $\ell$ . However,  $P_\ell^m$  is not, in general, a polynomial, since if  $m$  is odd, it carries a factor  $\sqrt{1 - x^2}$ :

$$P_2^0(x) = \frac{1}{2} (3x^2 - 1),$$

$$P_2^1(x) = (1 - x^2)^{1/2} \frac{d}{dx} \left[ \frac{1}{2} (3x^2 - 1) \right] = 3x \sqrt{1 - x^2},$$

$$P_2^2(x) = (1 - x^2) \frac{d}{dx} \left[ \frac{1}{2} (3x^2 - 1) \right] = 3x (1 - x^2) ,$$

etc. Since  $x = \cos \theta$  in the associated Legendre functions here,  $P_\ell^m(\cos \theta)$  is always a polynomial in  $\cos \theta$ , multiplied

Table V-1: **Some associated Legendre functions,  $P_\ell^m(\cos \theta)$ .**

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$P_1^1 = \sin \theta$	$P_3^3 = 15 \sin \theta (1 - \cos^2 \theta)$
$P_1^0 = \cos \theta$	$P_3^2 = 15 \sin^2 \theta \cos \theta$
$P_2^2 = 3 \sin^2 \theta$	$P_3^1 = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$
$P_2^1 = 3 \sin \theta \cos \theta$	$P_3^0 = \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta)$
$P_2^0 = \frac{1}{2} (3 \cos^2 \theta - 1)$	

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(if  $m$  is odd) by  $\sin \theta$  (since  $\sqrt{1 - \cos^2 \theta} = \sin \theta$ ). Some associated Legendre functions of  $\cos \theta$  are listed in Table (V-1).

- i) Notice that  $\ell$  must be a non-negative integer for the Rodrigues formula (Eq. V-27) to make any sense. Moreover, if  $|m| > \ell$ , then Eq. (V-26) says  $P_\ell^m = 0$ . For any given  $\ell$ , then, there are  $(2\ell + 1)$  possible values of  $m$ :

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell . \quad (\text{V-28})$$

- j) Eq. (V-24) is a second-order differential equation: It should have *two* linearly independent solutions, for some values of  $\ell$  and  $m$ . Where are the *other* solutions? Well, they exist as mathematical solutions to the equation, but they are *physically* unacceptable because they blow up at  $\theta = 0$  and/or  $\theta = \pi$ , and do not yield normalizable wave functions.

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**Example V-2.** Show that

$$\Theta(\theta) = A \ln[\tan(\theta/2)]$$

satisfies the  $\theta$  equation (Eq. V-24) for  $\ell = m = 0$ . This

is the unacceptable “second solution” — what's wrong with it?

**Solution:**

$$\frac{d\Theta}{d\theta} = \frac{A}{\tan(\theta/2)} \frac{1}{2} \sec^2\left(\frac{\theta}{2}\right) = \frac{A}{2} \frac{1}{\sin(\theta/2) \cos(\theta/2)} = \frac{A}{\sin \theta} .$$

So,

$$\frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) = \frac{d}{d\theta}(A) = 0 .$$

With  $\ell = m = 0$ , Eq. (V-24) reads

$$\frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) = 0 .$$

So,  $A \ln[\tan(\theta/2)]$  does satisfy Eq. (V-24). Note, however, that if  $\theta = 0$ , then  $\tan(\theta/2) = 0$  and

$$\Theta(0) = A \ln(0) = A(-\infty) \implies \boxed{\text{Blows up at } \theta = 0 .}$$

Also,

$$\Theta(\pi) = A \ln[\tan(\pi/2)] = A \ln(\infty) = A(\infty)$$

$$\implies \boxed{\text{Blows up at } \theta = \pi .}$$


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**k)** The volume element in spherical coordinates is

$$d^3\mathbf{r} = r^2 \sin \theta \, dr \, d\theta \, d\phi , \quad (\text{V-29})$$

so the normalizable condition of Equation (V-6) becomes

$$\int |\psi|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = \int |R|^2 r^2 \, dr \int |Y|^2 \sin \theta \, d\theta \, d\phi = 1 .$$

**l)** It is convenient to normalize  $R$  and  $Y$  individually:

$$\int_0^\infty |R|^2 r^2 \, dr = 1 \quad \text{and} \quad \int_0^{2\pi} \int_0^\pi |Y|^2 \sin \theta \, d\theta \, d\phi = 1 . \quad (\text{V-30})$$

- m) The normalized angular wave functions are called **spherical harmonics**:

$$Y_\ell^m(\theta, \phi) = \epsilon \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-|m|)!}{(\ell+|m|)!}} e^{im\phi} P_\ell^m(\cos \theta) , \quad (\text{V-31})$$

where  $\epsilon = (-1)^m$  for  $m > 0$  and  $\epsilon = 1$  for  $m \leq 0$ . Note from this equation that

$$Y_\ell^{-m} = (-1)^m Y_\ell^m. \quad (\text{V-32})$$

Spherical harmonics are orthogonal such that

$$\int_0^{2\pi} \int_0^\pi [Y_\ell^m(\theta, \phi)]^* [Y_{\ell'}^{m'}(\theta, \phi)] \sin \theta d\theta d\phi = \delta_{\ell\ell'} \delta_{mm'}. \quad (\text{V-33})$$

**Example V-3.** Use Equations (V-26), (V-27), and (V-31) to construct  $Y_0^0$  and  $Y_2^1$ . Check that they are normalized and orthogonal.

**Solution:**

From Eq. (V-31),

$$Y_0^0 = \sqrt{\frac{1}{4\pi} \frac{0!}{0!}} P_0^0(\cos \theta) = \frac{1}{\sqrt{4\pi}} P_0^0(\cos \theta),$$

where  $\epsilon = 1$ . From Eqs. (V-26) and (V-27),

$$P_0^0(\cos \theta) = P_0(\cos \theta) = \frac{1}{0!} = 1,$$

so

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} .$$

From Eq. (V-31),

$$Y_2^1 = -\sqrt{\frac{5}{4\pi} \frac{1}{3 \cdot 2}} e^{i\phi} P_2^1(\cos \theta) = -\sqrt{\frac{5}{24\pi}} e^{i\phi} P_2^1(\cos \theta),$$

where  $\epsilon = (-1)^1 = -1$ . From Eq. (V-26),

$$P_2^1(x) = \sqrt{1-x^2} \frac{d}{dx} P_2(x).$$

Then using Eq. (V-27)

$$\begin{aligned} P_2(x) &= \frac{1}{4 \cdot 2} \left( \frac{d}{dx} \right)^2 (x^2 - 1)^2 = \frac{1}{8} \frac{d}{dx} [2(x^2 - 1) 2x] \\ &= \frac{1}{8} \frac{d}{dx} [4x^3 - 4x] = \frac{1}{2} \frac{d}{dx} [x^3 - x] = \frac{1}{2} (3x^2 - 1); \end{aligned}$$

so

$$P_2^1(x) = \sqrt{1-x^2} \frac{d}{dx} \left[ \frac{3}{2} x^2 - \frac{1}{2} \right] = \sqrt{1-x^2} 3x.$$

Substituting  $\cos \theta$  for  $x$  gives

$$P_2^1(\cos \theta) = \sqrt{1-\cos^2 \theta} 3 \cos \theta = 3 \cos \theta \sin \theta,$$

and

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

Normalization:

$$\iint |Y_0^0|^2 \sin \theta d\theta d\phi = \frac{1}{4\pi} \left[ \int_0^\pi \sin \theta d\theta \right] \left[ \int_0^{2\pi} d\phi \right] = \frac{1}{4\pi} (2)(2\pi) = 1. \quad \checkmark$$

$$\begin{aligned} \iint |Y_2^1|^2 \sin \theta d\theta d\phi &= \frac{15}{8\pi} \int_0^\pi \sin^2 \theta \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{15}{4} \int_0^\pi \cos^2 \theta (1 - \cos^2 \theta) \sin \theta d\theta \\ &= \frac{15}{4} \left[ -\frac{\cos^3 \theta}{3} + \frac{\cos^5 \theta}{5} \right] \Big|_0^\pi \\ &= \frac{15}{4} \left[ \frac{2}{3} - \frac{2}{5} \right] = \frac{5}{2} - \frac{3}{2} = 1. \quad \checkmark \end{aligned}$$

Orthogonality:

$$\iint (Y_0^0)^* (Y_2^1) \sin \theta d\theta d\phi = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{15}{8\pi}} \left[ \int_0^\pi \sin^2 \theta \cos \theta d\theta \right] \left[ \int_0^{2\pi} e^{i\phi} d\phi \right].$$

But

$$\int_0^\pi \sin^2 \theta \cos \theta d\theta = \left( \frac{\sin^3 \theta}{3} \right) \Big|_0^\pi = 0$$

and

$$\int_0^{2\pi} e^{i\phi} d\phi = \frac{e^{i\phi}}{i} \Big|_0^{2\pi} = (-i \cos \phi + \sin \phi) \Big|_0^{2\pi} = (-i + i) = 0.$$

So,

$$\iint (Y_0^0)^* (Y_2^1) \sin \theta d\theta d\phi = 0. \quad \checkmark$$


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## 9. The Radial Equation.

- a) Note that the angular part of the wave function,  $Y(\theta, \phi)$  is the same for all spherically symmetric potentials, and is independent of this potential  $\Rightarrow V$  only affects the *radial* part of the wave function,  $R(r)$ , which is determined by the differential equation given in Eq. (V-14):

$$\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = \ell(\ell + 1) R. \quad (\text{V-34})$$

- b) This equation simplifies if we change variables: Let

$$u(r) \equiv r R(r), \quad (\text{V-35})$$

then using the quotient rule for derivatives we get

$$\begin{aligned} R &= \frac{u}{r} \\ \frac{dR}{dr} &= \frac{r(du/dr) - u}{r^2} \\ r^2 \left( \frac{dR}{dr} \right) &= r(du/dr) - u \\ \frac{d}{dr} \left[ r^2 \left( \frac{dR}{dr} \right) \right] &= \frac{d}{dr} \left( r \frac{du}{dr} \right) - \frac{du}{dr} \\ &= \frac{du}{dr} + r \frac{d^2 u}{dr^2} - \frac{du}{dr} = r \frac{d^2 u}{dr^2}. \end{aligned}$$



- c) Hence making the various substitutions for  $R$  in Eq. (V-34) we get

$$r \frac{d^2 u}{dr^2} - \frac{2mr^2}{\hbar^2} [V - E] \frac{u}{r} = \ell(\ell + 1) \frac{u}{r}$$

$$-\frac{\hbar^2}{2mr} \cdot r \frac{d^2 u}{dr^2} + \frac{\hbar^2}{2mr} \cdot \frac{2mur}{\hbar^2} [V - E] = -\frac{\hbar^2}{2mr} \cdot \ell(\ell + 1) \frac{u}{r} ,$$

or simplifying gives

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ V + \frac{\hbar^2}{2m} \frac{\ell(\ell + 1)}{r^2} \right] u = Eu .} \quad (\text{V-36})$$

- d) This is called the **radial equation** (note that  $m$  in this equation represents mass, and not the magnetic quantum number, as was the case in the angular equation).
- i) It is identical in form to the one-dimensional Schrödinger equation (Eq. III-8), except that the effective potential,

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m} \frac{\ell(\ell + 1)}{r^2} , \quad (\text{V-37})$$

contains an extra piece, the so-called **centrifugal term**,  $(\hbar^2/2m)[\ell(\ell + 1)/r^2]$ .

- ii) This centrifugal term tends to throw the particle outward (away from the origin), just like the centrifugal (pseudo-) force in classical mechanics.

- e) Meanwhile, the normalization condition becomes

$$\int_0^\infty |u|^2 dr = 1 . \quad (\text{V-38})$$

10. We cannot proceed any further without providing a specific potential. As an example, let's consider the **infinite spherical well**:

$$V(r) = \begin{cases} 0, & \text{if } r < a; \\ \infty & \text{if } r > a . \end{cases} \quad (\text{V-39})$$

- a) Outside the well the wave function is zero; inside the well the radial equation says

$$\frac{d^2u}{dr^2} = \left[ \frac{\ell(\ell+1)}{r^2} - k^2 \right] u , \quad (\text{V-40})$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar} . \quad (\text{V-41})$$

- b) For the boundary condition  $u(a) = 0$  for  $\ell = 0$ , we get

$$\frac{d^2u}{dr^2} = -k^2u \implies u(r) = A \sin(kr) + B \cos(kr) .$$

- i) However, the actual radial wave function is  $R(r) = u(r)/r$ , and  $[\cos(kr)/r]$  blows up as  $r \rightarrow 0$ . So in order for the wave function to be normalizable, we must chose  $B = 0$ .

- ii) This boundary condition then requires  $\sin(ka) = 0$  or  $ka = n\pi$ , for some integer  $n$ . From this, analogously to the 1-D infinite square well, the allowed energies that satisfy the boundary condition are

$$E_{n\ell} = E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad (n = 1, 2, 3, \dots) . \quad (\text{V-42})$$

- c) Normalizing  $u(r)$  yields  $A = \sqrt{2/a}$ . Using the solution to the angular part (see Example V-3),  $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$ , of the wave equation gives the complete wave equation:

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r} . \quad (\text{V-43})$$

- i) Notice that the *wave function* of stationary states are labeled by *three quantum numbers*,  $n$ ,  $\ell$ , and  $m$ :  $\psi_{n\ell m}(r, \theta, \phi)$ .

ii) The *energy*, however, depends only upon  $n$  and  $\ell$ :  $E_{n\ell} \implies$  the  $m$  quantum states are said to be degenerate with each other since they give the same energy.

d) The general solution to Equation (V-40) for an arbitrary integer  $\ell$  is

$$u(r) = Arj_\ell(kr) + Brn_\ell(kr) , \quad (\text{V-44})$$

where  $j_\ell(x)$  is the **spherical Bessel function** of order  $\ell$ , and  $n_\ell(x)$  is the **spherical Neumann function** of order  $\ell$ .

i) Bessel functions are defined as

$$j_\ell(x) \equiv (-x)^\ell \left( \frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\sin x}{x} . \quad (\text{V-45})$$

For example,

$$\begin{aligned} j_0(x) &= \frac{\sin x}{x} ; \\ j_1(x) &= (-x) \frac{1}{x} \frac{d}{dx} \left( \frac{\sin x}{x} \right) = \frac{\sin x}{x^2} - \frac{\cos x}{x} . \end{aligned}$$

ii) Meanwhile, Neumann functions are defined as

$$n_\ell(x) \equiv -(-x)^\ell \left( \frac{1}{x} \frac{d}{dx} \right)^\ell \frac{\cos x}{x} . \quad (\text{V-46})$$

For example,

$$\begin{aligned} n_0(x) &= -\frac{\cos x}{x} ; \\ n_1(x) &= -(-x) \frac{1}{x} \frac{d}{dx} \left( \frac{\cos x}{x} \right) = -\frac{\cos x}{x^2} - \frac{\sin x}{x} . \end{aligned}$$

iii) Note that the notation  $\left( \frac{1}{x} \frac{d}{dx} \right)^\ell$  has the following meaning: if we set  $\ell = 3$ , then

$$\left( \frac{1}{x} \frac{d}{dx} \right)^3 = \left\{ \frac{1}{x} \frac{d}{dx} \left[ \frac{1}{x} \frac{d}{dx} \left( \frac{1}{x} \frac{d}{dx} \right) \right] \right\} .$$

- iv) For small  $x$ , note that  $\sin x \approx x - x^3/3! + x^5/5! - \dots$  and  $\cos x \approx 1 - x^2/2 + x^4/4! - \dots$ , as such:

$$j_\ell \approx \frac{x^\ell}{(2\ell+1)!!} , \quad n_\ell \approx -\frac{(2\ell-1)!!}{x^{\ell+1}}, \quad \text{for } x \ll 1 , \quad (\text{V-47})$$

where the double “exclamation points” mean  $(2\ell+1)!! = 1 \cdot 3 \cdot 5 \cdot 7 \cdot \dots \cdot (2\ell+1)$  [*e.g.*, for  $\ell = 0$ ,  $(2\ell+1)!! = 1!! = 1$ ;  $\ell = 1$ ,  $(2\ell+1)!! = 3!! = 1 \cdot 3 = 3$ ; and  $\ell = 2$ ,  $(2\ell+1)!! = 5!! = 1 \cdot 3 \cdot 5 = 15$ , and note for the  $n_\ell$  equation that  $(-1)!! = (-1)! \equiv 1$  and  $0!! = 0! \equiv 1$ ]. So,

$$j_0(x) \approx 1; \quad n_0(x) \approx \frac{1}{x}; \quad j_1(x) \approx \frac{x}{3}; \quad n_1(x) \approx -\frac{1}{x^2} .$$

- v) As can be seen from these trends at small  $x$ , the Bessel functions remain finite at the origin, but the Neumann functions blow up there. As such,  $B_\ell = 0$ , so

$$R(r) = A j_\ell(kr) . \quad (\text{V-48})$$

- e) Now using the boundary condition,  $R(a) = 0$ , we must solve the equation

$$j_\ell(ka) = 0 , \quad (\text{V-49})$$

that is,  $(ka)$  is a zero of the  $\ell^{\text{th}}$ -order spherical Bessel function. Since spherical Bessel functions are oscillatory (see Figure V-1 and Table V-2), each one has an infinite number of zeros.

- f) The boundary condition requires that

$$k = \frac{1}{a} \beta_{n_\ell} , \quad (\text{V-50})$$

where  $\beta_{n_\ell}$  is the  $n^{\text{th}}$  zero of the  $\ell^{\text{th}}$  spherical Bessel function.

Table V-2: **The first four spherical Bessel functions.**

$$j_0 = \frac{\sin x}{x}$$

$$j_1 = \frac{\sin x}{x^2} - \frac{\cos x}{x}$$

$$j_2 = \left( \frac{3}{x^3} - \frac{1}{x} \right) \sin x - \frac{3}{x^2} \cos x$$

$$j_3 = \left( \frac{15}{x^4} - \frac{6}{x^2} \right) \sin x - \left( \frac{15}{x^3} - \frac{1}{x} \right) \cos x$$

Table V-3: **The first four spherical Neumann functions.**

$$n_0 = -\frac{\cos x}{x}$$

$$n_1 = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$$

$$n_2 = -\left( \frac{3}{x^3} - \frac{1}{x} \right) \cos x - \frac{3}{x^2} \sin x$$

$$n_3 = -\left( \frac{15}{x^4} - \frac{6}{x^2} \right) \cos x - \left( \frac{15}{x^3} - \frac{1}{x} \right) \sin x$$

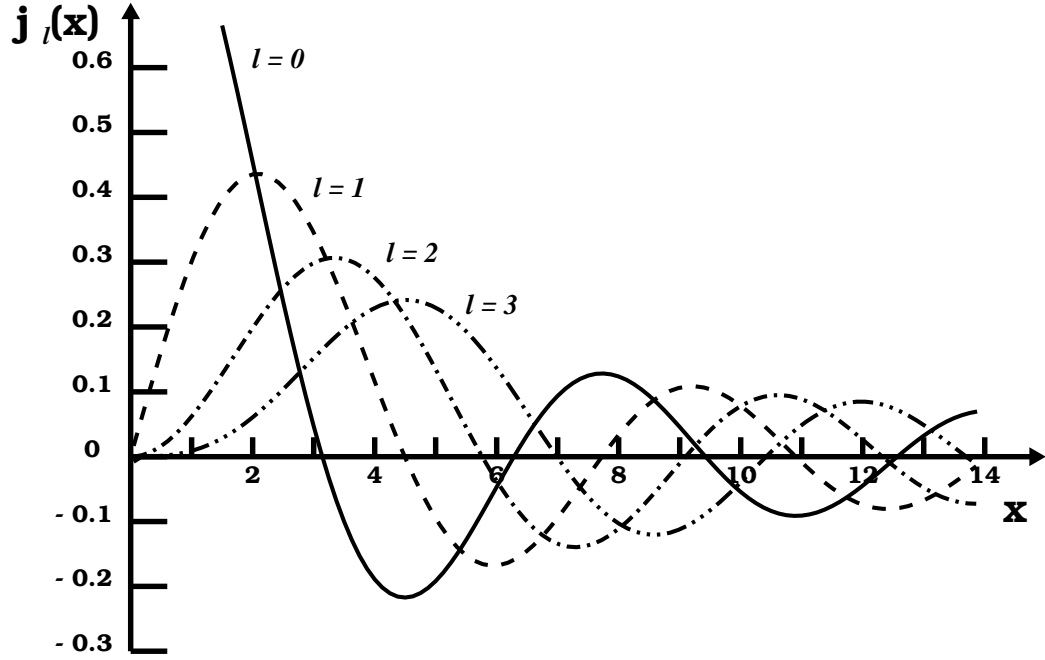


Figure V-1: Graphs of the first four spherical Bessel functions.

- g) The wave functions that result from the 3-D Schrödinger equation are

$$\psi_{nlm}(r, \theta, \phi) = A_{nl} j_l(\beta_{nl}r/a) Y_\ell^m(\theta, \phi) , \quad (\text{V-51})$$

with the constant  $A_{nl}$  to be determined by normalization.

- h) The allowed energies of these wave functions are

$$E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2 . \quad (\text{V-52})$$

Each energy level is  $(2\ell + 1)$ -fold degenerate, since there are  $(2\ell + 1)$  different values of  $m$  for each value of  $\ell$  (see Eq. V-28).

## B. The Hydrogen Atom.

### 1. The Potential Function.

a) The hydrogen atom consists of a relatively massive, essentially motionless, proton (placed at the origin) of charge  $+e$ , together with a relatively small mass electron of charge  $-e$  that circles around it, held in orbit by the mutual attraction of opposite charges.

b) From Coulomb's law, the potential energy (in SI units) is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} . \quad (\text{V-53})$$

c) We can use this potential then in our radial equation (Eq. V-36), giving

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[ -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u = Eu . \quad (\text{V-54})$$

d) We will solve this equation using the analytical solution technique used for the harmonic oscillator. Note that the Coulomb potential admits both *continuum* states (with  $E > 0$ ), describing electron-proton scattering and photoionization, and discrete *bound* states (with  $E < 0$ ), representing the hydrogen atom.

### 2. The Radial Wave Function.

a) We will now determine the bound states for hydrogen. To do this, we will simplify the notation by letting

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \quad (\text{V-55})$$

(note that  $\kappa$  is real since  $E < 0$  for bound states) and dividing Eq. (V-54) by  $E$  which gives

$$\frac{1}{\kappa^2} \frac{d^2u}{dr^2} = \left[ 1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \frac{1}{(\kappa r)} + \frac{\ell(\ell+1)}{(\kappa r)^2} \right] u . \quad (\text{V-56})$$

b) Then let

$$\rho \equiv \kappa r \quad \text{and} \quad \rho_o \equiv \frac{me^2}{2\pi\epsilon_o\hbar^2\kappa} , \quad (\text{V-57})$$

so that

$$\frac{d^2u}{d\rho^2} = \left[ 1 - \frac{\rho_o}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u . \quad (\text{V-58})$$

c) Next we examine the asymptotic form of the solutions. As  $\rho \rightarrow \infty$ , the constant term in the brackets dominates, so (approximately)

$$\frac{d^2u}{d\rho^2} = u .$$

d) The general solution to this equation is

$$u(\rho) = Ae^{-\rho} + Be^{\rho} ,$$

but  $e^{\rho}$  blows up as  $\rho \rightarrow \infty$ , so  $B = 0$ . As such

$$u(\rho) \sim Ae^{-\rho} \quad \text{for large } \rho . \quad (\text{V-59})$$

e) In the other extreme, as  $\rho \rightarrow 0$ , the centrifugal term dominates (when  $\ell > 0$ , though the result will still apply even when  $\ell = 0$ ), so (approximately) then

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

f) The general solution to this equation is

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell} ,$$

but  $\rho^{-\ell}$  blows up as  $\rho \rightarrow 0$ , so  $D = 0$ . Thus

$$u(\rho) \sim C\rho^{\ell+1} \quad \text{for small } \rho . \quad (\text{V-60})$$

g) The next step is to peel off the asymptotic behavior, by introducing the new function  $v(\rho)$ :

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho) , \quad (\text{V-61})$$



in the hope that  $v(\rho)$  will turn out to be simpler than  $u(\rho)$ .

**h)** Starting out, we get

$$\frac{du}{d\rho} = \rho^\ell e^{-\rho} \left[ (\ell + 1 - \rho)v + \rho \frac{dv}{d\rho} \right]$$

and

$$\begin{aligned} \frac{d^2u}{d\rho^2} = & \rho^\ell e^{-\rho} \left\{ \left[ -2\ell - 2 + \rho + \frac{\ell(\ell + 1)}{\rho} \right] v + \right. \\ & \left. 2(\ell + 1 - \rho) \frac{dv}{d\rho} + \rho \frac{d^2v}{d\rho^2} \right\} . \end{aligned}$$

**i)** In terms of  $v(\rho)$ , the radial equation (Eq. V-58) becomes

$$\rho \frac{d^2v}{d\rho^2} + 2(\ell + 1 - \rho) \frac{dv}{d\rho} + [\rho_\circ - 2(\ell + 1)]v = 0 . \quad (\text{V-62})$$

**j)** Finally, assume the solution to  $v(\rho)$  can be expressed as a power series in  $\rho$ :

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j . \quad (\text{V-63})$$

Differentiating gives

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j a_j \rho^{j-1} = \sum_{j=0}^{\infty} (j + 1) a_{j+1} \rho^j .$$

In the second sum, we replaced  $j$  with  $j + 1$ . Note that these two sums are still equivalent, even though they both start from  $j = 0$ , since the  $j = -1$  term equals zero in the second sum. Differentiating again gives

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j + 1) a_{j+1} \rho^{j-1} .$$

**k)** Inserting these into Equation (V-62) gives

$$\sum_{j=0}^{\infty} j(j + 1) a_{j+1} \rho^j + 2(\ell + 1) \sum_{j=0}^{\infty} (j + 1) a_{j+1} \rho^j$$

$$-2 \sum_{j=0}^{\infty} j a_j \rho^j + [\rho_{\circ} - 2(\ell + 1)] \sum_{j=0}^{\infty} a_j \rho^j = 0 .$$

1) Equating the coefficients of like powers gives

$$j(j+1) a_{j+1} + 2(\ell+1)(j+1) a_{j+1} - 2j a_j + [\rho_{\circ} - 2(\ell+1)] a_j = 0 ,$$

or

$$a_{j+1} = \left[ \frac{2(j + \ell + 1) - \rho_{\circ}}{(j + 1)(j + 2\ell + 2)} \right] a_j . \quad (\text{V-64})$$

To determine each coefficient, start with  $a_0 = A$  and determine  $A$  through normalization.

i) You might wonder why we didn't just start by using the series solution for  $u(\rho)$  in the first place. This is done primarily because a three-term recursion relation ( $a_{j+2}$ ,  $a_{j+1}$ , and  $a_j$ ) would result if the asymptotic  $e^{-\rho}$  term was not included in the solution. Such a recursion relation is much more difficult to handle than the one derived in Equation (V-64).

ii) For large  $j$  (this corresponds to large  $\rho$ ), the recursion relation becomes

$$a_{j+1} \cong \frac{2j}{j(j+1)} a_j = \frac{2}{j+1} a_j ,$$

so

$$a_j \cong \frac{2^j}{j!} A .$$

iii) Suppose for a moment that this were the *exact* result, then

$$v(\rho) = A \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = A e^{2\rho} ,$$

and hence

$$u(\rho) = A \rho^{\ell+1} e^{\rho} ,$$

which blows up at large  $\rho$ !

- iv) This is precisely the asymptotic behavior we didn't want at large  $\rho$ , since the wave functions would no longer be normalizable. There's only one way out of this dilemma: *The series must terminate*. There must be some maximum integer,  $j_{\max}$ , such that

$$a_{j_{\max}+1} = 0 \quad (\text{V-65})$$

beyond which all coefficients vanish automatically.

- v) With this definition, Equation (V-64) becomes

$$2(j_{\max} + \ell + 1) - \rho_{\circ} = 0 .$$

- vi) Defining

$$n \equiv j_{\max} + \ell + 1 \quad (\text{V-66})$$

(the so-called **principal quantum number**), we have

$$\rho_{\circ} = 2n . \quad (\text{V-67})$$

- m) The energy  $E$  is determined from  $\rho_{\circ}$  from Eqs. (V-55) and (V-56), so

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{m e^4}{8\pi^2 \epsilon_{\circ}^2 \hbar^2 \rho_{\circ}^2} . \quad (\text{V-68})$$

and the allowed energies are

$$E_n = - \left[ \frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_{\circ}} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots$$

(V-69)

- i) This is the famous **Bohr formula** — by any measure the most important result in all of quantum

mechanics. This equation (written in SI units) is equivalent to Equation (I-67), which is the Bohr formula given in the cgs unit system.

ii) Bohr obtained this result in 1913 by a serendipitous mixture of inapplicable classical physics and premature quantum theory (the Schrödinger equation did not come until 1924).

n) Combining Eqs. (V-57) and (V-67), we find that

$$\kappa = \left( \frac{me^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an} , \quad (\text{V-70})$$

where

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11} \text{ m} = 0.529 \text{ \AA}$$

(V-71)

is the so-called **Bohr radius** — the orbital radius of the ground state electron in hydrogen.

o) It follows from Eq. (V-57) that

$$\rho = \frac{r}{an} . \quad (\text{V-72})$$

p) From Eq. (V-12), the wave functions that describe the hydrogen atom are labeled by 3 quantum numbers ( $n$ ,  $\ell$ , and  $m$  corresponding to the “principal,” “orbital angular momentum,” and “magnetic” (also called “azimuthal”) quantum numbers, respectively):

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell}^m(\theta, \phi) , \quad (\text{V-73})$$

where (referring back to Eqs. V-36 and V-61):

$$R_{n\ell}(r) = \frac{1}{r} \rho^{\ell+1} e^{-\rho} v(\rho). \quad (\text{V-74})$$

- q) To determine  $v(\rho)$ , we use Eq. (V-67) in Eq. (V-64), which gives

$$a_{j+1} = \frac{2(j + \ell + 1 - n)}{(j + 1)(j + 2\ell + 2)} a_j . \quad (\text{V-75})$$

- r) The **ground state** is defined to be the state that has the lowest energy. This occurs when  $n = 1$ , so

$$E_1 = - \left[ \frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV}. \quad (\text{V-76})$$

This means that one would ionize the atom from the ground state if a photon energy of at least 13.6 eV is imparted on the atom.

- i) From Eq. (V-66), the  $n = 1$  state forces both  $j_{\max}$  and  $\ell$  to 0 (as such,  $m = 0$ ).

- ii) The wave function for the ground state then becomes

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi) . \quad (\text{V-77})$$

- iii) The recursion formula of Eq. (V-75) truncates after the first term ( $j = 0$  yields  $a_1 = 0$ ), so  $v(\rho)$  is a constant ( $a_0$ ) and

$$R_{10}(r) = \frac{a_0}{a} e^{-r/a} . \quad (\text{V-78})$$

- iv) Normalizing this equation gives

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|a_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr = |a_0|^2 \frac{a}{4} = 1 ,$$

so  $a_0 = 2/\sqrt{a}$ .

- v) Meanwhile,  $Y_0^0 = 1/\sqrt{4\pi}$ , which gives the final

ground state wave function of

$$\boxed{\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} .} \quad (\text{V-79})$$

s) If  $n = 2$ , the energy is

$$E_2 = \frac{-13.6 \text{ eV}}{4} = -3.4 \text{ eV}; \quad (\text{V-80})$$

this is the first excited state — or rather, *states*, since we can have either  $\ell = 0$  (in which case  $m = 0$ ) or  $\ell = 1$  (with  $m = -1, 0$ , or  $+1$ ), so there are actually four different states that share this energy.

i) If  $\ell = 0$ , the recursion relation gives

$$a_1 = -a_0 \text{ (using } j = 0\text{), and } a_2 = 0 \text{ (using } j = 1\text{),}$$

so  $v(\rho) = a_0(1 - \rho)$ , and hence

$$R_{20}(r) = \frac{a_0}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a} . \quad (\text{V-81})$$

ii) If  $\ell = 1$ , the recursion formula terminates the series after a single term, so  $v(\rho)$  is a constant, and we find

$$R_{21}(r) = \frac{a_0}{4a^2} r e^{-r/2a} . \quad (\text{V-82})$$

t) For arbitrary  $n$ , the possible values of  $\ell$  (consistent with Eq. V-66) are

$$\ell = 0, 1, 2, \dots, n - 1 . \quad (\text{V-83})$$

u) For each  $\ell$ , there are  $(2\ell + 1)$  possible values of  $m$ , so the total **degeneracy** of the energy level  $E_n$  is

$$d(n) = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2 . \quad (\text{V-84})$$

Table V-4: **The first few Laguerre polynomials,  $L_q(x)$ .**

---

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

---

Table V-5: **Some associated Laguerre polynomials,  $L_{q-p}^p(x)$ .**

---

$L_0^0$	$=$	1	$L_0^2$	$=$	2
$L_1^0$	$=$	$-x + 1$	$L_1^2$	$=$	$-6x + 18$
$L_2^0$	$=$	$x^2 - 4x + 2$	$L_2^2$	$=$	$12x^2 - 96x + 144$
$L_0^1$	$=$	1	$L_0^3$	$=$	6
$L_1^1$	$=$	$-2x + 4$	$L_1^3$	$=$	$-24x + 96$
$L_2^1$	$=$	$3x^2 - 18x + 18$	$L_2^3$	$=$	$60x^2 - 600x + 1200$

---

- v) The polynomial  $v(\rho)$  (defined by Equations V-63 and V-75) is a function well known to applied mathematicians; apart from normalization, it can be written as

$$v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho) , \quad (\text{V-85})$$

where

$$L_{q-p}^p \equiv (-1)^p \left( \frac{d}{dx} \right)^p L_q(x) \quad (\text{V-86})$$

is an **associated Laguerre polynomial** (see Table V-5), and

$$L_q(x) \equiv e^x \left( \frac{d}{dx} \right)^q (e^{-x} x^q) \quad (\text{V-87})$$

is the  $q$ -th **Laguerre polynomial** (see Table V-4).

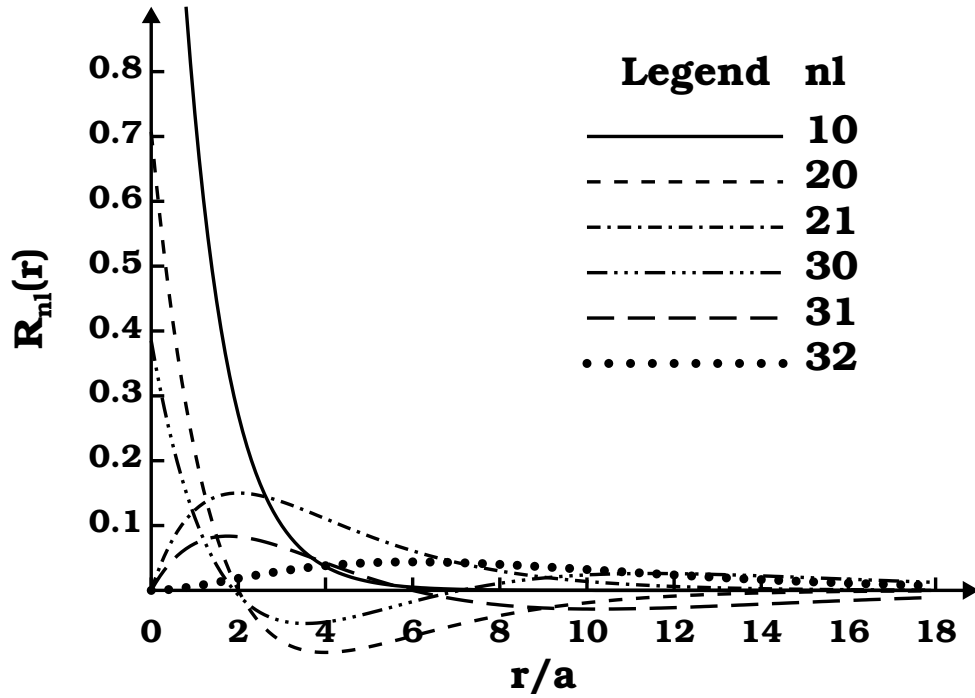


Figure V-2: Graphs of the first few hydrogen radial wave functions,  $R_{nl}(r)$  (note that the Bohr radius ‘ $a$ ’ in the calculation of  $R_{nl}(r)$  set to unity in this plot).

- w) With these associated Laguerre polynomials, we can now easily determine the radial wave equation (see Table V-6 and Figure V-2).
- x) From these polynomial functions, we can now write the final, “complete,” normalized wave functions for hydrogen:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^\ell L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{na}\right) Y_\ell^m(\theta, \phi) .$$

(V-88)

- y) Even though this equation is complicated, keep in mind that hydrogen is the only atom for which an analytic solution exists for its wave function. All other atoms require *perturbation theory* to describe their states.



Table V-6: The first few radial wave functions for hydrogen,  $R_{nl}(r)$ .

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$R_{10}$	$=$	$2a^{-3/2} \exp(-r/a)$
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$R_{20}$	$=$	$\frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a}\right) \exp(-r/2a)$
$R_{21}$	$=$	$\frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp(-r/2a)$

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$R_{30}$	$=$	$\frac{2}{\sqrt{27}} a^{-3/2} \left[1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a}\right)^2\right] \exp(-r/3a)$
$R_{31}$	$=$	$\frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a}\right) \left(\frac{r}{a}\right) \exp(-r/3a)$
$R_{32}$	$=$	$\frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a}\right)^2 \exp(-r/3a)$

---

- z) Of course, these wave functions for hydrogen are orthogonal:

$$\int \psi_{n\ell m}^* \psi_{n'\ell'm'} r^2 \sin \theta dr d\theta d\phi = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'} . \quad (\text{V-89})$$

3. With these complete wave functions for hydrogen and their associative eigenvalues, we can derive all of the equations that were presented in §I of the notes concerning the spectrum of hydrogen (see Eqs. I-14 through I-17 and Eqs. I-67 and I-68).

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**Example V-4.** What is the probability that an electron in the ground state of hydrogen will be found *inside the nucleus*?

- (a) First calculate the *exact* answer, assuming that the wave function (Eq. V-79) is correct all the way down to  $r = 0$ . Let  $b$  be the radius of the nucleus.

**Solution (a):**

$$P = \int |\Psi|^2 d^3r = \int_0^{2\pi} \int_{-\pi}^{\pi} \int_0^b |\Psi|^2 r^2 \sin \theta dr d\theta d\phi$$

$$\begin{aligned}
&= \int_0^{2\pi} d\phi \int_{-\pi}^{\pi} \sin \theta d\theta \int_0^b \left| \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \right|^2 r^2 dr \\
&= (2\pi)(2) \left( \frac{1}{\pi a^3} \int_0^b e^{-2r/a} r^2 dr \right) = \frac{4\pi}{\pi a^3} \int_0^b e^{-2r/a} r^2 dr \\
&= \frac{4}{a^3} \left[ -\frac{a}{2} r^2 e^{-2r/a} + \frac{a^3}{4} e^{-2r/a} \left( -\frac{2r}{a} - 1 \right) \right] \Big|_0^b \\
&= - \left( 1 + \frac{2r}{a} + \frac{2r^2}{a^2} \right) e^{-2r/a} \Big|_0^b,
\end{aligned}$$

or

$$P = 1 - \left( 1 + \frac{2b}{a} + \frac{2b^2}{a^2} \right) e^{-2b/a} .$$

- (b) Expand the result as a power series in the small number  $\epsilon \equiv 2b/a$ , and show that the lowest order term is the cubic:  $P \approx (4/3)(b/a)^3$ . This should be a suitable approximation, provided that  $b$  is much less than  $a$  (which it is).

**Solution (b):**

$$\begin{aligned}
P &= 1 - \left( 1 + \epsilon + \frac{1}{2} \epsilon^2 \right) e^{-\epsilon} \\
&\approx 1 - \left( 1 + \epsilon + \frac{1}{2} \epsilon^2 \right) \left( 1 - \epsilon + \frac{\epsilon^2}{2} - \frac{\epsilon^3}{3!} \right) \\
&\approx 1 - 1 + \epsilon - \frac{\epsilon^2}{2} + \frac{\epsilon^3}{6} - \epsilon + \epsilon^2 - \frac{\epsilon^3}{2} - \frac{\epsilon^2}{2} + \frac{\epsilon^3}{2} \\
&\approx \epsilon^3 \left( \frac{1}{6} - \frac{1}{2} + \frac{1}{2} \right) = \frac{1}{6} \epsilon^3 = \frac{1}{6} \left( \frac{2b}{a} \right)^3,
\end{aligned}$$

or

$$P \approx \frac{4}{3} \left( \frac{b}{a} \right)^3 .$$

(c) Alternatively, we might assume that  $\psi(r)$  is essentially constant over the (tiny) volume of the nucleus, so that  $P \approx (4/3)\pi b^3 |\psi(0)|^2$ . Check that you get the same answer this way.

**Solution (c):**

The ground state wave function is given by Eq. (V-79):

$$|\psi(0)|^2 = \left[ \frac{1}{\sqrt{\pi a^3}} e^0 \right]^2 = \frac{1}{\pi a^3} ,$$

thus

$$P \approx \left( \frac{4}{3} \right) \pi b^3 |\psi(0)|^2 = \left( \frac{4}{3} \right) \pi b^3 \frac{1}{\pi a^3} = \frac{4}{3} \left( \frac{b}{a} \right)^3 . \quad \checkmark$$

(d) Use  $b \approx 10^{-15}$  m and  $a \approx 0.5 \times 10^{-10}$  m to get a numerical estimate for  $P$ . Roughly speaking, this represents the “fraction of its time that the electron spends inside the nucleus.

**Solution (d):**

$$\begin{aligned} P &= \frac{4}{3} \left( \frac{10^{-15} \text{ m}}{0.5 \times 10^{-10} \text{ m}} \right)^3 = \frac{4}{3} (2 \times 10^{-5})^3 \\ &= \frac{4}{3} \cdot 8 \times 10^{-15} = \frac{32}{3} \times 10^{-15}, \end{aligned}$$

or

$$P = 1.07 \times 10^{-14} .$$

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**Example V-5.** Use the energy eigenvalue equation (*i.e.*, the Bohr formula given by Eq. V-69) to deduce the empirically derived Rydberg formula (*i.e.*, Eq. I-17) for the hydrogen atom.

**Solution:**

$$E_n = - \left[ \frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} .$$

Energy is related to a photon's wavelength by  $E = hc/\lambda$ . Setting the photon's energy equal to the energy difference between two bound states:

$$\begin{aligned}\frac{hc}{\lambda_{ji}} &= E_j - E_i \\ &= -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\left(\frac{1}{j^2} - \frac{1}{i^2}\right) \\ &= \left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\left(\frac{1}{i^2} - \frac{1}{j^2}\right),\end{aligned}$$

where  $j$  is the principle quantum number of the upper state in the transition and  $i$  is the lower state principle quantum number. Solving this for the wavenumber ( $\bar{\nu}_{ji} = 1/\lambda_{ji}$ ) we get

$$\bar{\nu}_{ji} = \frac{1}{\lambda_{ji}} = \frac{me^4}{8\epsilon_0^2 h^3 c} \left(\frac{1}{i^2} - \frac{1}{j^2}\right).$$

To be more precise here,  $m$  represents the reduced mass between the electron and proton and not the electron mass alone, so

$$\begin{aligned}m &= \frac{m_e M_A}{m_e + M_A} = \frac{m_e m_p}{m_e + m_p} = \frac{1.52367 \times 10^{-57} \text{ kg}^2}{1.67352 \times 10^{-27} \text{ kg}} \\ &= 9.10460 \times 10^{-31} \text{ kg} \approx m_e.\end{aligned}$$

Also, the other constants in this Rydberg formula are  $\epsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2 \text{ s}^2 / \text{kg m}^3$  [farad/meter] and  $e = 1.60219 \times 10^{-19} \text{ C}$ . Using the values for these physics constants, we can define and evaluate the Rydberg constant for hydrogen  $R$  to be

$$R = \frac{me^4}{8\epsilon_0^2 h^3 c} = 1.096776 \times 10^7 \text{ m}^{-1} = 109,677.6 \text{ cm}^{-1},$$

and the Rydberg equation becomes

$$\frac{1}{\lambda_{ji}} = R \left(\frac{1}{i^2} - \frac{1}{j^2}\right).$$

Hence proving the empirically derived Eq. (I-17) from quantum mechanics for hydrogen where  $Z = 1$ .