

1. Introduction to quantum mechanics. The Schrödinger equation.

At the end of the 19th century it was realized that even though equations of motions of classical mechanics work very well for large bodies such as bullets, stones, cannonballs, planets etc., they fail miserably when applied to small particles such as molecules and atoms, and their components - electrons and atomic nuclei. All attempts to simply modify the laws of classical mechanics to get them to work with small particles had also failed. Thus, a new theory had to be developed that would be able to describe the behavior of microscopic objects. Such theory is called quantum mechanics (QM). Quoting Michio Kaku, Professor of Theoretical Physics, The City College of New York,

"It is often stated that of all the theories proposed in this century, the silliest is quantum theory.

In fact, some say that the only thing that quantum theory has going for it is that it is unquestionably correct."

In quantum mechanics, the equations of motion described the Project 3 handout are replaced by the *Schrödinger equation*. The form of the Schrödinger equation depends on the physical situation, but the most general form is the *time-dependent Schrödinger equation*, which gives a description of a system evolving with time [1]:

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}, \quad (1)$$

where i is the imaginary unit, \hbar is Planck's constant divided by 2π (also called *reduced Planck's constant* or *Dirac's constant*), the symbol " $\partial/\partial t$ " indicates a partial derivative w.r.t. time t , Ψ is the *wavefunction* of the quantum system, and \hat{H} is the *Hamiltonian operator* (which characterizes the total energy of any given wave function and takes different forms depending on the situation) [1].

The most illustrative example is perhaps the *non-relativistic* Schrödinger equation for a single particle moving in an electric field (but not a magnetic field) [1]:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} \quad (2)$$

where m is the particle's mass, V is its potential energy, ∇^2 is the Laplacian [operator], and Ψ is the wavefunction (more precisely, in this context, it is called the "position-space wave function"). In plain language, it means "total energy equals kinetic energy plus potential energy" [1].

Given the particular differential operators involved, this is a linear partial differential equation [1]. To apply the Schrödinger equation, the Hamiltonian operator is set up for the system, accounting for the kinetic and potential energy of the particles constituting the system, then inserted into the Schrödinger equation [1]. The resulting partial differential equation is solved for the wavefunction, which contains information about the system [1].

The Laplacian [operator] present in equation (2) is defined as

$$\nabla^2 = \sum_{k=1}^n \frac{\partial^2}{\partial q_k^2} = \left(\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2} + \dots + \frac{\partial^2}{\partial q_n^2} \right) \quad (3)$$

where n is the number of parameters in a function to which we apply the Laplacian operator.

In fact, it turns out that classical mechanical quantities (observables) are represented by *linear operators* in quantum mechanics (Table 1) [2].

Table 1. Classical-mechanical observables and their corresponding quantum-mechanical operators [2].

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	\hat{X}	Multiply by x
	\mathbf{r}	$\hat{\mathbf{R}}$	Multiply by \mathbf{r}
Momentum	p_x	\hat{P}_x	$-i\hbar \frac{\partial}{\partial x}$
	\mathbf{p}	$\hat{\mathbf{P}}$	$-i\hbar \left(\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \right)$
Kinetic energy	T_x	\hat{T}_x	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
	T	\hat{T}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
	$V(x, y, z)$	$\hat{V}(x, y, z)$	Multiply by $V(x, y, z)$
Total energy	H	\hat{H}	$\hat{T} + \hat{V}$

An operator is a symbol that tells you to do something to whatever follows the symbol. For example, the Laplacian operator tells you to calculate second unmixed (pure) derivatives of a function and add them up. Operators are usually denoted by a capital letter with a carat over it, e.g. \hat{A} (the Laplacian operator is one of the exceptions to this rule). For example,

$$\hat{A}f(q) = g(q) \quad (4)$$

indicates the operator \hat{A} operates on $f(q)$ to give a new function $g(q)$ [2]. A *linear operator*, the only type that is used in quantum mechanics, is the one for which the following equality is true [2]:

$$\hat{A}[c_1 f_1(q) + c_2 f_2(q)] = \hat{A}c_1 f_1(q) + \hat{A}c_2 f_2(q) \quad (5)$$

where c_1 and c_2 are (possibly complex) constants. In addition to being linear, quantum mechanical operators are also *Hermitian*, i.e. [2]

$$\int_{\text{all space}} f^*(q) \hat{A}g(q) dq = \int_{\text{all space}} g(q) [\hat{A}f(q)]^* dq = \int_{\text{all space}} g(q) \hat{A}^* f^*(q) dq \quad (6)$$

where symbol “*” denotes a complex conjugate, i.e. f^* is the complex conjugate of the function f , and \hat{A}^* is the complex conjugate of the operator \hat{A} . This ensures that the *eigenvalues of quantum mechanical operators are real* and their *eigenfunctions are orthonormal*. A set of functions $f_i(q)$ ($i = 1 \dots n$) is said to be an orthonormal if [2]

$$\int_{\text{all space}} f_i^*(q) f_j(q) dq = \delta_{ij} \quad (7)$$

where δ_{ij} is the Kronecker delta

$$\delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases} \quad (8)$$

Indeed looking at equations (1) and (2), one can see that the Schrödinger equation is actually an *eigenvalue* problem, which in a very general form can be written as [2]

$$\hat{A}f(q) = af(q) \quad (9)$$

where a is a constant. The function $f(q)$ is called an *eigenfunction* of the operator \hat{A} , and a is called an *eigenvalue*.

While the time-dependent Schrödinger equation is the most general form of the Schrödinger equation, in this project we are going to consider only the *time-independent Schrödinger equation* as applied to atoms and molecules, which is given by [3]:

$$\hat{H}\Psi = E\Psi, \quad (10)$$

where E is the energy, Ψ is the wavefunction and \hat{H} is the Hamiltonian operator, which contains operators for the kinetic energies of all electrons, the Coulomb potential energies among all electrons and nuclei, and the kinetic energy of all nuclei. The wavefunction Ψ depends on spatial coordinates of *all* nuclei and electrons in the system, and spin coordinates of *all* electrons (which we omit for clarity). Wavefunctions that are solutions of the time-independent Schrödinger equation are called *stationary* because they are independent of time.

The most famous form of the time-independent Schrödinger equation is the *non-relativistic Schrödinger equation* for a single particle moving of mass m in an electric field (but not a magnetic field) [1]

$$\hat{H}\Psi(\mathbf{r}) = [\hat{T} + \hat{V}]\Psi(\mathbf{r}) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) \quad (11)$$

where \hat{T} is the kinetic energy operator and \hat{V} is the potential energy operator. The state of a quantum-mechanical system is completely specified by the wavefunction $\Psi(\mathbf{r})$ [2]. All possible information about the system can be derived from $\Psi(\mathbf{r})$. The wavefunction $\Psi(\mathbf{r})$ has the important property that $\Psi^*(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r}$ is the probability that the particle lies in the volume $d\mathbf{r}$, located at the position \mathbf{r} . Because the total probability of finding a particle somewhere must be unity (otherwise, such a particle does not exist!),

$$\int_{\text{all space}} \Psi^*(\mathbf{r})\Psi(\mathbf{r})d\mathbf{r} = 1 \quad (12)$$

Wavefunctions that satisfy equation (12) are said to be normalized [2].

If a system is in state described by a normalized wavefunction $\Psi(\mathbf{r})$, then the average value of the observable corresponding to \hat{A} is given by the expectation value $\langle a \rangle$ of the operator \hat{A} [2]:

$$\langle a \rangle = \int_{\text{all space}} \Psi^*(\mathbf{r})\hat{A}\Psi(\mathbf{r})d\mathbf{r} \quad (13)$$

If the wavefunction is *not* normalized, then

$$\langle a \rangle = \frac{\int_{\text{all space}} \Psi^*(\mathbf{r}) \hat{A} \Psi(\mathbf{r}) d\mathbf{r}}{\int_{\text{all space}} \Psi^*(\mathbf{r}) \Psi(\mathbf{r}) d\mathbf{r}} \quad (14)$$

2. The time-independent Schrödinger equation for a particle free to move in one dimension

Perhaps, the simplest example of the time-independent Schrödinger equation is for a particle of mass m that is free to move in one dimension [4,5]:

$$\hat{H}\psi(x) = E\psi(x) \quad (15)$$

$$[\hat{T} + \hat{V}]\psi(x) = E\psi(x) \quad (16)$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(x) \right] \psi(x) = E\psi(x) \quad (17)$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (18)$$

For a region of space where the potential energy is zero, we can set $V = 0$ and consider the equation [4,5]

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (19)$$

The general solutions of this equation are [4,5]

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx} \quad (20)$$

with A and B constants, as may be verified by substitution. However, it may be more convenient to use the *de Moivre's / Euler's theorem*

$$e^{\pm i\varphi} = \cos \varphi \pm i \sin \varphi \quad (21)$$

and write [4,5]:

$$\begin{aligned} \psi_k(x) &= Ae^{ikx} + Be^{-ikx} \\ &= A(\cos kx + i \sin kx) + B(\cos kx - i \sin kx) \\ &= (A + B) \cos kx + (A - B)i \sin kx \end{aligned} \quad (22)$$

If we absorb all numerical factors into two new coefficients C and D , then the general solutions (20) take the form [4,5]

$$\psi_k(x) = C \sin kx + D \cos kx \quad (23)$$

The energies for solutions (20) and (23) are given by [4,5]:

$$E_k = \frac{k^2 \hbar^2}{2m} \quad (24)$$

Note that we are now labeling both the wavefunctions and the energies (that is, the eigenfunctions and eigenvalues of \hat{H}) with the index k . These solutions are continuous, have continuous slope everywhere, are single-valued, and do not go to infinity, and so - in the absence

of any other information - are acceptable for all values of k . Because the energy of the particle is proportional to k^2 , all values of the energy are permitted. It follows that *the translational energy of a free particle is not quantized* [4,5].

In Mathematica, equation (19) can be solved using the DSolve[] option:

<https://reference.wolfram.com/language/ref/DSolve.html>

However, it is a good idea to always start a new Mathematica notebook with the command Clear["Global`*"] which clears the values for all symbols in the Global` context, except those that are protected [6]:

Input: Clear[Global`*];

Note that symbol “`” is not an apostrophe, it is the so-called “grave accent”:

https://en.wikipedia.org/wiki/Grave_accent

Now, let's type in the DSolve[] command for our differential equation:

Input: DSolve[- $\frac{\hbar^2}{2m}\psi''[x] == E * \psi[x], \psi[x], x]$

Note that we had to use a special “double struck” character \mathbb{E} (which can be entered as [Esc]dsE[Esc]) because the symbol E in Mathematica is reserved for the base of natural logarithm e , and is “protected”. The solution is:

Output: $\{\{\psi[x] \rightarrow C[1]\cos[\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}] + C[2]\sin[\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}]\}\}$

where C[1] and C[2] are constants. Now we can extract, and save the solution to a variable called, say, ψ :

Input: $\psi = \psi[x]/.\%[[1]]$

Output: $C[1]\cos[\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}] + C[2]\sin[\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}]$

Extracting the argument of Cos[] or Sin[] is more difficult. To extract the argument of cosine, and save it to, say, variable arg, type:

Input: arg = $\psi[[1,2]][[1,1;;5]]$

Output: $\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}$

In equation (23) the argument is labelled as kx , and we can do the same in Mathematica, and solve for the energy:

Input: Solve[arg == $k * x$, E]

Output: $\{\{E \rightarrow \frac{k^2 \hbar^2}{2m}\}\}$

Note that the expression for the energy evaluated in Mathematica is identical to that in equation (24). Saving the expression for the energy to variable E is easy:

Input: $E = E/. \%[[1]]$

Output: $\frac{k^2 \hbar^2}{2m}$

Not bad, eh?!

If you wish to execute the entire notebook automatically (one cell after another), use the “Evaluate Notebook” option in the “Evaluation” menu. Keep in mind, that *Mathematica* keeps definitions and assignments of all variables in memory as it executes notebook(s). Sometimes, you want to start over, and erase all those assignments. In this case, use option “Quit Kernel” →

“Local” in the same “Evaluation” menu, and re-evaluate the cells of interest, or use the “Evaluate Notebook” option to evaluate *all* cells in your notebook. To clear the output only, use the “Cell” → “Delete All Output” option.

3. The time-independent Schrödinger equation for a particle in a box

Now consider the same particle of mass m as discussed in the previous section, which is confined to a one-dimensional box (well) with impenetrable walls at $x = 0$ and $x = L$ shown in Figure 1 [4,5]. The potential energy is zero inside the box but rises abruptly to infinity at the walls. This model is an idealization of the potential energy of a gas-phase molecule that is free to move in a one-dimensional container [4,5]. However, it is also the basis of the treatment of the electronic structure of metals and of a primitive treatment of conjugated molecules. The particle in a box is also used in statistical thermodynamics in assessing the contribution of the translational motion of molecules to their thermodynamic properties [4,5]

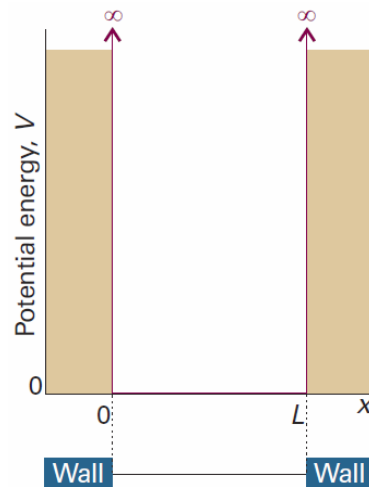


Figure 1. A particle in a one-dimensional region with impenetrable walls. Its potential energy is zero between $x = 0$ and $x = L$, and rises abruptly to infinity as soon as it touches the walls [4,5].

The Schrödinger equation for a particle of mass m when it is between the walls (and where $V = 0$) is the same as for a free particle (equation 19), so the general solutions given in equations (20), (23), and (24) are also the same [4,5]. Thus,

$$\text{For } 0 \leq x \leq L, \quad \psi_k(x) = C \sin kx + D \cos kx \quad E_k = \frac{k^2 \hbar^2}{2m} \quad (25)$$

When the particle touches the walls, its potential energy rises sharply to infinity. As a result, it is never found inside the material of the walls and its wavefunction is zero there. That is [4,5],

$$\text{For } x < 0 \text{ and } x > L, \quad \psi_n(x) = 0 \quad (26)$$

The requirement of the continuity of the wavefunction then implies that $\psi_k(x)$ as given by equation (25) must also be zero at the walls, for it must match the wavefunction inside the material of the walls, where the functions meet [4,5]. That is, the wavefunction must satisfy the following two *boundary conditions*, or constraints on the function at certain locations [4,5]:

$$\psi_k(0) = 0 \text{ and } \psi_k(L) = 0 \quad (27)$$

First, we consider the boundary condition $\psi_k(0) = 0$: since $x = 0$, the wavefunction becomes [4,5]

$$\psi_k(0) = C \sin k0 + D \cos k0 = 0 \quad (28)$$

Note that $\sin k0 = 0$ no matter what k and C are [4,5]. However, $\cos k0 = 1$, so the only way to satisfy this boundary condition is to set $D = 0$. Thus, the only acceptable wavefunctions are [4,5]

$$\psi_k(x) = C \sin kx \quad (29)$$

Now we apply the second boundary condition: $\psi_k(L) = 0$

$$\psi_k(L) = C \sin kL = 0 \quad (30)$$

We can not set $C = 0$ because then $\psi_k(x) = 0$ for all x , which would violate the normalization condition (equation 12), i.e. particle does not exist. In order for $\psi_k(L)$ to be zero without setting $C = 0$, the term $\sin kL$ should become zero [7]:

$$\sin kL = 0 \quad (31)$$

Obviously, this holds if

$$kL = n\pi \quad n = 1, 2, 3, \dots \quad (32)$$

Solving for k gives [7]

$$k = \frac{n\pi}{L} \quad n = 1, 2, 3, \dots \quad (33)$$

where n is a positive integer. Although there is no mathematical reason why n can't be a negative integer, use of negative integers adds nothing new to the solution (i.e. $n\pi = -n\pi$), so they are ignored. However, this is not always the case [7].

Substituting the expression for k into equations for $\psi_k(x)$ and E_k gives

$$\psi_n(x) = C \sin \frac{n\pi x}{L} \quad (34)$$

$$E_n = \frac{n^2 \hbar^2}{8mL^2} \quad (35)$$

where the definition for \hbar has been substituted in the last expression for energy [7]. The energy values depend on some constants and on n , which is restricted to positive integer values. This means that the energy cannot have just any value; it can have only values determined by \hbar , m , L , and - most importantly - n . The energy of the particle in the box is quantized, since the energy value is restricted to having only certain values. The integer n is called a *quantum number* [7].

Let's see if we can do the same in Mathematica. As always, we start with the `Clear["Global`*"]` command:

Input: `Clear[Global`*];`

Since we already know how to solve the time-independent Schrödinger equation for a free particle, we can follow the same approach while adding the first boundary condition ($\psi_k(0) = 0$):

Input: `DSolve[{-\frac{\hbar^2}{2*m}\psi''[x] == E * \psi[x], \psi[0] == 0}, \psi[x], x]`

Output: `{{\psi[x] \to C[2]Sin[\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}]}}`

Note how the cosine term disappears because the only way to satisfy the first boundary condition is to set $C[1]=0$. The second boundary condition has to be entered in manually.

First, we extract the sine argument and replace x with L :

Input: `solψ = ψ[x]/.%[[1]]`

Output: $C[2]\text{Sin}\left[\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}\right]$

Input: `arg = solψ[[2,1]]`

Output: $\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}$

Input: `arg = arg/.x → L`

Output: $\frac{\sqrt{2}L\sqrt{m}\sqrt{E}}{\hbar}$

In order for the sine function to evaluate to zero at L , the argument has to be equal to $n\pi$, where n is a positive integer. We do just that in Mathematica: solve the resulting equation for the energy, and save the solution in variable \mathbb{E} :

Input: `solE = Solve[arg == n * π, E]`

Output: $\{\{\mathbb{E} \rightarrow \frac{n^2\pi^2\hbar^2}{2L^2m}\}\}$

Input: `E = E/.solE[[1]]`

Output: $\frac{n^2\pi^2\hbar^2}{2L^2m}$

To simplify the expression for \mathbb{E} we use the definition of \hbar :

Input: `ħ = h/(2*π)`

Output: $\frac{h}{2\pi}$

Input: `E`

Output: $\frac{h^2n^2}{8L^2m}$

where the last expression is identical to equation (35).

The determination of the wavefunction is not complete. It must be normalized, i.e. multiplied by some constant N so that [7]

$$\int_0^L (N\psi(x))^*(N\psi(x))dx = 1 \quad (36)$$

The limits on the integral are 0 to L because the only region of interest for the nonzero wavefunction is from $x = 0$ to $x = L$. We assume that the constant C (equation 29) is a part of the normalization constant N that multiplies the sine component of the wavefunction. The integral to be evaluated is [7]

$$\int_0^L \left(N \sin \frac{n\pi x}{L}\right)^* \left(N \sin \frac{n\pi x}{L}\right) dx = 1 \quad (37)$$

The complex conjugate does not change anything inside the parentheses, since everything is a real number or real function, so:

$$N^2 \int_0^L \left(\sin \frac{n\pi x}{L}\right)^2 dx = 1 \quad (38)$$

which means that

$$N = \left(\int_0^L \left(\sin \frac{n\pi x}{L}\right)^2 dx\right)^{-1/2} \quad (39)$$

This integral can be evaluated by hand, but perhaps it is more elegant to let Mathematica do it. Recall that we already have wavefunction saved in variable $\text{sol}\psi$

$$C[2]\text{Sin}\left[\frac{\sqrt{2}\sqrt{m}x\sqrt{E}}{\hbar}\right]$$

Now, all we need is to integrate and solve for the constant $C[2]$, which is identical to coefficient N in equations (36)-(39). However, before doing so, it is a good idea to help Mathematica by specifying which variables are real numbers and which are integers:

Input: $\$Assumptions = \{x, m, h, L\} \in \text{Reals} \&\& n \in \text{Integers}$

Output: $(x|m|h|L) \in \text{Reals} \&\& n \in \text{Integers}$

Now we evaluate integral (38)

Input: $\text{solI} = \text{Integrate}[\text{sol}\psi^2, \{x, 0, L\}]$

Output: $\frac{1}{2}LC[2]^2$

, and solve for coefficient $C[2]$:

Input: $\text{solC} = \text{Solve}[\text{solI} == 1, C[2]]$

Output: $\{\{C[2] \rightarrow -\frac{\sqrt{2}}{\sqrt{L}}\}, \{C[2] \rightarrow \frac{\sqrt{2}}{\sqrt{L}}\}\}$

Which solution should we use? Actually, it does not matter because both solutions satisfy the normalization condition (36). However, it is customary to choose the positive normalization coefficient:

Input: $N = C[2]/.\text{solC}[[2]]$

Output: $\frac{\sqrt{2}}{\sqrt{L}}$

Note that because symbol N in Mathematica is protected (command $N[\text{expr}]$ gives the numerical value of expr), we have used a special “double struck” character \mathbb{N} (which can be entered as $[\text{Esc}]dsN[\text{Esc}]$). Now, let’s form a complete solution (called ψ) by replacing the coefficient $C[2]$ in $\text{sol}\psi$ with the expression for \mathbb{N} :

Input: $\text{sol}\psi = \text{sol}\psi/.C[2] \rightarrow \mathbb{N}$

Output: $\frac{\sqrt{2}\text{Sin}\left[\frac{\sqrt{m}\sqrt{\frac{h^2n^2}{L^2m}}\pi x}{h}\right]}{\sqrt{L}}$

Finally, simplify the expression for the wavefunction as follows:

Input: $\text{sol}\psi = \text{Assuming}[m > 0 \&\& L > 0 \&\& h > 0 \&\& n > 0, \text{FullSimplify}[\text{sol}\psi]]$

Output: $\frac{\sqrt{2}\text{Sin}\left[\frac{n\pi x}{L}\right]}{\sqrt{L}}$

Thus, the acceptable wavefunctions for a one-dimensional particle-in-a-box are given by

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \quad n = 1, 2, 3, \dots, \infty \quad (40)$$

The quantized energies of the particles in this box are

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (41)$$

Figure 2 shows the first six particle in a box wavefunctions plotted for a box with $0 \leq x \leq 1$. All of them go to zero at the sides of the box, as required by the boundary conditions. All of

them look like simple sine functions (which is what they are) with positive and negative values [7].

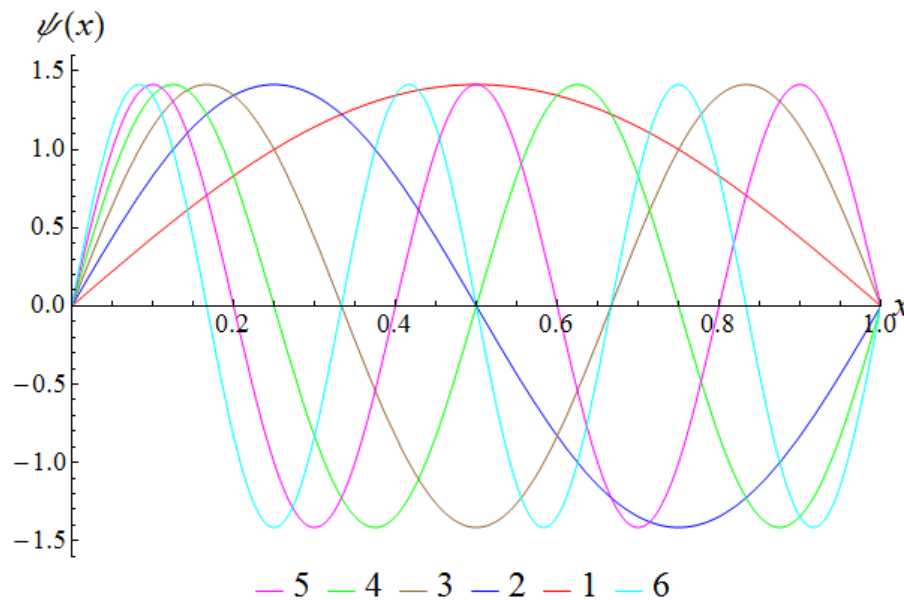


Figure 2. Plot of the first six particle in a box wavefunctions.

We produced these plots using the following procedure¹

1. Form a function, let's call it ψ , which is a function of n , x , and L :
 Input: $\psi[n, x, L] = \text{sol}\psi$
 Output: $\frac{\sqrt{2}\sin[\frac{n\pi x}{L}]}{\sqrt{L}}$
2. Check the definition of the generated function:
 Input: ψ
 Output: $\psi[n, x, L] = \frac{\sqrt{2}\sin[\frac{n\pi x}{L}]}{\sqrt{L}}$
3. Define some arbitrary chosen length of the box. Here, we use $L = 1$:
 $L = 1$
4. Define the maximum value of n for which we wish to plot the wavefunctions:
 $n_{\text{max}} = 6$
5. Initialize the array which will contain plots (there will be n_{max} of those):
 $\text{PlotPsi} = \text{Table}[0, \{n_{\text{max}}\}]$
6. Set default plot options:
 $\text{SetOptions}[\text{Plot}, \text{BaseStyle} \rightarrow \text{FontSize} \rightarrow 18,$
 $\text{PlotRange} \rightarrow \{\{0, L\}, \{-1.6, 1.6\}\}, \text{ImageSize} \rightarrow 600];$
 Note that we specified the plot range for both x ($0 \leq x \leq L$) and ψ ($-1.6 \leq \psi \leq 1.6$).

¹ We note that what follows is only one of many different ways (and certainly not the most elegant) one can generate plots in Mathematica.

7. Generate a color palette (make sure to have at least n_{max} colors in the palette):

color = {Red, Blue, Brown, Green, Magenta, Cyan}

8. Generate plots:

```
Do[
  PlotPsi[[n]] = Plot[
     $\psi[n, x, L]$ , {x, 0, L},
    PlotStyle → color[[n]],
    PlotLegends → Placed[LineLegend[{Style[n, 24]}], Bottom]
  ]
, {n, 1, nmax}]
```

9. Display plots:

```
Print[Show[PlotPsi, AxesLabel → {Style["x", Italic, 24],
Style[" $\psi(x)$ ", Italic, 24]}]];
```

Whew! Wasn't that fun?! Should you want to display wavefunctions for $n > 6$, simply modify the value n_{max} and extend the color palette. Yes, it is that easy!

4. The time-independent Schrödinger equation for a particle in a three-dimensional box

The one-dimensional particle in a box treatment can be expanded to two and three dimensions very easily. Because the treatments are similar, we consider just the three-dimensional system here [7]. The system consists of a particle of mass m confined to a box of length L_1 in the x -direction, L_2 in the y -direction, and L_3 in the z -direction [4,5]. Inside the box, the potential energy is zero and at the walls it is infinite. This system could be a model for a quantum mechanical system of a gas in a container of macroscopic dimensions or for an electron confined to a small cavity in a solid.

The Schrödinger equation for a particle in a three-dimensional box is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) = E \psi(x, y, z) \quad (42)$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E \psi(x, y, z) \quad (43)$$

We determine the acceptable wavefunctions for this system by trying another assumption [7]. Let us assume that the complete three-dimensional $\psi(x, y, z)$, which must be a function of x , y , and z , can be written as a product of three functions, each of which can be written in terms of only one variable [7]. That is:

$$\psi(x, y, z) = X(x)Y(y)Z(z) \quad (44)$$

where $X(x)$ is a function only of x (that is, independent of y and z), $Y(y)$ is a function solely of y , and $Z(z)$ is a function solely of z . Wavefunctions that can be written this way are said to be *separable*. Why make this particular assumption? Because then in the evaluation of the del-

squared part of the Schrödinger equation, each second derivative will act on only one of the separate functions and the others will cancel, making an ultimate solution of the Schrödinger equation that much simpler. This technique is called the *separation of variables*.

As a result, we arrive at three independent Schrödinger equations, each describing motion of the particle in a given Cartesian direction.

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} X(x) &= E_x X(x) \\ -\frac{\hbar^2}{2m} \frac{d^2}{dy^2} Y(y) &= E_y Y(y) \\ -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} Z(z) &= E_z Z(z) \end{aligned} \quad (45)$$

Obviously, all three equations have the same form as the Schrödinger equation for the one-dimensional particle in a box solved above [7]. Rather than having to re-derive solutions for the three-dimensional case, we can simply use the same functions, but with the appropriate labels for a three-dimensional system [7].

It follows that the total wavefunction $\psi(x, y, z)$ has the form [4,5]:

$$\psi_{n_1, n_2, n_3}(x, y, z) = \left(\frac{8}{L_1 L_2 L_3} \right)^{1/2} \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} \sin \frac{n_3 \pi z}{L_3} \quad (46)$$

Outside the box, the wavefunction is zero. The total energy of particle E is a sum of contributions due to motion of the particle in the three Cartesian directions which are assumed to be independent

$$E = E_x + E_y + E_z \quad (47)$$

Thus, the total energy of the particle in a three dimensional box is given by

$$E_n = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \frac{\hbar^2}{8m} \quad (48)$$

The quantum numbers n_1 , n_2 , and n_3 are all positive integers that can be varied independently.

Note that one boundary condition results in a single quantum number, and three boundary conditions produce three quantum numbers.

5. The time-independent Schrödinger equation for the hydrogen atom

The hydrogen atom is a very simple system that contains two particles, a proton and an electron, that are interacting via a Coulomb force. According to classical physics, the Coulomb interaction energy V between two point electric charges q_1 and q_2 (these are electric charges! not generalized coordinates...) is given by

$$V = \frac{q_1 q_2}{4\pi \epsilon_0 r} \quad (49)$$

where electric charges q_1 and q_2 are given in the unit of Coulomb, the distance between charges r is given in meters, and ϵ_0 is the vacuum permittivity, also called the permittivity of free space (see Table 7 in the Project 1 handout), and the resulting energy is in joules. The factor of $4\pi\epsilon_0$

arises because we are using SI units. Since the proton and the electron have charges of the same magnitude (equal to the elementary charge e), but different signs (the electron charge is $-e$, the proton charge is $+e$), equation (49) reduces to

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \quad (50)$$

With this in mind, the Schrödinger equation for the hydrogen atom can be written as

$$-\frac{\hbar^2}{2m_e}\nabla^2\Psi_T - \frac{\hbar^2}{2m_p}\nabla^2\Psi_T - \frac{e^2}{4\pi\epsilon_0 r} = E_T\Psi_T \quad (51)$$

where m_e is the mass of the electron, m_p is the mass of the proton, and the total wavefunction Ψ is a function of coordinates of both particles:

$$\Psi_T \equiv \Psi_T(x_e, y_e, z_e, x_p, y_p, z_p) \quad (52)$$

Note that the physical interpretation of equation (51) is quite simple: the first term is the kinetic energy of the electron, the second term is the kinetic energy of the proton, and the third term is the Coulomb potential energy of interaction between the two particles. Why the gravitational potential energy is not included? Well, for such light particles the gravitational energy is many orders of magnitude smaller than the Coulomb energy, so the former can be happily ignored!

A new problem arises when we note that the total energy, E_T , is made of two parts: 1) the translational motion of the atom as whole, and 2) the energy of motion of the electron w.r.t. the proton [8]. It is the latter portion of the energy in which we are interested.

Using the separation of variables technique, it is possible to separate out and discard the translational portion of the total wavefunction [8]. We introduce a new set of variables x_m, y_m, z_m which are Cartesian coordinates of the *center of mass* of the hydrogen atom, and the variables r, θ, ϕ , which are the *spherical (polar) coordinates* of the electron w.r.t. nucleus [8].

A coordinate of the center of mass of a system is, in general, given by

$$x_m = \frac{\sum_{i=1}^N x_i m_i}{M} \quad y_m = \frac{\sum_{i=1}^N y_i m_i}{M} \quad z_m = \frac{\sum_{i=1}^N z_i m_i}{M} \quad (53)$$

where N is the total number of particles, (x_i, y_i, z_i) are Cartesian coordinates of the i -th particle, and M is the total mass of the system defined as

$$M = \sum_{i=1}^N m_i \quad (54)$$

Keep in mind that the particle masses m_i should be in the same units in both expressions, and the units of (x_m, y_m, z_m) come out to be the same as the units of (x_i, y_i, z_i) . Also note that if a coordinate of the i -th particle is zero, it does not contribute to the coordinate of the center of mass.

For the hydrogen atom, the Cartesian coordinates of the center of mass are given by

$$x_m = \frac{m_p x_p + m_e x_e}{m_p + m_e} \quad y_m = \frac{m_p y_p + m_e y_e}{m_p + m_e} \quad z_m = \frac{m_p z_p + m_e z_e}{z_p + z_e} \quad (55)$$

and the transformation to spherical coordinates (Figure 3) are

$$x = r \sin \theta \cos \phi \quad (56)$$

$$y = r \sin \theta \sin \phi \quad (57)$$

$$z = r \cos \theta \quad (58)$$

By using these transformations, it is a straightforward procedure to obtain the Schrödinger equation in terms of Cartesian coordinates of the center of mass and the polar coordinates r, θ, ϕ [1-3,5-8]. The coordinates of the center of mass x_m, y_m, z_m obviously relate to the translational motion of the atom as a whole, and the r, θ, ϕ coordinates are seen to relate the coordinates of the electron x_e, y_e, z_e to the coordinates of the proton x_p, y_p, z_p .

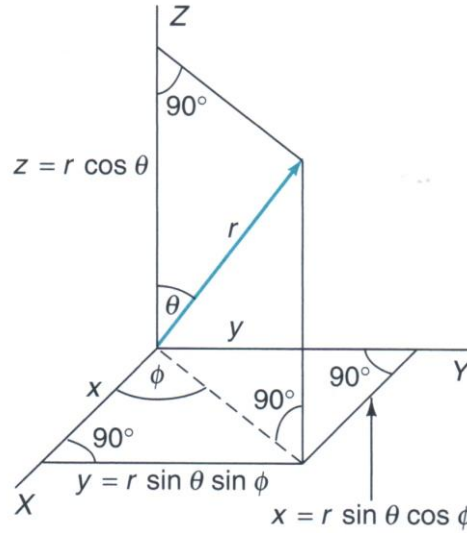


Figure 3. Transformation diagram for spherical coordinates

In terms of the new variables, the Schrödinger equation for the hydrogen atom becomes [8]:

$$-\frac{\hbar^2}{2(m_e + m_p)} \nabla_m^2 \Psi_T - \frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi_T}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi_T}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi_T}{\partial \theta} \right) \right] - \frac{e^2 \Psi_T}{4\pi\epsilon_0 r} = E_T \Psi_T \quad (59)$$

where

$$\nabla_m^2 = \left(\frac{\partial^2}{\partial x_m^2} + \frac{\partial^2}{\partial y_m^2} + \frac{\partial^2}{\partial z_m^2} \right) \quad (60)$$

and the parameter μ , called the *reduced mass*, is defined as [8]

$$\mu = \frac{m_e m_p}{m_e + m_p} \quad (61)$$

The total wavefunction Ψ_T is the function of x_m, y_m, z_m and r, θ, ϕ :

$$\Psi_T \equiv \Psi_T(x_m, y_m, z_m, r, \theta, \phi) \quad (62)$$

and the total energy E_T is sum of translational energy of the atom as a whole, E_{trans} , as well as the energy of the electron w.r.t. the proton, E [8].

It is now possible to perform the separation of variables. The total wavefunction Ψ_T is represented as a product of the two wavefunctions [8]:

$$\Psi_T(x_m, y_m, z_m, r, \theta, \phi) = \Psi_{\text{trans}}(x_m, y_m, z_m) \Psi(r, \theta, \phi) \quad (63)$$

where Ψ_{trans} is the translational wavefunction for the atom as a whole, and Ψ is the electronic wavefunction, i.e. wavefunction of the electron, that we are interested in. When this expression is substituted into the Schrödinger equation (59), the following two equations are obtained:

$$-\frac{\hbar^2}{2(m_e + m_p)} \nabla_m^2 \Psi_{\text{trans}}(x_m, y_m, z_m) = E_{\text{trans}} \Psi_{\text{trans}}(x_m, y_m, z_m) \quad (64)$$

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \right] \Psi(r, \theta, \varphi) - \frac{e^2 \Psi(r, \theta, \varphi)}{4\pi\epsilon_0 r} = E \Psi(r, \theta, \varphi) \quad (65)$$

The first of these equations (64) contains only the variables x_m, y_m, z_m with no potential energy term [8]. This is identical to the Schrödinger equation for a free particle, and therefore represents the translational energy of the atom as a whole. The second equation is called the *electronic Schrödinger equation* because it essentially describes the motion of the electron around the proton. This is the one we are interested in.

6. The hydrogen atom wavefunctions

The electronic Schrödinger equation for the hydrogen atom in the *atomic system of units*

$$\hat{H}\Psi = E\Psi \quad (66)$$

$$\hat{H} = -\frac{1}{2} \nabla^2 - \frac{1}{r} \quad (67)$$

can be solved exactly. Switching to the spherical coordinate system and using the separation of variables technique, we get:

$$\Psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi) \quad (68)$$

where the *radial function* $R(r)$ is the solution of the *radial equation*:

$$-\frac{1}{2r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \left[\frac{l(l+1)}{2r^2} - \frac{1}{r} - E \right] = 0 \quad (69)$$

and the *angular function* $Y(\theta, \varphi)$ is the solution of the *angular equation*:

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \varphi)}{\partial \theta} \right) + \frac{\partial^2 Y(\theta, \varphi)}{\partial \theta^2} + Y(\theta, \varphi) l(l+1) \sin^2 \theta = 0 \quad (70)$$

A. The radial function $R(r)$

The radial function $R_{nl}(r)$ is a function of two quantum numbers, n and l :

$$n = 1, 2, 3, \dots, \quad 0 \leq l \leq n - 1 \quad (71)$$

It is normalized as:

$$\int_0^\infty R_{nl}^*(r) R_{nl}(r) r^2 dr = 1 \quad (72)$$

Because functions $R_{nl}(r)$ are real:

$$\int_0^\infty R_{nl}^2(r) r^2 dr = 1 \quad (73)$$

The general form of $R_{nl}(r)$ is given by

$$R_{nl}(r) = N_{nl} \left(\frac{2}{n} \right)^{l+3/2} r^l e^{-r/n} L_{n-l-1}^{2l+1} \left(\frac{2r}{n} \right) \quad (74)$$

where N_{nl} is the normalization coefficient

$$N_{nl} = \left(\frac{(n-l-1)!}{2n[(n+l)!]^3} \right)^{1/2} \quad (75)$$

and the functions $L_{n-l-1}^{2l+1}(x)$ are called *associated Laguerre polynomials* [9]:

$$L_{n-l-1}^{2l+1}(x) = L_{i_{\max}}^{2l+1}(x) = \sum_{i=0}^{i_{\max}} \frac{(-1)^i [(n+l)!]^2 x^i}{i! (i_{\max} - i)! (2l+1+i)!} \quad (76)$$

In mathematics, the *associated Laguerre polynomials* are solutions to the *associated Laguerre differential equation* [10]:

$$x \frac{d^2 f(x)}{dx^2} + (q+1-x) \frac{df(x)}{dx} + pf(x) = 0 \quad (77)$$

where parameters p and q are constants. While it is tempting to program formula (76) explicitly, Mathematica can generate *generalized Laguerre polynomials* using command `LaguerreL[p,q,x]`

<https://reference.wolfram.com/language/ref/LaguerreL.html>

which are related to the *associated Laguerre polynomials* $L_p^q(x)$ as

$$L_p^q(x) = (p+q)! \text{LaguerreL}[p,q,x] \quad (78)$$

Note that there are several notations for the *associated Laguerre polynomials*, so one has to be extremely careful when generating these functions.

Off topic: In case you wonder, a special case of the *associated Laguerre differential equation* is the *Laguerre differential equation* [10]

$$x \frac{d^2 f(x)}{dx^2} + (1-x) \frac{df(x)}{dx} + pf(x) = 0, \quad p = \text{constant} \quad (79)$$

where the solutions $L_p(x)$ are called the [*unassociated*] *Laguerre polynomials* which are given by the *Rodrigues representation* (formula)

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} (x^n e^{-x}) \quad (80)$$

or by the sum

$$L_n(x) = \sum_{k=0}^n \frac{(-1)^k}{k!} \binom{n}{k} x^k \quad (81)$$

where $\binom{n}{k}$ is a *binomial coefficient*. The value of the binomial coefficient for nonnegative n and k is given explicitly by

$$\binom{n}{k} = \begin{cases} \frac{n!}{(n-k)!k!} & \text{for } 0 \leq k < n \\ 0 & \text{otherwise} \end{cases} \quad (82)$$

In Mathematica, the [unassociated] *Laguerre polynomials* can be readily generated using the `LaguerreL[n,x]` command:

<https://reference.wolfram.com/language/ref/LaguerreL.html>

What to do

What you should do now is construct radial functions $R_{nl}(r)$ in Mathematica or any other software, verify their normalizations (i.e. for each generated $R_{nl}(r)$ evaluate integral (73) either analytically, using command `Integrate[]`:

<https://reference.wolfram.com/language/ref/Integrate.html>

or numerically, using command `NIntegrate[]`:

<https://reference.wolfram.com/language/ref/NIntegrate.html>

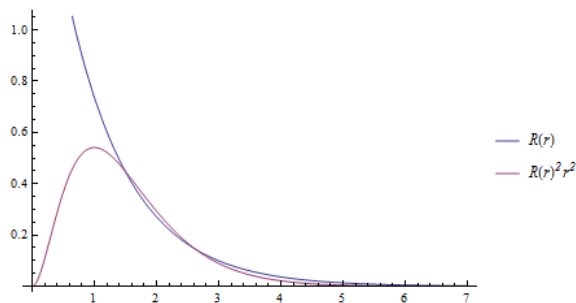
and plot (in 1-D, using the `Plot[]` command) the radial functions $R_{nl}(r)$ and probability densities $R_{nl}^2(r)r^2$ for $1 \leq n \leq 4$ and all allowed values of l . Plot $R_{nl}(r)$ together with $R_{nl}^2(r)r^2$ for each combination of n and l as shown in Figure 4.

Radial function: $n = 1, l = 0$

$n-l-1 = 0, 2l+1 = 1$, associated Laguerre polynomial = 1

function $R_{n1}(r) = 2 e^{-r}$

normalization integral = 1.0000000000000000

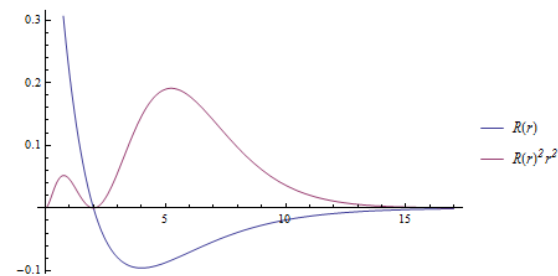


Radial function: $n = 2, l = 0$

$n-l-1 = 1, 2l+1 = 1$, associated Laguerre polynomial = $2(2-x)$

function $R_{n1}(r) = \frac{e^{-r/2} (2-r)}{2\sqrt{2}}$

normalization integral = 1.0000000000000000

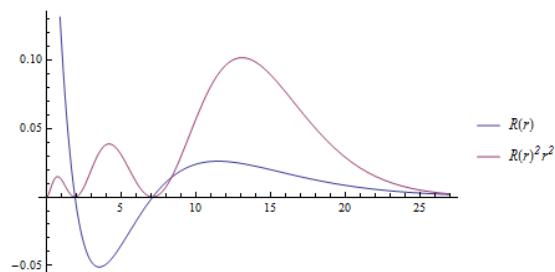


Radial function: $n = 3, l = 0$

$n-l-1 = 2, 2l+1 = 1$, associated Laguerre polynomial = $3(6-6x+x^2)$

function $R_{n1}(r) = \frac{2 e^{-r/3} (27-18r+2r^2)}{81\sqrt{3}}$

normalization integral = 1.0000000000000000

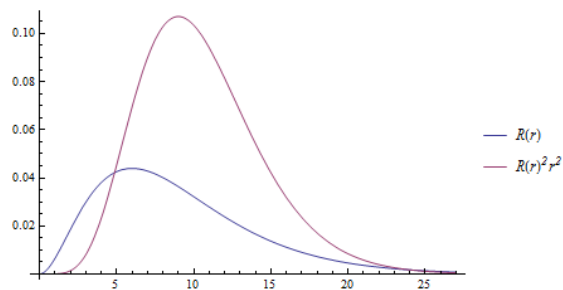


Radial function: $n = 3, l = 2$

$n-l-1 = 0, 2l+1 = 5$, associated Laguerre polynomial = 120

function $R_{n1}(r) = \frac{2}{81} \sqrt{\frac{2}{15}} e^{-r/3} r^2$

normalization integral = 1.0000000000000000

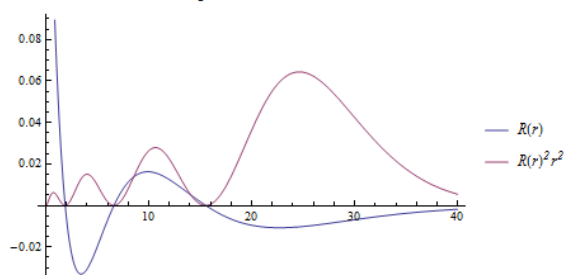


Radial function: $n = 4, l = 0$

$n-l-1 = 3, 2l+1 = 1$, associated Laguerre polynomial = $4(24-36x+20x^2-x^3)$

function $R_{n1}(r) = \frac{1}{768} e^{-r/4} (192-144r+24r^2-r^3)$

normalization integral = 1.0000000000000000



Radial function: $n = 4, l = 3$

$n-l-1 = 0, 2l+1 = 7$, associated Laguerre polynomial = 5040

function $R_{n1}(r) = \frac{e^{-r/4} r^3}{768\sqrt{35}}$

normalization integral = 1.0000000000000000

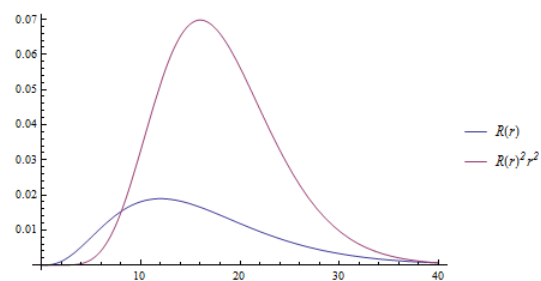


Figure 4. Sample plots of $R_{nl}(r)$ and $R_n^2(r)r^2$ for several combinations of n and l .

B. The angular function $Y(\theta, \varphi)$

The angular function $Y(\theta, \varphi) = Y_{l,m_l}(\theta, \varphi)$ is a function of two quantum numbers, l and m_l :

$$0 \leq l \leq n-1 \quad -l \leq m_l \leq +l \quad (83)$$

and is represented by *spherical harmonics* $Y_l^m(\theta, \varphi)$ [11]

$$Y_{l,m_l}(\theta, \varphi) = Y_l^m(\theta, \varphi) \quad (84)$$

Note that from now on we assume that $m = m_l$ which simplifies the notation. In mathematics, spherical harmonics $Y_l^m(\theta, \varphi)$ are the angular part of the solutions for the *Laplace equation* [12,13]:

$$\nabla^2 f(r, \theta, \varphi) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 f}{\partial \varphi^2} = 0 \quad (85)$$

Spherical harmonics $Y_l^m(\theta, \varphi)$ are normalized such that [14]

$$\int_0^{2\pi} \int_0^\pi Y_l^m(\theta, \varphi)^* Y_l^{m'}(\theta, \varphi) \sin \theta d\theta d\varphi = \delta_{ll'} \delta_{mm'} \quad (86)$$

where symbol “*” denotes complex-conjugate, and δ_{ij} is the Kronecker delta

$$\delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases} \quad (87)$$

Spherical harmonics $Y_l^m(\theta, \varphi)$ that obey equation (86) are often called *wavefunction-normalized*. The general form of $Y_l^m(\theta, \varphi)$ is given by [14,15,16,17]:

$$Y_l^m(\theta, \varphi) = (-1)^{m+|m|} \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\varphi} \quad (88)$$

where functions $P_l^m(x)$ are the *associated Legendre polynomials* [14,18]. Note that here we follow the notation used in Mathematica [6,19,20] according to which the Condon-Shortley phase $(-1)^m = (-1)^{|m|}$ [21] is included in the definition of the *associated Legendre polynomials* [22,14]

$$P_l^{|m|}(x) = (-1)^{|m|} (1-x^2)^{|m|/2} \frac{d^{|m|} P_l(x)}{dx^{|m|}} \quad (89)$$

$$P_l^{-|m|}(x) = (-1)^{|m|} \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(x)$$

which makes it unnecessary to include the Condon-Shortley phase in the definition of $Y_l^m(\theta, \varphi)$. Note that in the Arfken notation [12] the Condon-Shortley phase $(-1)^m = (-1)^{|m|}$ is included in the definition of $Y_l^m(\theta, \varphi)$, and thus excluded from the definition of the associated Legendre polynomial $P_l^m(x)$. The associated Legendre polynomials for the positive and negative values of m are related to each other via the following relationship:

$$P_l^m(x) = (-1)^{|m|} \frac{(l+m)!}{(l-m)!} P_l^{-m}(x) \quad (90)$$

which is valid regardless whether m is positive or negative. Equations (89) and (90) are consistent with Mathematica's function LegendreP[l, m, x]:

<https://reference.wolfram.com/language/ref/LegendreP.html>

The associated Legendre polynomials $P_l^m(x)$ are solutions to the *associated Legendre differential equation* [23]:

$$(1-x^2)\frac{d^2f(x)}{dx^2} - 2x\frac{df(x)}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2}\right]f(x) = 0 \quad (91)$$

where l is a positive integer and $m = 0, \dots, l$. The *associated Legendre polynomials* can be defined in terms of the ordinary (unassociated) *Legendre polynomials* $P_l(x)$ [24]:

$$P_l^m(x) = (-1)^m (1-x^2)^{m/2} \frac{d^m P_l(x)}{dx^m} \quad (92)$$

In mathematics, the *Legendre polynomials* are solutions to *Legendre's differential equation* [25]:

$$(1-x^2)\frac{d^2f(x)}{dx^2} - 2x\frac{df(x)}{dx} + l(l+1)f(x) = 0 \quad (93)$$

and can be generated using the *formula of Rodrigues*:

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n \quad (94)$$

In Mathematica, the ordinary (unassociated) Legendre polynomials $P_l(x)$ can be generated using the `LegendreP[l, x]` command:

<https://reference.wolfram.com/language/ref/LegendreP.html>

Fortunately, there is no need to struggle with the *associated Legendre polynomials*, *Legendre polynomials*, and the *Rodrigues formula* in Mathematica because it can readily generate spherical harmonics $Y_l^m(\theta, \phi)$ of any order using the `SphericalHarmonicY[l, m, \theta, \phi]` command:

<https://reference.wolfram.com/language/ref/SphericalHarmonicY.html>

What to do

There are several issues with plotting spherical harmonics as defined above. First, only functions with $m = 0$ are real - all other spherical harmonics contain imaginary components (try it now!). Second, these functions are defined in terms of angles (θ, ϕ) while most plots are usually done in the Cartesian frame (x, y, z) . Thus, rather than plotting complex spherical harmonics $Y_l^m(\theta, \phi)$, we are going to work with *real spherical harmonics* $y_l^m(\theta, \phi)$ which are the normalized *linear combinations* of complex spherical harmonics $Y_l^m(\theta, \phi)$ [26,27,28]

$$y_l^m(\theta, \phi) = \begin{cases} \frac{i}{\sqrt{2}} (Y_l^m(\theta, \phi) - (-1)^m Y_l^{|m|}(\theta, \phi)) & \text{if } m < 0 \\ Y_l^0(\theta, \phi) & \text{if } m = 0 \\ \frac{1}{\sqrt{2}} (Y_l^{-m}(\theta, \phi) + (-1)^m Y_l^m(\theta, \phi)) & \text{if } m > 0 \end{cases} \quad (95)$$

Upon the separation of a complex function $Y_l^m(\theta, \phi)$ into the real $\text{Re}[Y_l^m(\theta, \phi)]$ and imaginary $\text{Im}[Y_l^m(\theta, \phi)]$ parts, the *real spherical harmonic function* $y_l^m(\theta, \phi)$ can be also defined as [29]:

$$y_l^m(\theta, \phi) = \begin{cases} \sqrt{2} \text{Im}[Y_l^{|m|}(\theta, \phi)] & \text{if } m < 0 \\ Y_l^0(\theta, \phi) & \text{if } m = 0 \\ \sqrt{2} \text{Re}[Y_l^{|m|}(\theta, \phi)] & \text{if } m > 0 \end{cases} \quad (96)$$

The real spherical harmonics $y_l^m(\theta, \varphi)$ have the same orthonormality properties (equation 86) as $Y_l^m(\theta, \varphi)$:

$$\int_0^{2\pi} \int_0^\pi y_l^m(\theta, \varphi) y_l^{m'}(\theta, \varphi) \sin \theta d\theta d\varphi = \delta_{ll'} \delta_{mm'} \quad (97)$$

The real spherical harmonics with $m > 0$ differ from those with $m < 0$ by multiplication of the *cosine* or *sine* functions, respectively:

$$y_l^{|m|}(\theta, \varphi) = N_{lm} P_l^{|m|}(\cos \theta) \cos(|m|\varphi) \quad (98)$$

$$y_l^{-|m|}(\theta, \varphi) = N_{lm} P_l^{|m|}(\cos \theta) \sin(|m|\varphi)$$

$$y_l^0(\theta, \varphi) = N_{lm} P_l^0(\cos \theta)$$

where

$$N_{lm} = \left[\frac{(2l+1)}{2(1+\delta_{m,0})\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} \quad (99)$$

, and functions $P_l^m(x)$ are the associated Legendre polynomials [6,14,19], or simply as:

$$y_l^m(\theta, \varphi) = (-1)^{|m|} N_{l,m} P_l^{|m|}(\cos \theta) \begin{cases} \cos(|m|\varphi), m > 0 \\ \sin(|m|\varphi), m < 0 \\ 1, m = 0 \end{cases} \quad (100)$$

where $\delta_{i,j}$ is the Kronecker delta function. The functions

$$P_l^{|m|}(\cos \theta) \begin{cases} \cos(|m|\varphi) \\ \sin(|m|\varphi) \end{cases} =: T_l^m(\theta, \varphi) \quad (101)$$

are often called the *tesseral harmonics* [22,30,31]. Note that because no well-established notation exists for *tesseral harmonics*, we shall denote these functions as $T_l^m(\theta, \varphi)$.

Now define the *real spherical harmonics* function using any definition given above. We like the Which[] command because it allows several tests to be performed in sequence:

<https://reference.wolfram.com/language/ref/Which.html>

The second step is to convert *real spherical harmonics* $y_l^m(\theta, \varphi)$ from the spherical coordinate system (θ, φ) to the Cartesian frame (x, y, z) . It is not very difficult. The spherical harmonics, both the real and complex, can be transformed from the spherical coordinate system (r, θ, φ) to the Cartesian frame (x, y, z) using well-known relationships [12]:

$$\begin{aligned} x &= r \sin \theta \cos \varphi \\ y &= r \sin \theta \sin \varphi \\ z &= r \cos \theta \end{aligned} \quad (102)$$

where $\theta \in [0, \pi]$ and $\varphi \in [0, 2\pi)$.

Of course, the reverse transformations are given by

$$\begin{aligned} r &= (x^2 + y^2 + z^2)^{1/2} \\ \cos \theta &= \frac{z}{(x^2 + y^2 + z^2)^{1/2}} = \frac{z}{r} \\ \tan \varphi &= \frac{y}{x} \end{aligned} \tag{103}$$

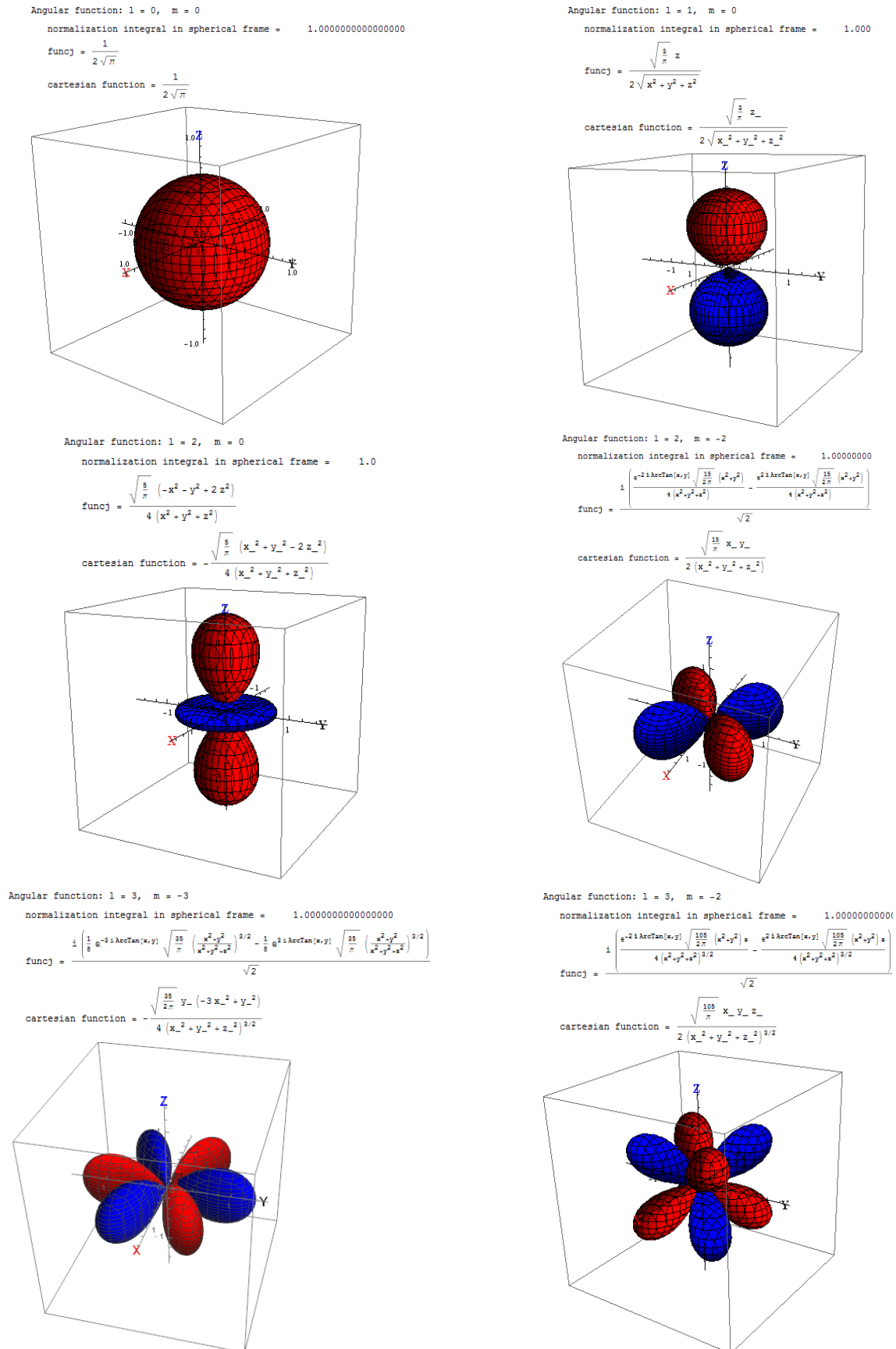
Now define (θ, φ) in terms of (x, y, z) in Mathematica, and plug those into the expression for *real spherical harmonics* $y_l^m(\theta, \varphi)$. Let Mathematica `FullSimplify[]` the expressions

<https://reference.wolfram.com/language/ref/FullSimplify.html>

and you get a nice and clean representation of real spherical harmonics in Cartesian frame $y_l^m(x, y, z)$. For each function generated verify its normalization, i.e. calculate (analytically or numerically) integral (97) in either Cartesian frame (by integrating over x , y , and z) or spherical frame (by integrating over θ and φ). Now augment the resulting functions with a simple exponential e^{-r} and use the `ContourPlot3D[]` command:

<https://reference.wolfram.com/language/ref/ContourPlot3D.html>

to produce three-dimensional isosurface (isocontour) plots of the *real Cartesian spherical harmonics* $y_l^m(x, y, z)$ for $0 \leq l \leq 3$ and all allowed values of m . Use the **blue color** to represent the negative isosurface, and **red** for positive. Also, plot the Cartesian axes X , Y , and Z centered at $(0,0,0)$, and label them. Several sample plots are shown in Figure 5.

Figure 5. Sample plots of $y_l^m(x, y, z)$ for several allowed combinations of l and m .

C. The complete hydrogen wavefunction

The complete hydrogen wavefunctions are given by

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_l^m(\theta, \varphi) \quad (104)$$

The normalization condition is

$$\int_0^\infty r^2 \int_0^\pi \sin \theta \int_0^{2\pi} \psi_{nlm}^*(r, \varphi, \theta) \psi_{nlm}(r, \theta, \varphi) d\varphi d\theta dr = 1 \quad (105)$$

Because the Hamiltonian operator \hat{H} is Hermitian, the functions $\psi_{nlm}(r, \theta, \varphi)$ must also be orthogonal. This orthogonality relationship is given by

$$\int_0^\infty r^2 \int_0^\pi \sin \theta \int_0^{2\pi} \psi_{n'l'm'}^*(r, \varphi, \theta) \psi_{nlm}(r, \theta, \varphi) d\varphi d\theta dr = \delta_{nn'} \delta_{ll'} \delta_{mm'} \quad (106)$$

where δ 's are Kronecker deltas.

What to do

Note that for plotting purposes we should replace complex spherical harmonics in the spherical coordinate system $Y_l^m(\theta, \varphi)$ with real spherical harmonics in the Cartesian frame $y_l^m(x, y, z)$, thus creating a Cartesian representation of the complete hydrogen wavefunction $\psi_{nlm}(x, y, z)$. It does not make much sense to plot these in 3D using `ContourPlot3D[]` because the internal structure given by $R_{nl}(r)$ will be lost - we would only see the angular part (i.e. spherical harmonics). So, what you need to do is create 2D plots of $\psi_{nlm}(x, y, z)$ for $1 \leq n \leq 4$ (and all allowed combinations of l and m) in the three main Cartesian planes (x, y) , (x, z) and (y, z) . Use either the contour representation `ContourPlot[]`:

<https://reference.wolfram.com/language/ref/ContourPlot.html>

or the probability density representation `DensityPlot[]`

<https://reference.wolfram.com/language/ref/DensityPlot.html>

, whichever you like. Label coordinate axes. Make sure that for each combination n , l and m the three plots are located next to each other (use command `Row`). In addition, verify the normalization of each $\psi_{nlm}(x, y, z)$ or $\psi_{nlm}(r, \theta, \varphi)$ by appropriate integration in the Cartesian or spherical coordinate system, respectively. Several sample plots are shown in Figure 6.

That's it!

Submit your project file to D2L by the due date/time.

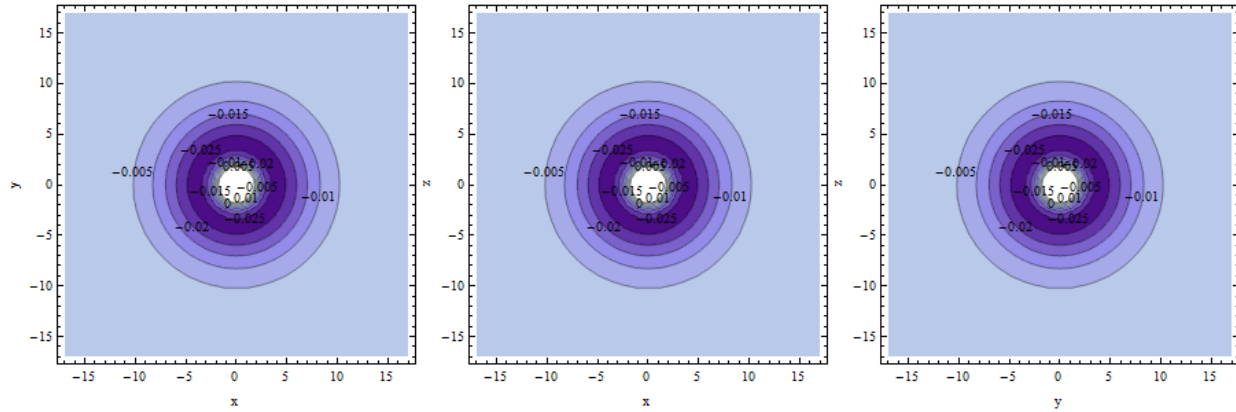
ψ for $n = 2, l = 0, m = 0$

$$\text{radial function} = \frac{e^{-\frac{r_-}{2}} (2 - r_-)}{2\sqrt{2}}$$

$$\text{angular function} = \frac{1}{2\sqrt{\pi}}$$

$$\text{total function} = -\frac{e^{-\frac{1}{2}\sqrt{x_-^2 + y_-^2 + z_-^2}} (-2 + \sqrt{x_-^2 + y_-^2 + z_-^2})}{4\sqrt{2\pi}}$$

normalization check = 0.9999999832240090



a) $n = 2, l = 0, m = 0$

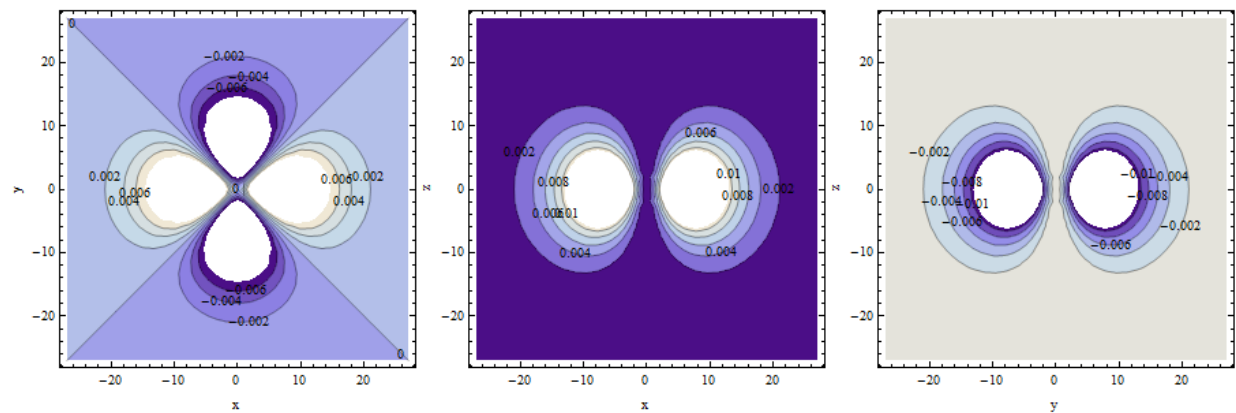
ψ for $n = 3, l = 2, m = 2$

$$\text{radial function} = \frac{2}{81} \sqrt{\frac{2}{15}} e^{-\frac{r_-}{3}} r_-^2$$

$$\text{angular function} = \frac{\frac{e^{-2i \arctan[x,y] \sqrt{\frac{15}{2\pi}} (x^2+y^2)}}{4(x^2+y^2+z^2)} + \frac{e^{2i \arctan[x,y] \sqrt{\frac{15}{2\pi}} (x^2+y^2)}}{4(x^2+y^2+z^2)}}{\sqrt{2}}$$

$$\text{total function} = \frac{e^{-\frac{1}{3}\sqrt{x_-^2 + y_-^2 + z_-^2}} (x_-^2 - y_-^2)}{81\sqrt{2\pi}}$$

normalization check = 0.9999999934371880



b) $n = 3, l = 2, m = 2$

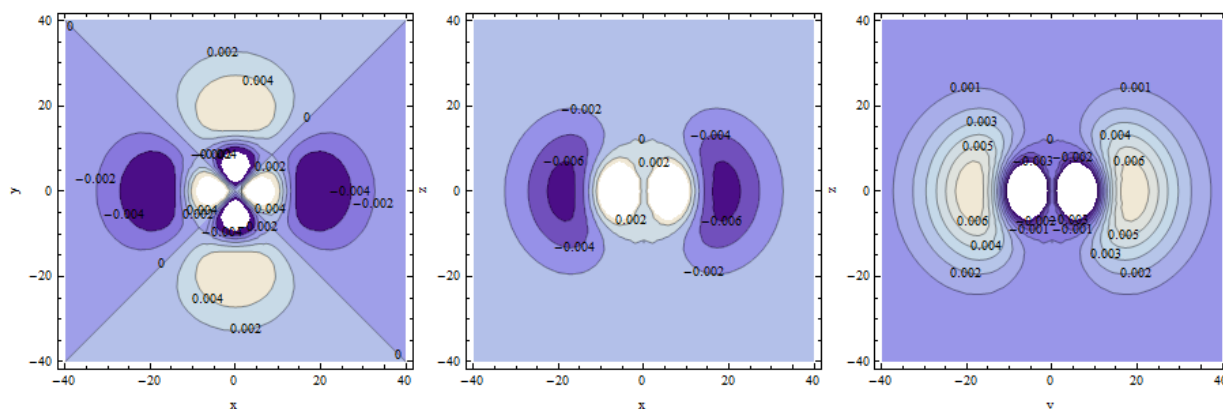
ψ for $n = 4, l = 2, m = 2$

$$\text{radial function} = \frac{e^{-\frac{r}{4}} \left(6 - \frac{r}{2}\right) r^2}{384 \sqrt{5}}$$

$$\text{angular function} = \frac{\frac{e^{-2i \text{ArcTan}[x,y]} \sqrt{\frac{15}{2\pi}} (x^2+y^2)}{4 (x^2+y^2+z^2)} + \frac{e^{2i \text{ArcTan}[x,y]} \sqrt{\frac{15}{2\pi}} (x^2+y^2)}{4 (x^2+y^2+z^2)}}{\sqrt{2}}$$

$$\text{total function} = -\frac{e^{-\frac{1}{4}\sqrt{x^2+y^2+z^2}} (x^2 - y^2) (-12 + \sqrt{x^2+y^2+z^2})}{1024 \sqrt{3\pi}}$$

$$\text{normalization check} = 0.9999999958062230$$



c) $n = 4, l = 2, m = 2$

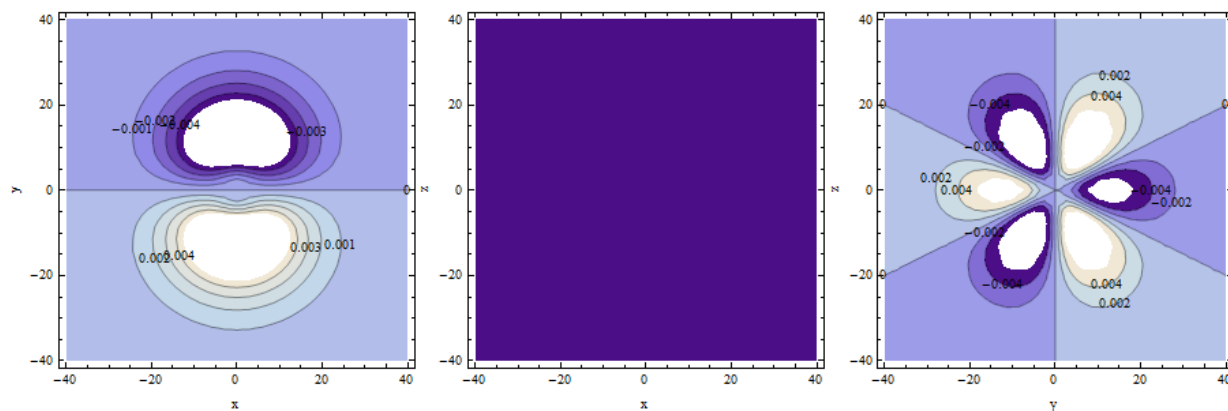
ψ for $n = 4, l = 3, m = -1$

$$\text{radial function} = \frac{e^{-\frac{r}{4}} r^3}{768 \sqrt{35}}$$

$$\text{angular function} = \frac{1}{\sqrt{2}} \left[-\frac{e^{-i \text{ArcTan}[x,y]} \sqrt{\frac{21}{\pi}} (x^2+y^2-4z^2) \sqrt{\frac{x^2+y^2}{x^2+y^2+z^2}}}{8 (x^2+y^2+z^2)} + \frac{e^{i \text{ArcTan}[x,y]} \sqrt{\frac{21}{\pi}} (x^2+y^2-4z^2) \sqrt{\frac{x^2+y^2}{x^2+y^2+z^2}}}{8 (x^2+y^2+z^2)} \right]$$

$$\text{total function} = -\frac{e^{-\frac{1}{4}\sqrt{x^2+y^2+z^2}} y_- (x_-^2 + y_-^2 - 4z_-^2)}{1024 \sqrt{30\pi}}$$

$$\text{normalization check} = 1.0000000038829990$$



d) $n = 4, l = 3, m = -1$

Figure 6. Sample plots of $\psi_{nlm}(x, y, z)$ for several allowed combinations of n, l , and m .

Note that in the xz plane ($y=0$) in **d**) the function is zero for *any* combination of x and z .

Such plane is called a ‘nodal plane’ – you should see quite a few of those.

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