Schrodinger Equation — Three Dimensions

The Hydrogen Atom

Completed and Analyzed in class, May 2, 2025

This is our last notebook. In the previous notebook, we did Schrodinger's equation for a free particle confined to a two-dimensional disk. The idea was to show you a problem that has some of the flavor of the full three-dimensional problem.

Now we will do analyze the most famous three-dimensional problem in quantum mechanics: the Hydrogen atom.

Time-Independent Schrodinger Equation in Three Dimensions

To go to three dimensions we now have second derivatives with respect to x, y, and z:

```
In[83]:=  - ℏ²/(2 μ) (Derivative[2, 0, 0][ψ][x, y, z] +

              Derivative[0, 2, 0][ψ][x, y, z] + Derivative[0, 0, 2][ψ][x, y, z]) +
          potential[x, y, z] × ψ[x, y, z] == energy ψ[x, y, z]  // TraditionalForm
```

Out[83]//TraditionalForm=

$$\text{potential}(x, y, z)\, \psi(x, y, z) - \frac{\hbar^2 \left(\psi^{(0,0,2)}(x, y, z) + \psi^{(0,2,0)}(x, y, z) + \psi^{(2,0,0)}(x, y, z) \right)}{2 \mu} = \text{energy}\, \psi(x, y, z)$$

Spherical Polar Coordinates

Just as in Harper and Tahm's External Rifle Ballistics notebook, it makes a load of progress toward a solution to switch to the spherical polar coordinates. The Wikipedia has a nice graphic:
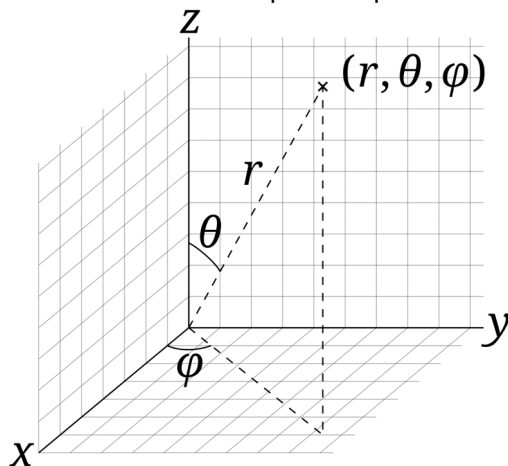
The only thing to note about the Wikipedia's graphic is that we usually have the *x*-coordinate pointing right, and the *y*-coordinate going into the paper, so you have to imagine rotating the coordinates by 90° (counter-clockwise looking down on the $x - y$ plane), relative to what they have shown.

Now that we know what polar coordinates are, there is another, even nastier calculation that determines how the sum of three second derivatives becomes a sum of derivatives with respect to *r*, *θ*, and *φ*:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r}\frac{\partial \psi}{\partial r} + \frac{1}{r^2 \sin^2 \theta}\left(\sin\theta\frac{\partial^2 \psi}{\partial \theta^2} + \cos\theta\frac{\partial \psi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2 \theta}\frac{\partial^2 \psi}{\partial \phi^2}$$

Of course, I am not going to mess with that. You just have to trust that this combination of derivatives is what comes out of a lot of multi-variable calculus steps.

Electron Orbiting a Hydrogen Nucleus

The above theory lets us rewrite, in polar coordinates, the time-independent Schrodinger equation for an electron orbiting a Hydrogen nucleus:

In[84]:=
```
hydrogenAtomProblem = Module[{ℏ = 1, μ = 1},
    - ℏ²/2 μ (Derivative[2, 0, 0][ψ][r, θ, ϕ] + 2/r Derivative[1, 0, 0][ψ][r, θ, ϕ] +
         1/r² Sin[θ]² (Sin[θ] Derivative[0, 2, 0][ψ][r, θ, ϕ] +
            Cos[θ] Derivative[0, 1, 0][ψ][r, θ, ϕ]) +
         1/r² Sin[θ]² Derivative[0, 0, 2][ψ][r, θ, ϕ]) + potential[
        r] × ψ[r, θ, ϕ] == energy ψ[r, θ, ϕ]];
```

Typesetting this equation for Mathematica makes it look even more complicated than it already is, so here is a screenshot of the combination of second derivatives from Howie Haber's UC Santa Cruz Physics 116C class that uses some special notation to make the second-derivatives especially elegant:

In spherical coordinates, the Laplacian is given by

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

The Great Simplification Again — Separation of Variables

Once again our next step is the "separation of variables" trick. We ***guess*** that $\psi(r, \theta, \phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$.

To save myself a boatload of typesetting, I am again going to screenshot Howie Haber's notes:

We shall solve Laplace's equation,

$$\vec{\nabla}^2 T(r, \theta, \phi) = 0, \tag{2}$$

using the method of separation of variables, by writing

$$T(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi).$$

Inserting this decomposition into the Laplace equation and multiplying through by $r^2/R\Theta\Phi$ yields

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Theta}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{d^2\Phi}{d\phi^2} = 0.$$

Hence,

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = -m^2, \tag{3}$$

where $-m^2$ is the separation constant, which is chosen negative so that the solutions for $\Phi(\phi)$ are periodic in ϕ,

$$\Phi(\phi) = \begin{cases} e^{im\phi} \\ e^{-im\phi} \end{cases} \qquad \text{for } m = 0, 1, 2, 3, \ldots.$$

Note that m must be an integer since ϕ is a periodic variable and $\Phi(\phi + 2\pi) = \Phi(\phi)$. In the case of $m = 0$, the general solution is $\Phi(\phi) = a\phi + b$, but we must choose $a = 0$ to be consistent with $\Phi(\phi + 2\pi) = \Phi(\phi)$. Hence in the case of $m = 0$, only one solution is allowed.

One can now recast eq. (3) in the following form,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = -\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m^2}{\sin^2\theta} = \ell(\ell+1), \tag{4}$$

Adding the Boundary Conditions — Quantum Numbers

Some of the boundary conditions have already been mentioned in the screenshotted notes above. In particular, we have to have $\Phi(2\pi) = \Phi(0)$. Another boundary condition is that the wave function has to vanish as $r \to \infty$. Another boundary condition is that at $r = 0$ where the nucleus is, the wave function can blow up, but only in a very controlled way. The reason it can blow up at all is that the potential is the Coulomb potential which is

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

and this potential blows up at $r = 0$. I mention these boundary conditions, because without them you would have no idea statements like m must be an integer comes from. You have now worked with boundary conditions enough to know that they commonly force a discrete set of solutions.

You will see that there are three integers in the exact solutions of the Hydrogen atom. They correspond to the total energy, the total angular momentum, and the component of the angular momentum around the axis that we have chosen as the polar axis in our polar coordinates. These integers are

called *"quantum numbers."*

The quantum numbers are important because you have to specify them in order to specify which solution of the Schrodinger Equation for the Hydrogen atom you are talking about, and equally important, because they correspond to important physical quantities. The are usually denoted as n, l, and m, and their direct correspondence is to the energy, the angular momentum, and the component of the angular momentum in the z-direction of the electron orbiting the Hydrogen nucleus. As we get into the exact solutions, this will become clearer.

The Exact Solutions — Spherical Harmonics

Without further ado, let's start writing down the exact solutions. Thanks to the separation of variables trick, they can be written as $R(r)\,\Theta(\theta)\,\Phi(\phi)$, but $\Theta(\theta)\,\Phi(\phi)$ portion is usually grouped together to make functions of θ and ϕ known as the "spherical harmonics." Traditionally they are written as $Y_l^m(\theta, \phi)$ and happily, Mathematica knows these functions. For example, here is the function with $l = 3$ and $m = 1$:

In[85]:= `SphericalHarmonicY[3, 1, θ, ϕ]`

Out[85]=

$$-\frac{1}{8}\, e^{i\,\phi}\, \sqrt{\frac{21}{\pi}}\, \left(-1 + 5\,\mathrm{Cos}[\theta]^2\right)\,\mathrm{Sin}[\theta]$$

The ϕ-dependence is pleasantly simple, it is just $e^{im\phi}$ which in this case, with $m = 1$, is just $e^{i\phi}$. When you do the complex absolute value of a spherical harmonic, the ϕ-dependence goes away. That means that

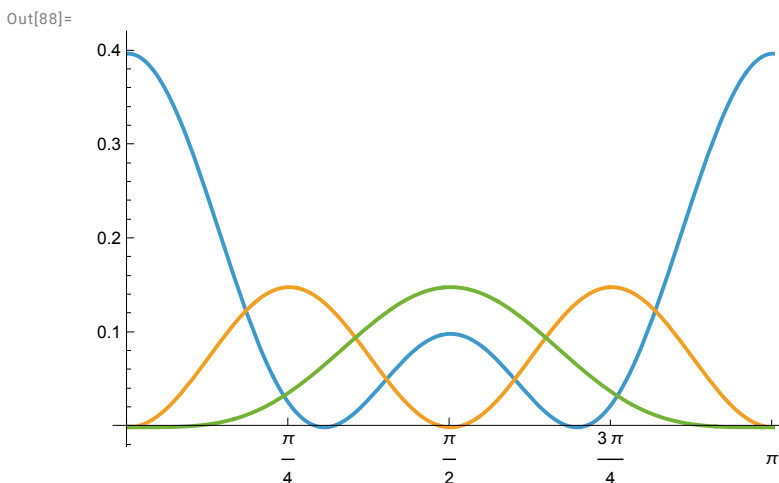In[86]:= `(* Abs[SphericalHarmonicY[3,1,θ,ϕ]]`^{2}`:=Abs[SphericalHarmonicY[3,1,θ,0]]`^{2} `*)`

Since we'll be squaring these a lot let's have a shorthand:

In[87]:= `ylmSquared[l_, m_, θ_] := Abs[SphericalHarmonicY[l, m, θ, 0]]`^{2}

Let's plot a few of these from the north pole ($\theta = 0$) to the south pole ($\theta = \pi$):

In[88]:= `Plot[{ylmSquared[2, 0, θ], ylmSquared[2, 1, θ], ylmSquared[2, 2, θ]},`
   `{θ, 0, Pi}, Ticks → {{0, Pi / 4, Pi / 2, 3 Pi / 4, Pi}, Automatic}]`

Out[88]=

Further down in this notebook, we will be doing three-dimensional visualizations, so don't think you have to glean too much from the above plots.

The Exact Solutions — Radial Wave Functions

```
In[89]:= R[n_, l_, r_] := 2/n² Sqrt[Factorial[n - 1 - l]/Factorial[n + l]³] (2 r/n)^l

         Exp[-r / n] Factorial[n + l] LaguerreL[n - l - 1, 2 l + 1, 2 r / n];
```
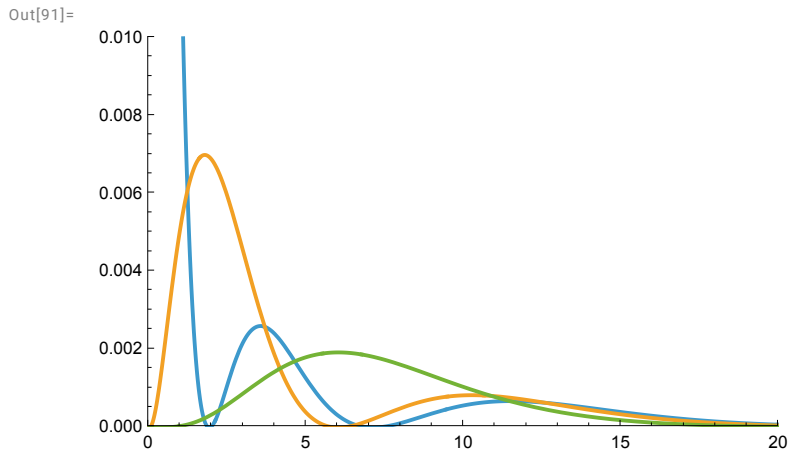
We'll be squaring these too, so it might be handy to define:

```
In[90]:= rnlSquared[n_, l_, r_] := Abs[R[n, l, r]]²
```

Let's look at a few with $n = 3$, and $l = 0, 1,$ and 2.

```
In[91]:= Plot[{rnlSquared[3, 0, r], rnlSquared[3, 1, r], rnlSquared[3, 2, r]},
         {r, 0, 20}, Ticks → {Range[0, 10, 1], 0, 1}, PlotRange → {{0, 20}, {0, 0.01}}]
```

Out[91]=

When someone starts jabbering away about orbital shells, it is these functions that they are referring to.

Normalization

The super-messy formulas above were messy in part because these solutions are normalized, so thankfully, there is no further messiness due to normalization.

Allowed Quantum Numbers and Total Energy

Not all combinations of quantum numbers n, l, and m are allowed. The only ones that correspond to solutions are in these these ranges:

$n = 1, 2, 3, 4,$ etc.
$l = 0, 1, 2, ..., n - 1$
$m = -l, -l + 1, ..., -1, 0, 1, ..., l - 1, l$

The total energy is entirely determined by the value of n and if you choose all the units conveniently the

$$-\frac{1}{n^2}$$

$\boldsymbol{n}$

$n = 1, 2, 3, 4,$ etc.

$l = 0, 1, 2, ..., n - 1$

$m = -l, -l + 1, ..., -1, 0, 1, ..., l - 1, l$

total energy is just $-\frac{1}{n^2}$. ***All you need to know to know the energy is n, so it is known as the "principle quantum number."***

You might be wondering what a minus sign is doing in the total energy. It is there because the Coulomb potential is attractive and it gets more and more negative as the electron gets closer to the nucleus. So there is positive kinetic energy and negative potential energy, and the latter outweighs the former.

If you had an electron with total positive energy (kinetic plus potential), it would fly away from the Hydrogen atom (leaving the proton sitting alone, as a positive ion). A bound electron has negative total energy.

Visualization — s, p, d, and f Orbitals for the $n = 4$ Principle Quantum Number

The s, p, d, and f orbitals are old names for the $l = 0$, $l = 1$, $l = 2$, and $l = 3$ spherical harmonics. The history is that when experimentalists were discovering the spectral lines of Hydrogen, they named them "sharp," "principle," "diffuse," and "fine."

The $l = 0$ orbitals aren't very interesting to visualize because they are spherically symmetric. However, ***because I have chosen n = 4*** (which is a little uncommon)***, there is nevertheless some interesting structure in the density plot.***

In[92]:= `DensityPlot3D[rnlSquared[4, 0, ToSphericalCoordinates[{x, y, z}]〚1〛]` ×
`  ylmSquared[0, 0, ToSphericalCoordinates[{x, y, z}]〚2〛],`
`  {x, -30, 30}, {y, -30, 30}, {z, -30, 30}]`
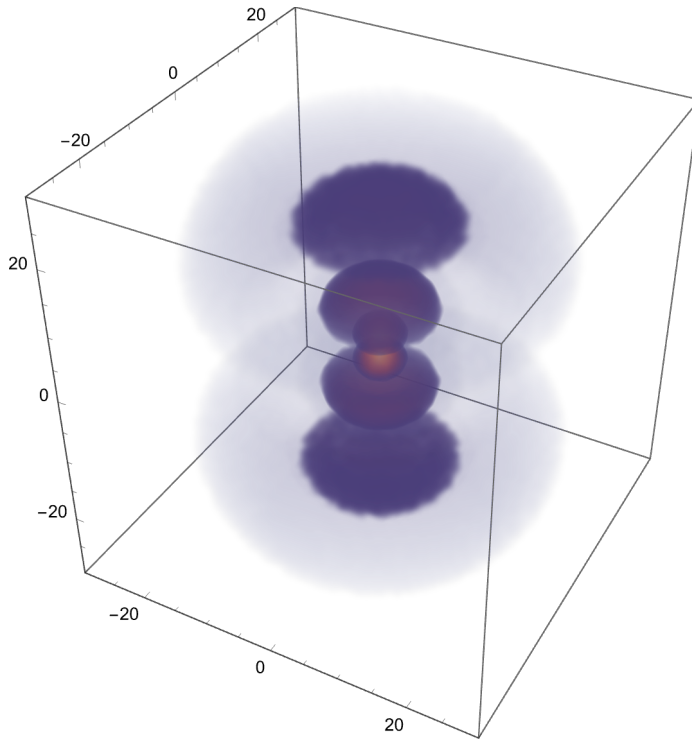
Out[92]=
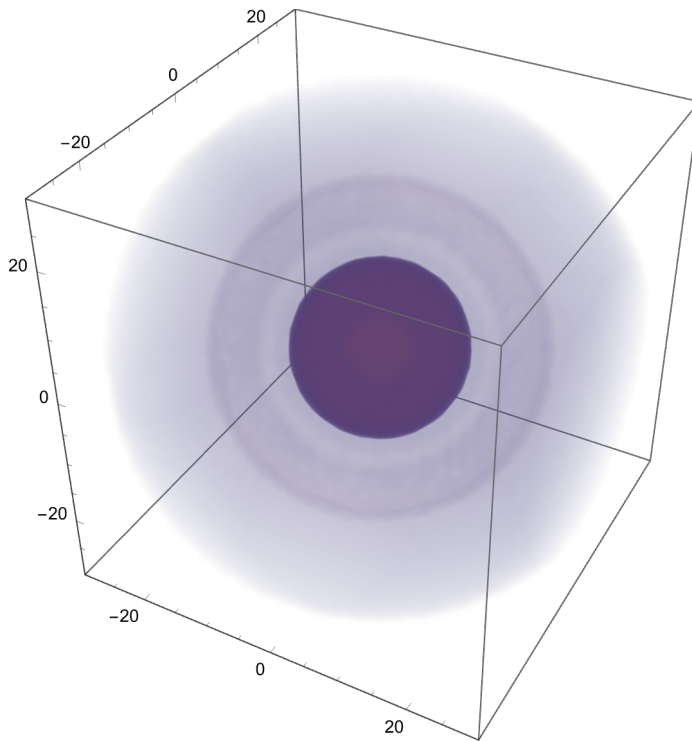
If $n = 4$, then $l = 0$, $l = 1$, $l = 2$, and $l = 3$ are allowed, and so $n = 4$, $l = 1$ is the first interesting orbital to visualize. They can have $m = -1$, 0, or $+1$.

Let's see if we can visualize the $n = 4$, $l = 1$, $m = 0$ probability distribution:

In[93]:= `DensityPlot3D[rnlSquared[4, 1, ToSphericalCoordinates[{x, y, z}]⟦1⟧]` ×
`    ylmSquared[1, 0, ToSphericalCoordinates[{x, y, z}]⟦2⟧],`
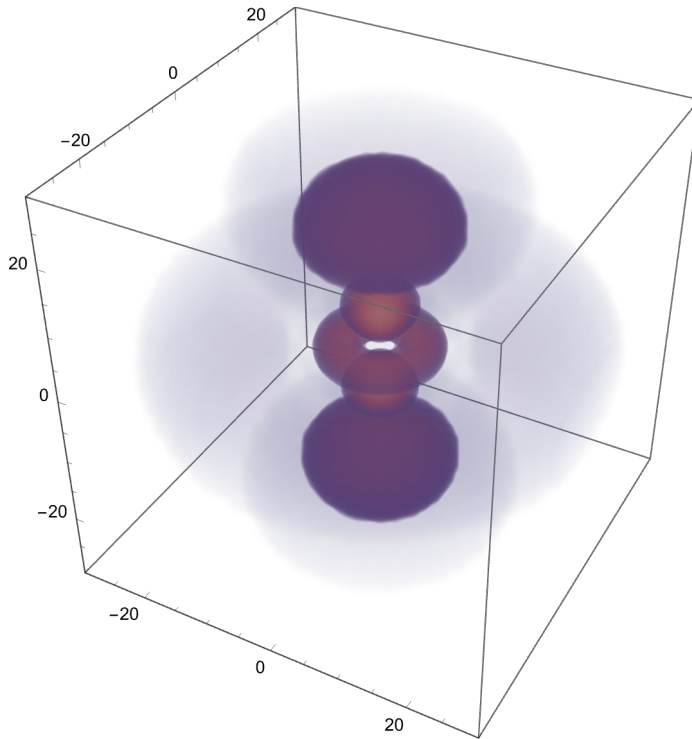`  {x, -30, 30}, {y, -30, 30}, {z, -30, 30}]`

Out[93]=

To do *d* orbitals, we can try the $n = 4$, $l = 2$, $m = 0$ probability distribution:

In[94]:= `DensityPlot3D[rnlSquared[4, 2, ToSphericalCoordinates[{x, y, z}]〚1〛] ×`
    `ylmSquared[2, 0, ToSphericalCoordinates[{x, y, z}]〚2〛],`
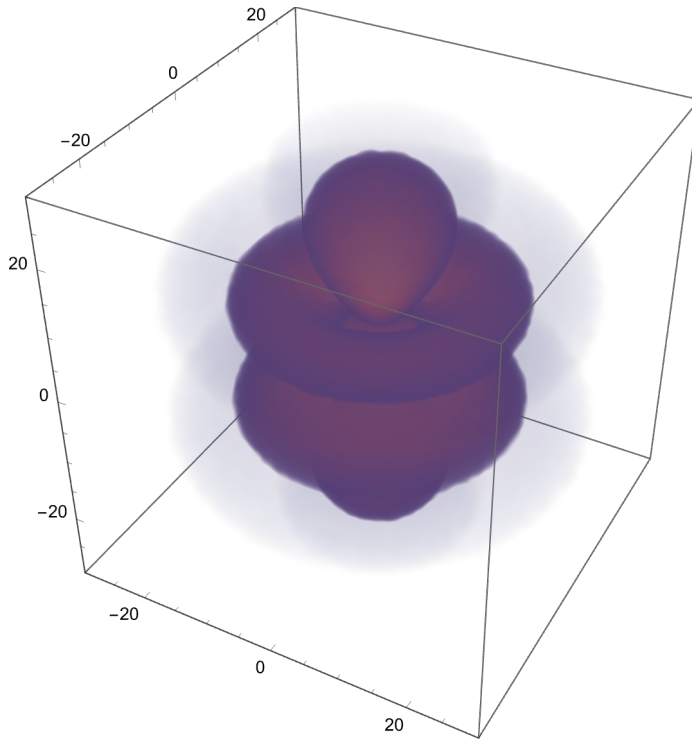 `{x, -30, 30}, {y, -30, 30}, {z, -30, 30}]`

Out[94]=

To do f orbitals, we can try the $n = 4$, $l = 3$, $m = 0$ probability distribution:

In[95]:= `DensityPlot3D[rnlSquared[4, 3, ToSphericalCoordinates[{x, y, z}]〚1〛]` ×
`  ylmSquared[3, 0, ToSphericalCoordinates[{x, y, z}]〚2〛],`
` {x, -30, 30}, {y, -30, 30}, {z, -30, 30}]`

Out[95]=

These are famous shapes (although to level the energy playing field I have always chosen $n = 4$ which again I should mention is a little uncommon). Physical chemists spend a lot of time trying to figure out what molecules are likely to form based on how these shapes might interlock with neighboring shapes.

Time-Dependence

To get time-dependence, we are going to have to make mixtures (superpositions) of quantum states with different energies. Also, this is going to necessitate dealing with the full complex values. Let's try a mixture of $n = 2$, $l = 1$, and $m = +1$, $n = 1$, $l = 0$, and $m = 0$, and $n = 2$, $l = 1$, and $m = -1$ and see what we get.

In[161]:=

```
mixture[t_, r_, θ_, ϕ_] :=
  1
  ─ Exp⎡Sqrt[-1] ─ t⎤ R[2, 1, r] SphericalHarmonicY[2, 1, θ, ϕ] +
  2   ⎣        4 ⎦
       1
     ──────── Exp[Sqrt[-1] t] R[1, 0, r] SphericalHarmonicY[1, 0, θ, ϕ] +
     Sqrt[2]
  1            1
  ─ Exp⎡Sqrt[-1] ─ t⎤ R[2, 1, r] SphericalHarmonicY[2, -1, θ, ϕ];
  2   ⎣        4 ⎦
```

`mixtureSquared[t_, r_, θ_, ϕ_] := Abs[mixture[t, r, θ, ϕ]]`^{2}

Three-dimensional plots are going to be expensive to animate, so let's confine ourselves to the $θ = π/2$

plane and do two-dimensional plots. To further conserve computational power, I am going to pre-render these for 40 time steps:
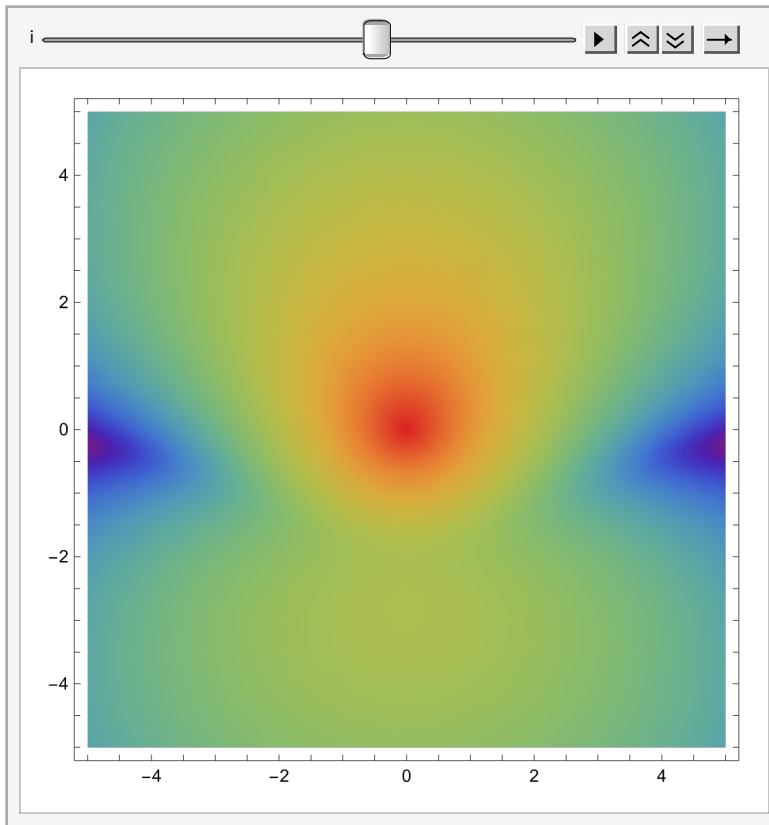
In[167]:=

```
prerenders =
  Array[DensityPlot[Log[mixtureSquared[(# - 1) (8 Pi)/(3 × 40), ToPolarCoordinates[{x, y}]〚1〛,
      Pi/2, ToPolarCoordinates[{x, y}]〚2〛]], {x, -5, 5},
    {y, -5, 5}, MaxRecursion → 6, PerformanceGoal → "Quality",
    ClippingStyle → Automatic, ColorFunction → "Rainbow"] &, 40];
```

Once the pre-rendering finishes, we'll try animation:

In[168]:=

```
Animate[prerenders〚i〛, {i, 1, 40, 1}, AnimationRunning → False]
```

Out[168]=

I of course should continue working on the quality of this output if I really want it to show up and down motion well. The flashing is artifacts.

In addition to seeing wave functions going up and down in the *y*-direction, we should be able to see them going around:

In[169]:=

```
anotherMixture[t_, r_, θ_, ϕ_] :=
    1
   ——— Exp[Sqrt[-1] 1/4 t] R[2, 1, r] SphericalHarmonicY[2, 1, θ, ϕ] +
  Sqrt[2]

    1
   ——— Exp[Sqrt[-1] t] R[1, 0, r] SphericalHarmonicY[1, 0, θ, ϕ];
  Sqrt[2]

anotherMixtureSquared[t_, r_, θ_, ϕ_] := Abs[anotherMixture[t, r, θ, ϕ]]^2


morePrerenders = Array[DensityPlot[Log[anotherMixtureSquared[(# - 1) 8 Pi/(3 × 40),

      ToPolarCoordinates[{x, y}][[1]], Pi/2, ToPolarCoordinates[{x, y}][[2]]]],

    {x, -5, 5}, {y, -5, 5}, MaxRecursion → 6, PerformanceGoal → "Quality",
    ClippingStyle → Automatic, ColorFunction → "Rainbow"] &, 40];


Animate[morePrerenders[[i]], {i, 1, 40, 1}, AnimationRunning → False]
```

Out[172]=
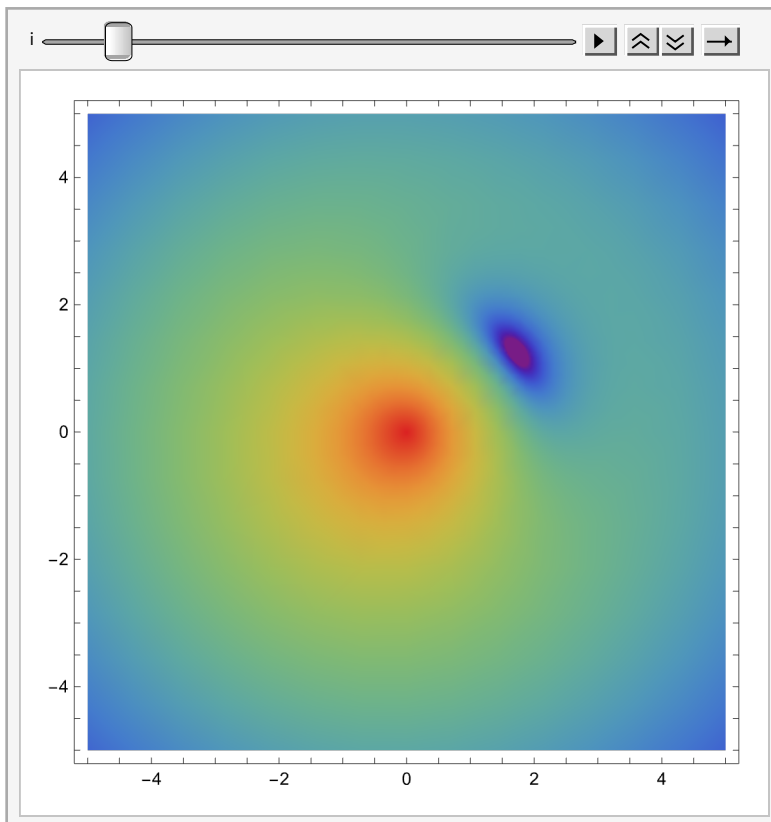
Again there are artifacts that could be improved upon, but I was pleased to actually get an electron going in a circle, and I hope you are too.

Conclusion (What was the Point?)

If you think stuff like this is insanely cool, you might want to spend a few years getting a degree in physics.

If on the other hand, it is nice, but you have had enough and would rather do something else, then the point of all this was to quickly expose you to some mathematics and problem solutions that you are very unlikely to see unless you become a physicist or a physical chemist. Oscillations and waves are everywhere around us, and you have now seen behind the curtain, with Mathematica's help in doing large amounts of algebra and computation, into some things that are otherwise not easily revealed.