Let's solve the Hydrogen Atom!

Step 1: Expressing the Schrödinger equation for the H atom

We begin with the basic, 3-dimensional, form for the Schrödinger equation for an electron within an electostatic potential, $V = -k\frac{e^2}{r}$, produced by the proton.

$$E\psi = -\frac{\hbar^2}{2m_e}\nabla^2\psi - k\frac{e^2}{r_e}\psi. \tag{1}$$

The Laplacian, $\nabla^2 = \vec{\nabla}\cdot\vec{\nabla}$, in Cartesian coordinates takes the simple form $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. However, the system at hand has spherical symmetry (specifically, the potential does) and thus spherical coordinates are the more natural units to use in this case. Thus, the first major task is to express the Schrödinger equation in spherical coordinates. Before that there is one small adjustment to make to the mass.

1a: Reduced mass, m

The first form introduced considered an electron of mass m orbiting a proton (of mass M), but considered the proton to be fixed. However, as in any orbiting system the objects orbit about the center of mass. Thus both the proton and electron will be in motion about this point (excuse the overly classical phrasing there). Realistically, we ought to be considering a *two object* system. So let's rewrite the equation to take both into account,

$$i\hbar\Psi(r_p, r_e, t) = -\frac{\hbar^2}{2m_p}\nabla_p^2\Psi(r_p, r_e, t) - \frac{\hbar^2}{2m_e}\nabla_e^2\Psi(r_p, r_e, t) - k\frac{e^2}{|r_e - r_p|}\Psi(r_p, r_e, t). \tag{2}$$

Where we have returned to the full time-dependent form for a moment. Well, this does not look like fun! It's a seven dimensional partial differential equation.[1] As in classical mechanics it's more useful to transform to enter of mass coordinates. Thus we define,

$$\begin{aligned}
R &= \frac{m_p r_p + m_e r_e}{m_p + m_e} && \text{position of center of mass.}\\
r &\equiv r_e - r_p && \text{relative position}\\
P &\equiv p_p + p_e && \text{total momentum}\\
p &= \frac{m_e p_p - m_p p_e}{m_p + m_e} && \text{“relative momentum”.}\\
M &= m_p + m_e && \text{total mass} \quad (= 938.272 + 0.51099\ MeV/c^2 = 938.783\ MeV/c^2)\\
m &= \frac{m_e m_p}{m_e + m_p} && \text{reduced mass} \quad \left(= \frac{479.448}{938.783} = 0.5107\ MeV/c^2\right)
\end{aligned}$$

With these definitions we can transform to the center of mass frame. You can verify the following (see appendix A),

$$\frac{p_e^2}{2m_e} + \frac{p_p^2}{2m_p} = \frac{p^2}{2m} + \frac{P^2}{2M} \tag{3}$$

We can now express the Schrödinger equation in terms of the coordinates R and r,

$$i\hbar\Phi(r, R, t) = -\frac{\hbar^2}{2M}\nabla_R^2\Phi(r, R, t) - \frac{\hbar^2}{2m}\nabla_r^2\Phi(r, R, t) - k\frac{e^2}{r}\Phi(r, R, t). \tag{4}$$

Since the potential is not a function of the center of mass coordinate R, this is a separable equation thus we can define, $\Phi(r, R, t) = f(R, t)\Psi(r, t)$ and obtain two different equations,

$$\begin{aligned}
i\hbar\frac{\partial f(R,t)}{\partial t} &= -\frac{\hbar^2}{2M}\nabla_R^2 f(R,t)\\
i\hbar\frac{\partial \Psi(r,t)}{\partial t} &= -\frac{\hbar^2}{2m}\nabla_r^2\psi(r,t) - k\frac{e^2}{r}\Psi(r,t)
\end{aligned} \tag{5}$$

[1] For those of you paying close attention you might worry about mixing these two momenta and two coordinates. It's ok since $[r_p, \nabla_e] = [r_e, \nabla_p] = 0$.

The first equation deals with the motion of the center of mass, which we can ignore in what follows. Thus we only consider the second equation and, as before, noting that the potential is not a function of time, we have energy eigenstates. Thus the time dependent wavefunction can be expressed as the product $\Psi(r,t) = e^{\frac{-iEt}{\hbar}}\psi(r)$. This gives us the time independent equation,

$$E\psi(r) = -\frac{\hbar^2}{2m}\nabla^2\psi(r) - \frac{e^2}{r}\psi(r). \tag{6}$$

All that hard work just changed our initial equation (1) by replacing m_e by the reduced mass and r_e with r. We have also absorbed the constant k into e (i.e. now $e = \sqrt{k}e$).[2]

The next step is to express the Laplacian in spherical coordinates.

1a: The Laplacian in spherical coordinates

Choosing spherical coordinates with origin at the center of mass we have

$$r^2 = x^2 + y^2 + z^2, \qquad x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = \cos\theta, \tag{7}$$

where the Cartesian coordinates are centered at the center of mass. Notice that the potential function in (6) is already expressed in spherical coordinates. It *only* remains to express the Laplacian in spherical coordinates.

[2]Note, if you follow this discussion in Park (pg 183), it is slightly different, and there the notation uses μ to represent the reduced mass. But do not that $\mu = m = m_e(1 - \frac{1}{1837})$

Appendix A: Transforming to CM frame

First using the transformations for the center of mass frame we can verify relation (3) by calculating the following (ignoring the $\frac{1}{2}$ factor that goes along for the ride),

$$\begin{aligned}
\frac{p^2}{m}+\frac{P^2}{M} &= \left[\frac{(m_e p_p - m_p p_e)^2}{M^2 m}\right] + \left\{\frac{(p_e+p_p)^2}{M}\right\} \\
&= \left[\frac{m_e^2 p_p^2 - 2m_e m_p p_e p_p + m_p^2 p_e^2}{M^2 m}\right] + \left\{\frac{p_e^2 + 2p_e p_p + p_p^2}{M}\right\} \\
&= \left[\frac{m_e^2 p_p^2 - 2m_e m_p p_e p_p + m_p^2 p_e^2}{M^2 \frac{m_e m_p}{M}}\right] + \left\{\frac{p_e^2 + 2p_e p_p + p_p^2}{M}\right\} \\
&= \left[\frac{m_e^2 p_p^2}{M m_e m_p} - \frac{2p_e p_p}{M} + \frac{m_p^2 p_e^2}{M m_e m_p}\right] + \left\{\frac{p_e^2 + 2p_e p_p + p_p^2}{M}\right\} \qquad \text{cross terms cancel, yayness!} \\
&= \left[\frac{m_e p_p^2}{M m_p} + \frac{m_p p_e^2}{M m_e}\right] + \left\{\frac{p_e^2 + p_p^2}{M}\right\} = \frac{p_p^2}{M}\left(\frac{m_e}{m_p}+1\right) + \frac{p_e^2}{M}\left(\frac{m_p}{m_e}+1\right) \\
&= \frac{p_p^2}{M}\left(\frac{m_e}{m_p}+\frac{m_p}{m_p}\right) + \frac{p_e^2}{M}\left(\frac{m_p}{m_e}+\frac{m_p}{m_p}\right) = \frac{p_p^2}{m_p} + \frac{p_e^2}{m_e}
\end{aligned}$$

And we're done.

Appendix B: Free QM particle on a cylinder.

In order to work up to how to find the Laplacian in spherical coordinates examine the easier case of cylindrical coordinates. The following is a question and solution to an optional question given out.

Let's extend the solution of a particle on a ring to the next higher dimension. Consider a free QM particle on an infinite cylinder (that is, a cylinder of finite radius R but of infinite extent in the z direction).

The general form of the time-independent Schrödinger equation for a free particle is,

$$E\psi = -\frac{\hbar^2}{2m}\nabla^2\psi \tag{8}$$

The problem is identical to the one asked in a previous set. However now the wavefunction is periodic in ϕ but unconstrained in the z direction. Since the system is rotationally invariant about z, the best coordinate system to use is cylindrical coordinates. Thus, look back at the optional notes posted on the web site to find the Laplacian expressed in cylindrical coordinates. Luckily, it simplifies since $\rho = R$ is a constant -that is, cancel any term that has a derivative with respect to ρ.

To proceed, see if you can separate this equation. That is, write the wavefunction as a product of two functions, one of z and one of ϕ, like: $\psi(z,\phi) = Z(z)\Phi(\phi)$. Insert this into the equation above and see if you can express it in a form,

$$\text{function of } \Phi \text{ only} = \text{function of } Z \text{ only}$$

Since these are two independent variables, and this expression is always true, they must equal the same constant. Call it $-K^2$. You should be able to solve the Φ easily, as it is identical to the cases we have dealt with. Then apply the periodic condition to the Φ equation.

Once you determine the condition that determines K^2, examine the Z equation, which can be easily solved. Since there is no constraint in this direction, the general solution is the solution.

Solution

It is easy to see that the coordinates on the cylinder can be expressed as either cylindrical coordinates or as Cartesian coordinates with one have a periodic constraint. Continue to call the coordinate parallel to the axis of symmetry z and call the perpendicular coordinate, tangent to the surface, x. Clearly $x = R\phi$ and is periodic in 2π. As there is no ρ dependence the two-diemnsional Laplacian is easy to find,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{R^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}.$$

The equation is,

$$\begin{aligned}
E\psi &= -\frac{\hbar^2}{2m}\nabla^2\psi \\
-\frac{2mE}{\hbar^2}\psi &= \nabla^2\psi = \frac{1}{R^2}\frac{\partial^2\psi}{\partial\phi^2} + \frac{\partial^2\psi}{\partial z^2} \\
-\frac{2mER^2}{\hbar^2}\psi &= \frac{\partial^2\psi}{\partial\phi^2} + R^2\frac{\partial^2\psi}{\partial z^2} \\
\frac{\partial^2\psi}{\partial\phi^2} &= -\frac{2mER^2}{\hbar^2}\psi - R^2\frac{\partial^2\psi}{\partial z^2}
\end{aligned}$$

This form suggest that we can factorize the solution as $\psi = \Phi Z$. Inserting we get.

$$Z\frac{\partial^2\Phi}{\partial\phi^2} = -\frac{2mER^2}{\hbar^2}\Phi Z - R^2\Phi\frac{\partial^2 Z}{\partial z^2}$$

Divide this whole equation by ΦZ to get,

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -\frac{2mER^2}{\hbar^2} - \frac{R^2}{Z}\frac{\partial^2 Z}{\partial z^2}$$

Since these are functions of independently varying variables, they must equal the same constant. Call this constant $-K^2$.

$$\frac{\partial^2\Phi}{\partial\phi^2} = -K^2\Phi$$

The solution to this equation is,

$$\Phi(\phi) = A\cos(K\phi) + B\sin(K\phi)$$

Since this function must be periodic, $\Phi(\phi) = \Phi(\phi + 2\pi)$ we get that K must be an integer, n.

This leaves the Z equation as,

$$\begin{aligned}
-n^2 &= -\frac{2mER^2}{\hbar^2} - \frac{R^2}{Z}\frac{\partial^2 Z}{\partial z^2} \\
-n^2 Z &= -\frac{2mER^2}{\hbar^2}Z - R^2\frac{\partial^2 Z}{\partial z^2} \\
\frac{\partial^2 Z}{\partial z^2} &= \left[\frac{n^2}{R^2} - \frac{2mE}{\hbar^2}\right] Z \equiv \kappa^2 Z
\end{aligned}$$

It appears that the type of solution will depend on the state n. Thus the general state is,

$$Z(z) = Ce^{\sqrt{\kappa}z} + De^{-\sqrt{\kappa}z}$$

O9.2: Free QM Particle on a sphere.

So, you've solved the free quantum particle on a ring, step up a dimension if you dare. The next higher dimensional closed, bounded space is a 2-sphere.

Aside: The mathematical term for the the two dimensional surface of a ball is sphere (often written $S = \partial B$, where B represents the ball*, the three dimensional object, which has a boundary that is the sphere. The general statement is that if you have an n dimensional ball, the surface is the $n-1$-dimensional boundary, the $n-1$ sphere: formally $S^{n-1} = \partial B^n$. So the 2-sphere (like the surface of the Earth) is the boundary of of the 3-ball (the whole Earth). Lastly, the boundary of a boundary is zero (for any dimension). That is, $\partial S^n = \partial\partial B^{n+1} = 0$.*

Back to the problem. The problem is identical to the one asked in a previous set however now we use spherical coordinates. Thus, look back at the optional notes posted on the web site to find the Laplacian expressed in spherical coordinates. Luckily, it simplifies since r is a constant -that is, cancel any term that has a derivative with respect to r. The general form of the time-independent Schrödinger equation for a free particle is,

$$E\psi = -\frac{\hbar^2}{2m}\nabla^2\psi \tag{9}$$

where ∇^2, the Laplacian, needs to be expressed in the appropriate coordinates.

To proceed, see if you can separate this equation. That is, write the wavefunction as a product of two functions, one of θ and one of ϕ, like: $\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi)$. Insert this into (9) above and see if you can express it in a form,

$$\text{function of } \Phi \text{ only} \quad = \quad \text{function of } \Theta \text{ only}$$

Since these are two independent variables, and this expression is always true, they must equal the same constant. Call it $-K^2$. You should be able to solve the Φ easily, as it is identical to the cases we have dealt with. Then apply the periodic condition to Φ. You should find what K is.

Then examine the other side. This is the hard part.

Once you have the differential equation for Θ express it in terms of $\cos\theta$. I.e. define $x = \cos\theta$ and rewrite the differential equation in terms of x. You should use the chain rule to do this,

$$\frac{\partial \Theta}{\partial \theta} \quad = \quad \frac{\partial \cos\theta}{\partial \theta}\frac{\partial \Theta}{\partial \cos\theta} = -\sin\theta \frac{\partial \Theta}{\partial \cos\theta} = -\sqrt{1-x^2}\frac{\partial \Theta}{\partial x}$$

Once you have the differential equation in terms of x, look it up. I will give you some hints. Search *associated Legendre polynomials* on wikipedia. Once you see what the solutions are, search *spherical harmonics* on wikipedia. Study the solutions to see what the form they take.

Spherical harmonics come into play in many areas, from solutions of the Hydrogen atom to the WMAP results.

Brute force method of obtaining Laplacian

Ok, let's just roll up our sleeves, be real physicists, and just crank out the transformation from Cartesian coordinates to spherical coordinates. Well, I am scared of this so let's make it slightly easier. Let's find the Laplacian on the 2-sphere, then extrapolate that to full 3-dimensional space. (I know that the last step is not too much trouble so that is why I am suggesting to do it that way). By the LPP (Lazy Physicist Principle), I want to simplify the notation so I do not get carpal tunnel syndrome by the time I am done. We know we will be dealing with a lot of sines and cosines, thus I will write them in the short hand notation of s and c. Then the relations between the two systems can be given by,

$$x = Rs\theta c\phi \qquad y = Rs\theta s\phi \qquad z = Rc\theta$$

We will also need the inverse relationships,

$$R = \sqrt{x^2+y^2+z^2} \qquad \theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right) \qquad \phi = \cos^{-1}\frac{x}{\sqrt{x^2+y^2}} = \sin^{-1}\frac{y}{\sqrt{x^2+y^2}}$$

I will also be handling a large amount of derivatives. So I will use a shorthand notation for partial derivatives as well,

$$\frac{\partial f}{\partial x} \equiv f_x \qquad \frac{\partial^2 f}{\partial^2 x} \equiv f_{xx} \qquad \frac{\partial^2 f}{\partial x \partial y} \equiv f_{xy}$$

When we analyze out Laplacian we must always be aware that it acts on a function. Thus we will keep a general function $f(x, y, z$ or $f(\theta, \phi)$ that is being acted upon. Thus we want to transform,

$$\nabla^2 f = f_{xx} + f_{yy} + f_{zz} = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \tag{10}$$

To begin we evaluate the basic partials,

$$\begin{aligned} x_\theta &= Rc\theta c\phi & x_\phi &= -Rs\theta s\phi \\ y_\theta &= Rc\theta s\phi & y_\phi &= Rs\theta c\phi \\ z_\theta &= -Rs\theta & z_\phi &= 0 \end{aligned}$$

In what follows we will mainly need the inverse partials,

$$\begin{aligned}
\theta_x &= \frac{\partial}{\partial x}\cos^{-1}\frac{z}{r} = \left(\frac{-1}{\sqrt{1-\frac{z^2}{r^2}}}\right)\left(-\frac{z}{r^2}\frac{\partial r}{\partial x}\right) = \left(\frac{z}{r\sqrt{r^2-z^2}}\right)\left(\frac{-\frac{1}{2}2x}{r}\right) = -\frac{zx}{r^2\sqrt{x^2+y^2}} = -\frac{c\theta s\theta c\phi}{rs\theta} = \frac{-1}{r}c\theta c\phi \\
\theta_y &= \frac{\partial}{\partial y}\cos^{-1}\frac{z}{r} = \left(\frac{-1}{\sqrt{1-\frac{z^2}{r^2}}}\right)\left(-\frac{z}{r^2}\frac{\partial r}{\partial y}\right) = \left(\frac{z}{r\sqrt{r^2-z^2}}\right)\left(\frac{-\frac{1}{2}2y}{r}\right) = \frac{zy}{r^2\sqrt{x^2+y^2}} = \frac{c\theta s\theta s\phi}{rs\theta} = \frac{1}{r}c\theta s\phi \\
\theta_z &= \frac{\partial}{\partial z}\sin^{-1}\frac{z}{r} = \left(\frac{-1}{\sqrt{1-\frac{z^2}{r^2}}}\right)\left(-\frac{z}{r^2}\frac{\partial r}{\partial z} - \frac{1}{r^2}\right) = \frac{1}{r^2}\left(\frac{z}{\sqrt{r^2-z^2}}\right)\left(-\frac{1}{2}2y\right) = \frac{zy}{r^2\sqrt{x^2+y^2}} = \frac{c\theta s\theta s\phi}{rs\theta} = \frac{1}{r}c\theta s\phi \\
\phi_x &= \frac{\partial}{\partial x}\cos^{-1}\frac{x}{\sqrt{x^2+y^2}} = \frac{-\frac{y}{x^2}2x}{1+(\frac{y}{x})^2} = \frac{-2\frac{s\phi}{c\phi}}{1+\frac{s^2\phi}{c^2\phi}} = -2s\phi c\phi = \qquad \theta_y = \qquad \theta_z =
\end{aligned} \tag{11}$$

Let's work on the first term in (10) and note that the intermediate result will translate directly to the later two terms.

$$\begin{aligned}
\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x}\frac{\partial}{\partial x}f &= \frac{\partial}{\partial x}\left(\frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}\right) f = \frac{\partial}{\partial x}\left(\frac{\partial r}{\partial x}\frac{\partial f}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial f}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial f}{\partial \phi}\right) = \frac{\partial}{\partial x}(r_x f_r + \theta_x f_\theta + \phi_x f_\phi) \\
&= \left(r_x\frac{\partial}{\partial r} + \theta_x\frac{\partial}{\partial \theta} + \phi_x\frac{\partial}{\partial \phi}\right)(r_x f_r + \theta_x f_\theta + \phi_x f_\phi) \\
&= r_x\left[r_{rr} f_r + r_r f_{rr} + \theta_{rr} f_\theta + \theta_r f_{rr} + \phi_{rr} f_\phi + \phi_r f_{\phi r}\right] \\
&\quad + \theta_x\left[(r_{x\theta} f_\theta + r_x f_{\theta x}) + (\theta_{x\theta} f_\theta + \theta_x f_{\theta\theta}) + (\phi_{x\theta} f_\phi + \phi_x f_{\phi\theta})\right] + \phi_x\left[(\theta_{x\phi} f_\theta + \theta_x f_{\theta\phi}) + (\phi_{x\phi} f_\phi + \phi_x f_{\phi\phi})\right]
\end{aligned} \tag{12}$$

Note that to obtain the $\frac{\partial^2}{\partial y^2}, \frac{\partial^2}{\partial z^2}$ expressions, we just substitute for x in this expression (although notice that the z relation will not have any dependence on ϕ). Also, notice in this expression that R will always appear as $\frac{1}{R^2}$, which can be factored out and ignored (replace at end).

Let's list out all of the derivatives we need, first for x

$$\begin{array}{lll}
\theta_x = \dfrac{1}{c\theta c\phi} & \theta_{x\theta} = \dfrac{s\theta}{c^2\theta c\phi} & \theta_{x\phi} = \dfrac{s\phi}{c\theta c^2\phi} \\
\phi_x = \dfrac{-1}{s\theta s\phi} & \phi_{x\theta} = \dfrac{c\theta}{s^2\theta s\phi} & \phi_{x\phi} = \dfrac{c\phi}{s\theta s^2\phi} \\
\theta_y = \dfrac{1}{c\theta s\phi} & \theta_{y\theta} = \dfrac{s\theta}{c^2\theta s\phi} & \theta_{y\phi} = \dfrac{-c\phi}{c\theta s^2\phi} \\
\phi_y = \dfrac{1}{s\theta c\phi} & \phi_{y\theta} = \dfrac{-c\theta}{s^2\theta c\phi} & \phi_{y\phi} = \dfrac{s\phi}{s\theta c^2\phi} \\
\theta_z = \dfrac{-1}{s\theta} & \theta_{z\theta} = \dfrac{c\theta}{s^2\theta} & \theta_{z\phi} = 0
\end{array}$$

Now it's just the task of inserting these derivatives and simplifying.

$$\begin{aligned}
\frac{\partial^2 f}{\partial x^2} &= \theta_x\left[(\theta_{x\theta}f_\theta + \theta_x f_{\theta\theta}) + (\phi_{x\theta}f_\phi + \phi_x f_{\phi\theta})\right] + \phi_x\left[(\theta_{x\phi}f_\theta + \theta_x f_{\theta\phi}) + (\phi_{x\phi}f_\phi + \phi_x f_{\phi\phi})\right] \\
&= \frac{1}{c\theta c\phi}\left[\left(\frac{s\theta}{c^2\theta c\phi}f_\theta + \frac{1}{c\theta c\phi}f_{\theta\theta}\right) + \left(\frac{c\theta}{s^2\theta s\phi}f_\phi + \frac{-1}{s\theta s\phi}f_{\phi\theta}\right)\right] \\
&\quad + \frac{-1}{s\theta s\phi}\left[\left(\frac{s\phi}{c\theta c^2\phi}f_\theta + \frac{1}{c\theta c\phi}f_{\theta\phi}\right) + \left(\frac{c\phi}{s\theta s^2\phi}f_\phi + \frac{-1}{s\theta s\phi}f_{\phi\phi}\right)\right] \\
&= \left(\frac{s\theta}{c^3\theta c^2\phi} - \frac{s\phi}{s\theta c\theta s\phi c^2\phi}\right)f_\theta + \left(\frac{1}{s^2\theta c\phi s\phi} - \frac{c\phi}{s^2\theta s^3\phi}\right)f_\phi + \frac{1}{c^2\theta c^2\phi}f_{\theta\theta} - \frac{1}{s^2\theta s^2\phi}f_{\phi\phi} - \frac{2}{c\theta s\theta c\phi s\phi}f_{\theta\phi}
\end{aligned}$$

Now for the y term,

$$\begin{aligned}
\frac{\partial^2 f}{\partial y^2} &= \theta_y\left[(\theta_{y\theta}f_\theta + \theta_y f_{\theta\theta}) + (\phi_{y\theta}f_\phi + \phi_y f_{\phi\theta})\right] + \phi_y\left[(\theta_{y\phi}f_\theta + \theta_y f_{\theta\phi}) + (\phi_{y\phi}f_\phi + \phi_y f_{\phi\phi})\right] \\
&= \frac{1}{c\theta s\phi}\left[\left(\frac{s\theta}{c^2\theta s\phi}f_\theta + \frac{1}{s\theta c\phi}f_{\theta\theta}\right) + \left(\frac{s\theta}{c^2\theta s\phi}f_\phi + \frac{1}{s\theta c\phi}f_{\phi\theta}\right)\right] \\
&\quad + \frac{1}{s\theta c\phi}\left[\left(\frac{-c\phi}{c\theta s^2\phi}f_\theta + \frac{1}{c\theta s\phi}f_{\theta\phi}\right) + \left(\frac{-c\theta}{s^2\theta c\phi}f_\phi + \frac{1}{s\theta c\phi}f_{\phi\phi}\right)\right] \\
&= \left(\frac{s\theta}{c^3\theta s^2\phi} - \frac{c\phi}{s\theta c\theta c\phi s^2\phi}\right)f_\theta + \left(\frac{s\theta}{c^3\theta s^2\phi} - \frac{c\theta}{s^3\theta c^2\phi}\right)f_\phi + \frac{1}{c^2\theta s^2\phi}f_{\theta\theta} - \frac{1}{s^2\theta c^2\phi}f_{\phi\phi} + \frac{2}{c\theta s\theta c\phi s\phi}f_{\theta\phi}
\end{aligned}$$

Lastly, consider the z term,

$$\frac{\partial^2 f}{\partial z^2} = \theta_z\left[\theta_{z\theta}f_\theta + \theta_z f_{\theta\theta}\right] = \frac{-1}{s\theta}\left[\frac{c\theta}{s^2\theta}f_\theta + \frac{-1}{s\theta}f_{\theta\theta}\right] = \frac{-c\theta}{s^3\theta}f_\theta + \frac{1}{s^2\theta}f_{\theta\theta}$$

Now we add it all together, grouping terms by f. Notice first of all that the cross term $f_{\theta\phi}$ vanishes (the last two terms in the first two relations).

$$
\begin{aligned}
R^2\nabla^2 f &= \left(\frac{s\theta}{c^3\theta c^2\phi} - \frac{1}{s\theta c\theta c^2\phi} + \frac{s\theta}{c^3\theta s^2\phi} - \frac{1}{s\theta c\theta s^2\phi} - \frac{c\theta}{s^3\theta}\right) f_\theta \\
&\quad + \left(\frac{1}{s^2\theta c\phi s\phi} - \frac{c\phi}{s^2\theta s^3\phi} + \frac{s\theta}{c^3\theta s^2\phi} - \frac{c\theta}{s^3\theta c^2\phi}\right) f_\phi \\
&\quad + \left(\frac{1}{c^2\theta c^2\phi} + \frac{1}{c^2\theta s^2\phi} + \frac{1}{s^2\theta}\right) f_{\theta\theta} + \left(\frac{1}{s^2\theta c^2\phi} + \frac{1}{s^2\theta s^2\phi}\right) f_{\phi\phi} \\
&= \left(\left[\frac{s\theta}{c^3\theta} - \frac{1}{s\theta c\theta}\right]\left(\frac{1}{c^2\phi} + \frac{1}{s^2\phi}\right) - \frac{c\theta}{s^3\theta}\right) f_\theta \\
&\quad + \left(\frac{1}{s^2\theta c\phi s\phi} - \frac{c\phi}{s^2\theta s^3\phi} + \frac{s\theta}{c^3\theta s^2\phi} - \frac{c\theta}{s^3\theta c^2\phi}\right) f_\phi \\
&\quad + \left(\frac{1}{c^2\theta c^2\phi} + \frac{1}{c^2\theta s^2\phi} + \frac{1}{s^2\theta}\right) f_{\theta\theta} + \left(\frac{1}{s^2\theta c^2\phi} + \frac{1}{s^2\theta s^2\phi}\right) f_{\phi\phi}
\end{aligned} \tag{13}
$$

References

[1] Gordon Baym, *Lectures on Quantum Mechanics* Benjamin/Cummings Pub., ©1973 (chapter 7).