Two- and Three-Dimensional Rotationally-Symmetric Potentials

The three-dimensional potential well is pretty hard to solve. We'll start off with the two-dimensional one.

The Two-Dimensional Schrödinger Equation in Polar Coordinates

We'll get bogged down if I try to show you the Schrödinger Equation in Polar Coordinates. I will just give it to you:

$$E_n\,\psi(r,\,\phi) = -\frac{\hbar^2}{2\,m}\left[\frac{\partial^2\psi(r,\phi)}{\partial r^2} + \frac{1}{r}\,\frac{\partial\psi(r,\phi)}{\partial r} + \frac{1}{r^2}\,\frac{\partial^2\psi(r,\phi)}{\partial\phi^2}\right] + V(r,\,\phi)\,\psi(r,\,\phi)$$

If you want to derive this thing, you have to use multi-variable calculus rules to convert the $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$ that appears in Schrodinger's equation in Cartesian coordinates into $\frac{\partial^2}{\partial r^2} + \frac{1}{r}\,\frac{\partial}{\partial r} + \frac{1}{r^2}\,\frac{\partial^2}{\partial\phi^2}$. If you really want, here is somebody who wrote it up completely, https://www.math.ucdavis.edu/~saito/courses/21C.w11/polar-lap.pdf, and below is an excerpt.

In the rest of this section, θ is the polar angle instead of ϕ, because that is typically what is named in 2-d. But I prefer ϕ above because this is the gateway to 3-d.

Recall that **Laplace's equation** in $\mathbb{R}^2$ in terms of the usual (i.e., **Cartesian**) (x, y) coordinate system is:

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = u_{xx} + u_{yy} = 0. \tag{1}$$

The Cartesian coordinates can be represented by the polar coordinates as follows:

$$\begin{cases} x = r\cos\theta; \\ y = r\sin\theta. \end{cases} \tag{2}$$

Let us first compute the partial derivatives of x, y w.r.t. r, θ:

$$\begin{cases} \dfrac{\partial x}{\partial r} = \cos\theta, & \dfrac{\partial x}{\partial \theta} = -r\sin\theta; \\ \dfrac{\partial y}{\partial r} = \sin\theta, & \dfrac{\partial y}{\partial \theta} = r\cos\theta. \end{cases} \tag{3}$$

To do so, let's compute $\frac{\partial u}{\partial r}$ first. We will use the **Chain Rule** since (x, y) are functions of (r, θ) as shown in (2).

$$\begin{aligned} \frac{\partial u}{\partial r} &= \frac{\partial u}{\partial x}\frac{\partial x}{\partial r} + \frac{\partial u}{\partial y}\frac{\partial y}{\partial r} \\ &= \frac{\partial u}{\partial x}\cos\theta + \frac{\partial u}{\partial y}\sin\theta \quad \text{using (3)} \\ &= \cos\theta\frac{\partial u}{\partial x} + \sin\theta\frac{\partial u}{\partial y}. \end{aligned} \tag{4}$$

So they did that much very tidy work, and they got $\frac{\partial u}{\partial r}$ in terms of derivatives with respect to x and y. If you want to understand what is going on rather than just manipulating symbols, you really need to draw pictures!!

Anyway, the next thing they do is compute $\frac{\partial^2 u}{\partial r^2}$, which is just repeating step 4 to get a second derivative. Then they need to do $\frac{\partial u}{\partial \theta}$. Finally they complete the second derivatives by doing $\frac{\partial^2 u}{\partial \theta^2}$.

The next thing is to make the dimensionally-sensible combination $\frac{\partial^2 u}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2}$ and simplify. They discover,

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}$$

and that is what goes into Schrödinger's equation.

The Rotationally Symmetric Case and the Separation of Variables Ansatz

If the potential is rotationally symmetric it doesn't depend on ϕ, so we have:

$$E_n\, \psi(r,\, \phi) = -\frac{\hbar^2}{2\,m}\left[\frac{d^2\, \psi\,(r,\phi)}{dr^2} + \frac{1}{r}\, \frac{\mathrm{d}\psi(r,\phi)}{dr} + \frac{1}{r^2}\, \frac{d^2\, \psi\,(r,\phi)}{d\phi^2}\right] + V(r)\, \psi(r,\, \phi)$$

The ansatz for solving this is

$$\psi(r,\, \phi) = \psi(r)\, \Phi(\phi)$$

where $\Phi(\phi)$ is an unknown function of ϕ.

$$E_n\, \psi(r)\, \Phi(\phi) = -\frac{\hbar^2}{2\,m}\left[\frac{d^2\, \psi(r)}{dr^2} + \frac{1}{r}\, \frac{\mathrm{d}\psi(r)}{dr}\right] \Phi(\phi) + \frac{1}{r^2}\, \frac{d^2\, \Phi(\phi)}{\mathrm{d}\phi^2}\, \psi(r)\, \Big] + V(r)\, \psi(r)\, \Phi(\phi)$$

Multiply through by $\frac{r^2}{R(r)\, \Phi(\phi)}$

$$r^2\, E_n = -\frac{\hbar^2}{2\,m}\left[r^2\, \frac{d^2\, R(r)}{dr^2} + r\, \frac{dR(r)}{dr}\right] \frac{1}{R(r)} - \frac{\hbar^2}{2\,m}\, \frac{1}{\Phi(\phi)}\, \frac{d^2\, \Phi(\phi)}{\mathrm{d}\phi^2} + r^2\, V(r)$$

Rearrange

$$r^2\, E_n + \frac{\hbar^2}{2\,m}\left[r^2\, \frac{d^2\, R(r)}{dr^2} + r\, \frac{dR(r)}{dr}\right] \frac{1}{R(r)} - r^2\, V(r) = -\frac{\hbar^2}{2\,m}\, \frac{1}{\Phi(\phi)}\, \frac{d^2\, \Phi(\phi)}{\mathrm{d}\phi^2}$$

All of the ϕ-dependence is on the RHS!! No ϕ-dependence is on the LHS. The LHS and the RHS must be independent of ϕ! But the RHS by the same type of argument is independent of r! So the LHS and the RHS must depend on neither ϕ nor r. They are some constant!

Let’s call the constant $\frac{\hbar^2}{2m} l^2$. Of course, it could be a negative constant, and I am predisposing you against that by putting in l^2 and $\frac{\hbar^2}{2m} l^2$ must be greater than or equal to zero, but you’ll see that this is true in a moment. With this constant,

$$-\frac{\hbar^2}{2m} \frac{1}{\Phi(\phi)} \frac{d^2 \Phi(\phi)}{d\phi^2} = \frac{\hbar^2}{2m} l^2$$

or

$$\frac{d^2 \Phi(\phi)}{d\phi^2} = -l^2 \Phi(\phi)$$

The $\Phi(\phi)$ that does this is $\Phi(\phi) = e^{i l \phi}$. If the constant had been negative, then $\Phi(\phi)$ would have grown or decayed exponentially. WHAT IS WRONG WITH THAT? Well, we can’t have discontinuity or kinks going from $\phi = 0$ to $\phi = 2\pi$, and the exponentials can’t satisfy that. The bottom line is that the constant is indeed positive, and furthermore, to have continuity and no kinks at $\phi = 0$ to $\phi = 2\pi$, l has to be an integer.

Now that we know l, from solving the ϕ equation, we put it back in to the r equation.

$$r^2 E_n + \frac{\hbar^2}{2m}\left[r^2 \frac{d^2 R(r)}{dr^2} + r \frac{dR(r)}{dr}\right] \frac{1}{R(r)} - r^2 V(r) = -\frac{\hbar^2}{2m} l^2$$

Multiplying through by $\frac{R(r)}{r^2}$ we have

$$E_n R(r) + \frac{\hbar^2}{2m}\left[\frac{d^2 R(r)}{dr^2} + \frac{1}{r} \frac{dR(r)}{dr}\right] - V(r) R(r) = -\frac{\hbar^2}{2m} l^2 \frac{R(r)}{r^2}$$

or

$$E_n R(r) = -\frac{\hbar^2}{2m}\left[\frac{d^2 R(r)}{dr^2} + \frac{1}{r} \frac{dR(r)}{dr}\right] + V(r) \psi(r) + \frac{\hbar^2}{2m} l^2 \frac{R(r)}{r^2}$$

This last equation is often a bear to solve, but the nice thing is that it looks just like a 1-d Schrodinger equation. There are two constants in it that change from solution to solution. They are E_n and l. We emphasize that the wave function will depend on these things by subscripting it as $R_{n,l}(r)$. E_n might depend on l, so we give it a subscript too.

$$E_{n,l} R_{n,l}(r) = -\frac{\hbar^2}{2m}\left[\frac{d^2 R_{n,l}(r)}{dr^2} + \frac{1}{r} \frac{dR_{n,l}(r)}{dr}\right] + V(r) R_{n,l}(r) + \frac{\hbar^2}{2m} l^2 \frac{R_{n,l}(r)}{r^2}$$

The next thing that is generally done is to define a new dimensionless radial coordinate:

$$\rho \equiv \frac{\sqrt{2\, m E_{n,l}}}{\hbar}\, r$$

Then the equation is:

$$E_{n,l}\, R_{n,l}(\rho) = -\frac{\hbar^2}{2\,m}\,\frac{2\,m E_{n,l}}{\hbar^2}\left[\frac{d^2 R_{n,l}(\rho)}{d\rho^2} + \frac{1}{\rho}\,\frac{dR_{n,l}(\rho)}{d\rho}\right] + V\left(\frac{\hbar}{\sqrt{2\,m E_{n,l}}}\,\rho\right) R_{n,l}(\rho) + \frac{\hbar^2}{2\,m}\, l^2\, \frac{2\,m E_{n,l}}{\hbar^2}\,\frac{R_{n,l}(\rho)}{\rho^2}$$

or, dividing through by $E_{n,l}$

$$R_{n,l}(r) = -\left[\frac{d^2 R_{n,l}(\rho)}{d\rho^2} + \frac{1}{\rho}\,\frac{dR_{n,l}(\rho)}{d\rho}\right] + \frac{V\left(\frac{\hbar}{\sqrt{2 m E_{n,l}}}\,\rho\right) R_{n,l}(\rho)}{E_{n,l}} + l^2\,\frac{R_{n,l}(\rho)}{\rho^2}$$

or,

$$\left(\rho^2 - l^2\right) R_{n,l}(\rho) + \left[\rho^2\,\frac{d^2 R_{n,l}(\rho)}{d\rho^2} + \rho\,\frac{dR_{n,l}(\rho)}{d\rho}\right] - \rho^2\,\frac{V\left(\frac{\hbar}{\sqrt{2 m E_{n,l}}}\,\rho\right) R_{n,l}(\rho)}{E_{n,l}} = 0$$

SchroSolver

I believe it is common to define a new function $P_{n,l}(\rho) = \rho^\alpha R_{n,l}(\rho)$ and then to choose α to put the equation into a form that has no first derivative, $\frac{dP_{n,l}(\rho)}{d\rho}$. We could do that! It’s good chain rule practice. It just involves studying the terms in the square brackets. Can you see why we would do it?

Even without doing it, if you believe there is a choice of α which makes the first derivative go away, it is pretty clear that we get a differential equation that looks like:

$$\left(\rho^2 - l^2 + \text{some constant involving } \alpha\right) \rho^\alpha\, P_{n,l}(\rho) + \rho^{2+\alpha}\,\frac{d^2 P_{n,l}(\rho)}{d\rho^2} - \rho^{2+\alpha}\,\frac{V\left(\frac{\hbar}{\sqrt{2 m E_{n,l}}}\,\rho\right) P_{n,l}(\rho)}{E_{n,l}} = 0$$

Can’t we solve this for $\frac{d^2 P_{n,l}(\rho)}{d\rho^2}$ and then throw SchroSolver at it?

That is exactly what Moore has done when he gives you the choice in the pop-up list to study Hydrogen.

The Three-Dimensional Schrödinger Equation in Polar Coordinates

I said the two-dimensional case was the gateway to the three-dimensional case. Here is Schrodinger's equation in three dimensions:

$$E_n\,\psi(r,\,\theta,\,\phi) = -\frac{\hbar^2}{2\,m}\left[\frac{\partial^2\psi(r,\theta,\phi)}{\partial r^2} + \frac{2}{r}\,\frac{\partial\psi(r,\theta,\phi)}{\partial r} + \frac{1}{r^2\sin\theta}\,\frac{\partial}{\partial\theta}\,\frac{\partial(\sin\theta\cdot\psi(r,\theta,\phi))}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\,\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}\right] + V(r)\,\psi(r,\,\theta,\,\phi).$$

This is definitely getting worse, but the game that is played to solve it is exactly the one that was played in 2-d. You make the ansatz

$$\psi(r,\,\theta,\,\phi) = \psi(r)\,Y(\theta,\,\phi)$$

You rearrange and argue that you have a LHS that only involves r and $\psi(r)$ and a RHS that only involves θ, ϕ, and $Y(\theta,\,\phi)$. In the end you discover what is on the following three pages, which is a set of functions $Y_{l,m}(\theta,\,\phi)$ that depend on two integers l and m. They are called the spherical harmonics.

There is more about the $Y_{l,m}(\theta,\,\phi)$ at https://mathworld.wolfram.com/SphericalHarmonic.html

Summary of Three-Dimensional Case

If you never take any more quantum mechanics, there are three things to know about the three-dimensional case.

(1) There is a function $R(r)$ that captures the radial dependence of $\psi(r,\,\theta,\,\phi)$. Furthermore, $R(r)$ is indexed by two integers n and l. So the radial dependence is given by $R_{n,l}(r)$. You already know lots about these functions on general grounds and you can study them in SchroSolver.

(2) There are functions $Y_{l,m}(\theta,\,\phi)$ that capture the angular dependence of $\psi(r,\,\theta,\,\phi)$. They solve a differential equation that *only* involves a constant l^2. The fact that the constant doesn't depend on m is called degeneracy.

(3) The wave functions that solve Hydrogen in total depend three constants, n, l, and m, but it turns out that E only depends on n! This is further degeneracy!

Spherical Harmonic

The spherical harmonics $Y_l^m(\theta, \phi)$ are the angular portion of the solution to Laplace's equation in spherical coordinates where azimuthal symmetry is not present. Some care must be taken in identifying the notational convention being used. In this entry, θ is taken as the polar (colatitudinal) coordinate with $\theta \in [0, \pi]$, and ϕ as the azimuthal (longitudinal) coordinate with $\phi \in [0, 2\pi)$. This is the convention normally used in physics, as described by Arfken (1985) and the Wolfram Language (in mathematical literature, θ usually denotes the longitudinal coordinate and ϕ the colatitudinal coordinate). Spherical harmonics are implemented in the Wolfram Language as SphericalHarmonicY[*l*, *m*, *theta*, *phi*].

Spherical harmonics satisfy the spherical harmonic differential equation, which is given by the angular part of Laplace's equation in spherical coordinates. Writing $F = \Phi(\phi)\Theta(\theta)$ in this equation gives

$$\frac{\Phi(\phi)}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{\Theta(\theta)}{\sin^2\theta}\frac{d^2\Phi(\phi)}{d\phi^2} + l(l+1)\Theta(\theta)\Phi(\phi) = 0. \tag{1}$$

Multiplying by $\sin^2\theta / (\Theta\Phi)$ gives

$$\left[\frac{\sin\theta}{\Theta(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + l(l+1)\sin^2\theta\right] + \frac{1}{\Phi(\phi)}\frac{d^2\Phi(\phi)}{d\phi^2} = 0. \tag{2}$$

Using separation of variables by equating the ϕ-dependent portion to a constant gives

$$\frac{1}{\Phi(\phi)}\frac{d^2\Phi(\phi)}{d\phi^2} = -m^2, \tag{3}$$

which has solutions

$$\Phi(\phi) = A e^{-im\phi} + B e^{im\phi}. \tag{4}$$

Plugging in (3) into (2) gives the equation for the θ-dependent portion, whose solution is

$$\Theta(\theta) = P_l^m(\cos\theta), \tag{5}$$

where $m = -l, -(l-1), ..., 0, ..., l-1, l$ and $P_l^m(z)$ is an associated Legendre polynomial. The spherical harmonics are then defined by combining $\Phi(\phi)$ and $\Theta(\theta)$,

$$Y_l^m(\theta, \phi) \equiv \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}\, P_l^m(\cos\theta)\, e^{im\phi}, \tag{6}$$

where the normalization is chosen such that

$$\begin{aligned}&\int_0^{2\pi}\int_0^{\pi} Y_l^m(\theta,\phi)\,\bar{Y}_{l'}^{m'}(\theta,\phi)\sin\theta\,d\theta\,d\phi\\ &=\int_0^{2\pi}\int_{-1}^{1} Y_l^m(\theta,\phi)\,\bar{Y}_{l'}^{m'}(\theta,\phi)\,d(\cos\theta)\,d\phi\\ &=\delta_{m m'}\,\delta_{l l'}\end{aligned} \tag{7}$$

(Arfken 1985, p. 681). Here, $\bar{z}$ denotes the complex conjugate and $\delta_{m n}$ is the Kronecker delta. Sometimes (e.g., Arfken 1985), the Condon-Shortley phase $(-1)^m$ is prepended to the definition of the spherical harmonics.

The spherical harmonics are sometimes separated into their real and imaginary parts,

$$Y_l^{ms}(\theta,\phi)\equiv\sqrt{\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}}\,P_l^m(\cos\theta)\sin(m\phi) \tag{8}$$

$$Y_l^{mc}(\theta,\phi)\equiv\sqrt{\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}}\,P_l^m(\cos\theta)\cos(m\phi). \tag{9}$$

The spherical harmonics obey

$$Y_l^{-l}(\theta,\phi)=\frac{1}{2^l\,l!}\sqrt{\frac{(2l+1)!}{4\pi}}\,\sin^l\theta\,e^{-il\phi} \tag{10}$$

$$Y_l^0(\theta,\phi)=\sqrt{\frac{2l+1}{4\pi}}\,P_l(\cos\theta) \tag{11}$$

$$Y_l^{-m}(\theta,\phi)=(-1)^m\,\bar{Y}_l^m(\theta,\phi), \tag{12}$$

where $P_l(x)$ is a Legendre polynomial.

Integrals of the spherical harmonics are given by

$$\begin{aligned}&\int_0^{2\pi}\int_0^{\pi} Y_{l_1}^{m_1}(\theta,\phi)\,Y_{l_2}^{m_2}(\theta,\phi)\,Y_{l_3}^{m_3}(\theta,\phi)\sin\theta\,d\theta\,d\phi\\ &=\sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix}l_1 & l_2 & l_3\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1 & l_2 & l_3\\ m_1 & m_2 & m_3\end{pmatrix},\end{aligned} \tag{13}$$

where $\begin{pmatrix}l_1 & l_2 & l_3\\ m_1 & m_2 & m_3\end{pmatrix}$ is a Wigner 3j-symbol (which is related to the Clebsch-Gordan coefficients). Special cases include

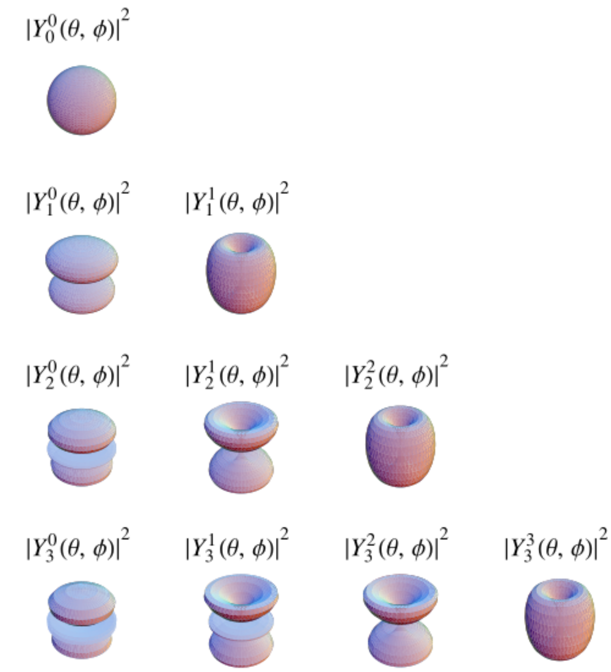
$$\int_0^{2\pi}\int_0^{\pi} Y_L^M(\theta,\phi)\,Y_0^0(\theta,\phi)\,\bar{Y}_L^M(\theta,\phi)\sin\theta\,d\theta\,d\phi=\frac{1}{\sqrt{4\pi}} \tag{14}$$

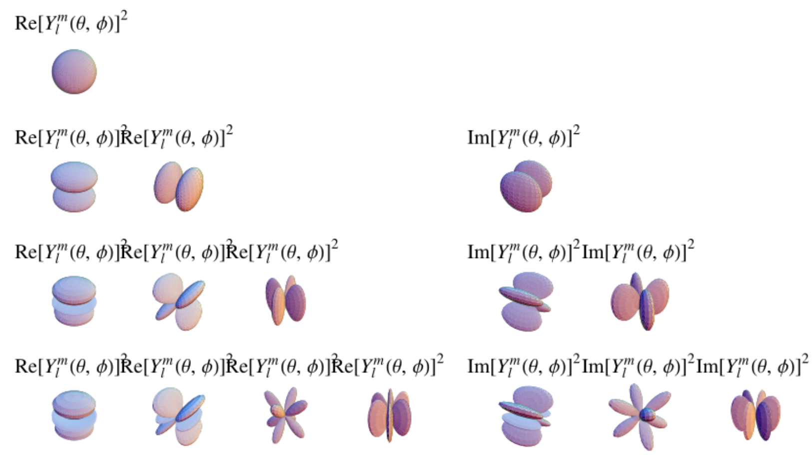
$$\int_0^{2\pi}\int_0^{\pi} Y_L^M(\theta,\phi)\,Y_1^0(\theta,\phi)\,\bar{Y}_{L+1}^M(\theta,\phi)\sin\theta\,d\theta\,d\phi=\sqrt{\frac{3}{4\pi}}\sqrt{\frac{(L+M+1)(L-M+1)}{(2L+1)(2L+3)}} \tag{15}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_L^M(\theta,\phi)\,Y_1^1(\theta,\phi)\,\bar{Y}_{L+1}^{M+1}(\theta,\phi)\sin\theta\,d\theta\,d\phi=\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(L+M+1)(L+M+2)}{(2L+1)(2L+3)}} \tag{16}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_L^M(\theta,\phi)\,Y_1^1(\theta,\phi)\,\bar{Y}_{L-1}^{M+1}(\theta,\phi)\sin\theta\,d\theta\,d\phi=-\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(L-M)(L-M-1)}{(2L-1)(2L+1)}} \tag{17}$$

(Arfken 1985, p. 700).





The above illustrations show $|Y_l^m(\theta, \phi)|^2$ (top), $\Re[Y_l^m(\theta, \phi)]^2$ (bottom left), and $\Im[Y_l^m(\theta, \phi)]^2$ (bottom right). The first few spherical harmonics are

$$Y_0^0(\theta, \phi) = \frac{1}{2} \frac{1}{\sqrt{\pi}} \quad (18)$$

$$Y_1^{-1}(\theta, \phi) = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin\theta \, e^{-i\phi} \quad (19)$$

$$Y_1^0(\theta, \phi) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos\theta \quad (20)$$

$$Y_1^1(\theta, \phi) = -\frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin\theta \, e^{i\phi} \quad (21)$$

$$Y_2^{-2}(\theta, \phi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2\theta \, e^{-2i\phi} \quad (22)$$