Schrödinger equation in 3D

The generalization to three dimensions is straightforward. Schrödinger's equation says

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi;$$

the Hamiltonian operator $\hat{H}$ is obtained from the classical energy

$$\frac{1}{2}mv^2 + V = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V$$

by the standard prescription (applied now to y and z, as well as x):

$$p_x \rightarrow -i\hbar\frac{\partial}{\partial x}, \quad p_y \rightarrow -i\hbar\frac{\partial}{\partial y}, \quad p_z \rightarrow -i\hbar\frac{\partial}{\partial z},$$

or

$$\boxed{\mathbf{p} \rightarrow -i\hbar\nabla,}$$

Schrödinger equation in 3D

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

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},$$

is the **Laplacian**, in cartesian coordinates.

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

$$\int |\Psi|^2\, d^3\mathbf{r} = 1,$$

with the integral taken over all space.

Schrödinger equation in 3D

If V is independent of time, there will be a complete set of stationary states,

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

where the spatial wave function ψ_n satisfies the time-*independent* Schrödinger equation:

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi.}$$

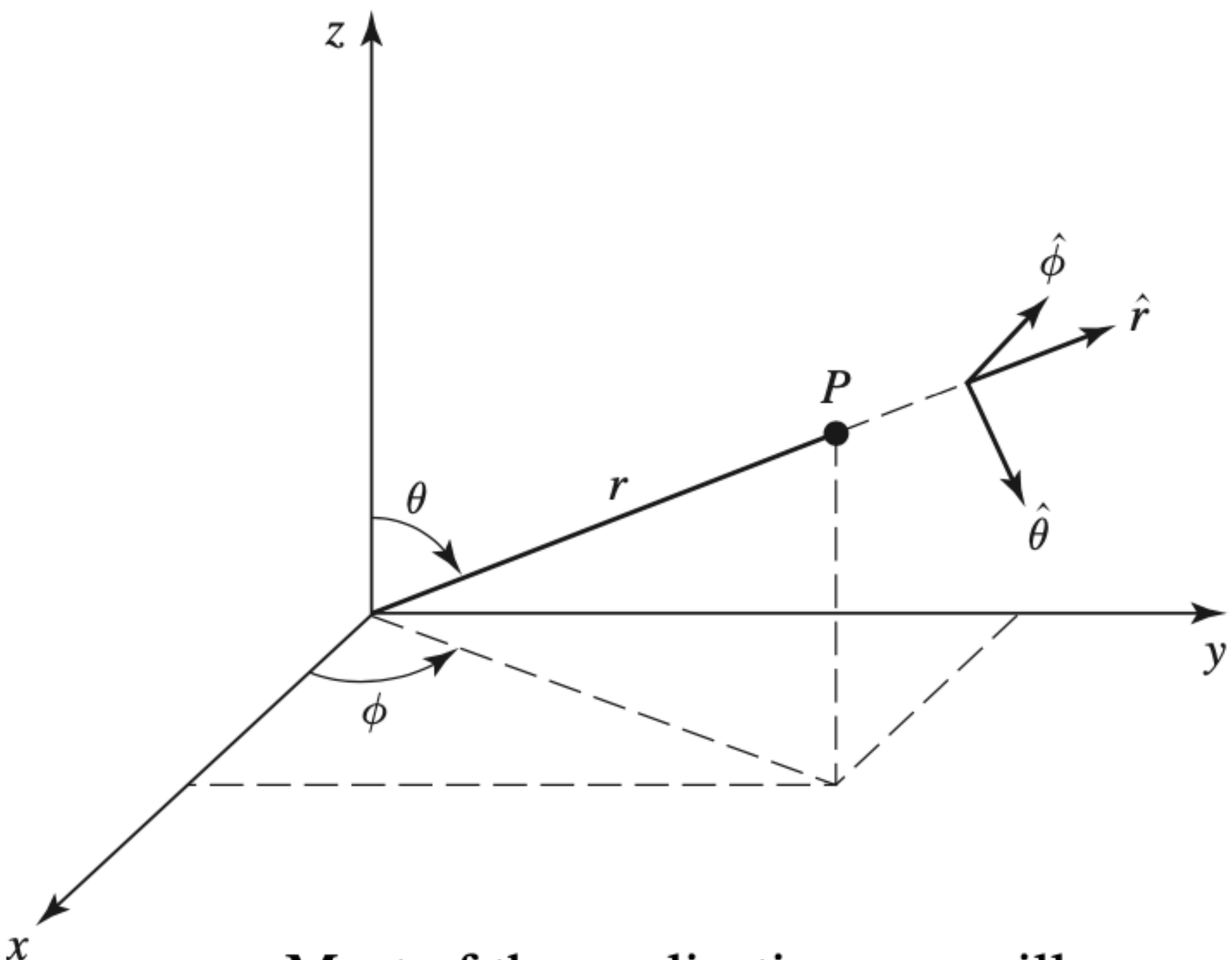
The general solution to the (time-*dependent*) Schrödinger equation is

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

with the constants c_n determined by the initial wave function, $\Psi(\mathbf{r}, 0)$, in the usual way. (If the potential admits continuum states, then the sum in Equation 4.9 becomes an integral.)

Schrödinger equation in spherical coordinates:

Spherical coordinates: radius r, polar angle θ, and azimuthal angle ϕ.



Most of the applications we will encounter involve **central potentials**, for which V is a function only of the distance from the origin, $V(\mathbf{r}) \rightarrow V(r)$. In that case it is natural to adopt **spherical coordinates**, (r, θ, ϕ) (Figure 4.1). In spherical coordinates the Laplacian takes the form[1]

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

Schrödinger equation in spherical coordinates:

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

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

Variable separation:

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

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

Dividing by YR and multiplying by $-2mr^2/\hbar^2$:

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

Schrödinger equation in spherical coordinates:

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

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

The Radial Equation

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

The Angular Equation

The Angular Equation

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

Multiplying by: $Y\sin^2\theta$.

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

Separation of variables: $Y(\theta,\phi)=\Theta(\theta)\,\Phi(\phi)$.

Dividing by: $\Theta\Phi$

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

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

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2.$$

Solution for Φ:

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \boxed{\Phi(\phi) = e^{im\phi}.}$$

where *m* can be positive or negative.

when ϕ advances by 2π, we return to the same point in space.

$$\Phi(\phi + 2\pi) = \Phi(\phi).$$

$$\exp[im(\phi + 2\pi)] = \exp(im\phi), \text{ or } \exp(2\pi im) = 1.$$

m must be an integer: $m = 0, \pm 1, \pm 2, \ldots.$

Solution for Θ:

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

The solution reads:

$$\Theta(\theta) = A P_\ell^m(\cos\theta)$$

where P_l^m is the **associated Legendre function**, defined by:

$$P_\ell^m(x) \equiv (-1)^m \left(1 - x^2\right)^{m/2} \left(\frac{d}{dx}\right)^m P_\ell(x),$$ for $m \geq 0$

and $P_l(x)$ is the ℓ_{th} **Legendre polynomial**, defined by the **Rodrigues formula**:

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

Solution for ϴ:

For negative values of *m*:

$$P_\ell^{-m}(x) = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(x).$$

$P_\ell(x)$ is a polynomial (of degree ℓ) in x, and is even or odd according to the parity of ℓ.

$P_\ell{}^m(x)$ is not, in general, a polynomial — if m is odd it carries a factor of $(1-x^2)^{0.5}$

ℓ must be a non-negative *integer.*

If $m > \ell$, $P_\ell{}^m = 0$. For any given ℓ, then, there are $(2\ell + 1)$ possible values of m:

$$\ell = 0,\ 1,\ 2, \ldots \quad \Rightarrow \quad m = -\ell,\ -\ell+1,\ \ldots,\ -1,\ 0,\ 1, \ldots,\ \ell-1,\ \ell.$$

Solution for ϴ:

For negative values of *m*:

$$P_\ell^{-m}(x) = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(x).$$

First Legendre polynomials:

$$P_0 = 1$$

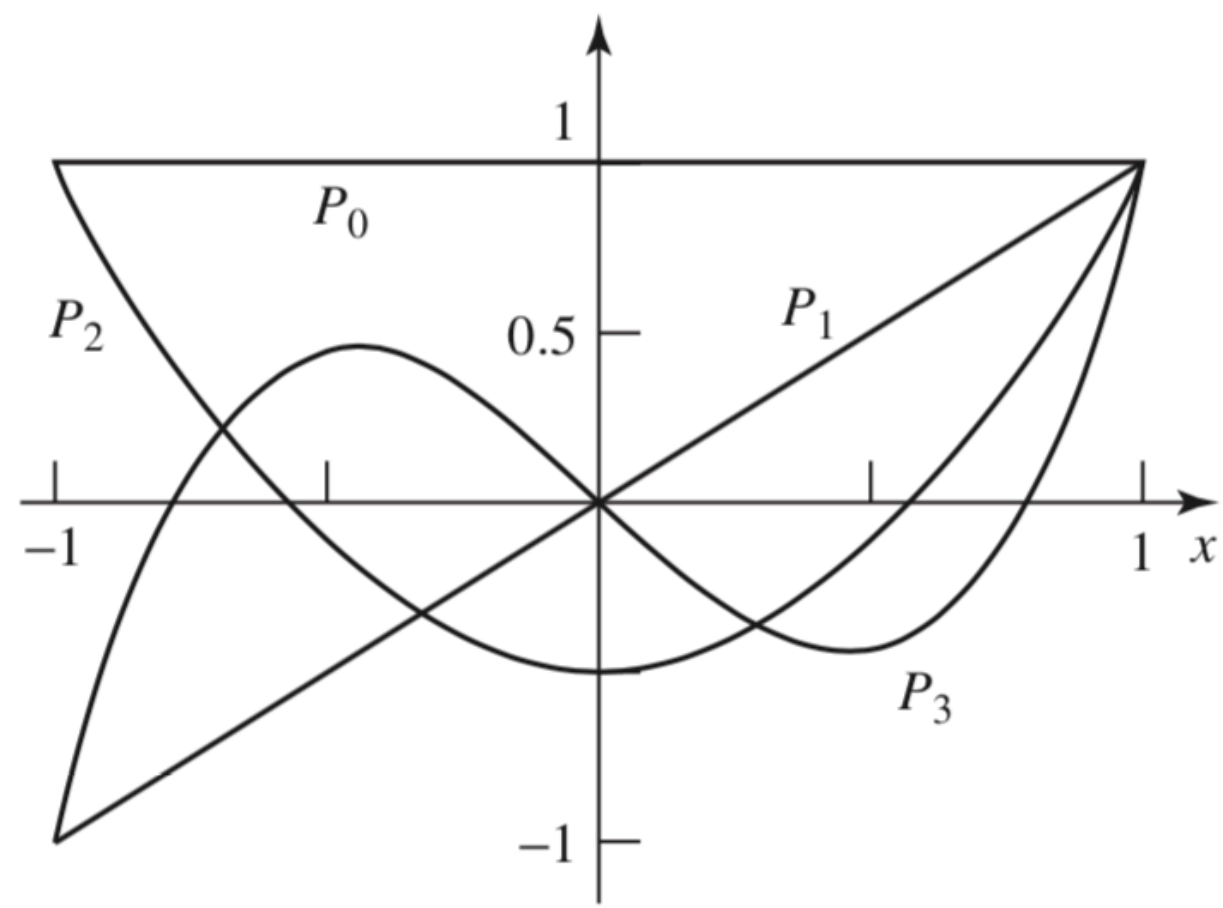
$$P_1 = x$$

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

$$P_3 = \frac{1}{2}(5x^3 - 3\mathrm{x})$$

$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

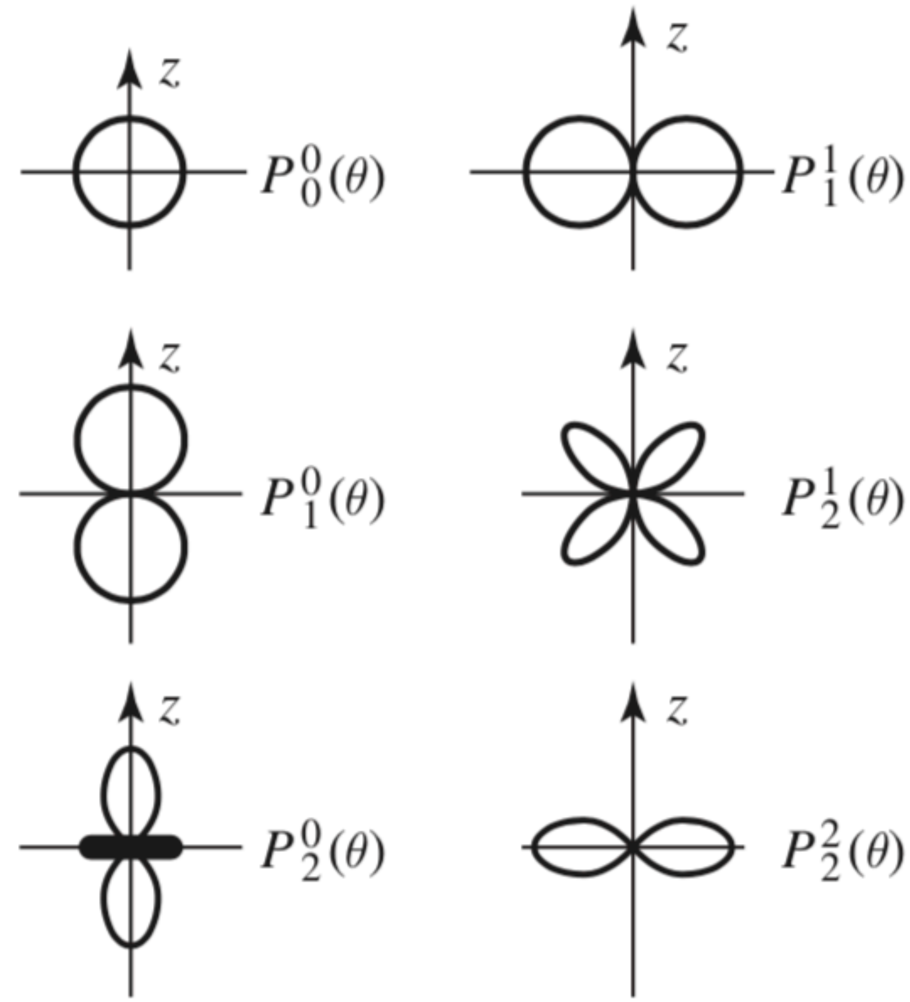
$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$



Solution for Θ:

We need $P_\ell{}^m(\cos\theta)$, and $(1 - \cos^2\theta)^{0.5} = \sin\theta$, so $P_\ell{}^m(\cos\theta)$ is always a polynomial in cos θ, multiplied — if *m* is odd—by sin θ .

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = -\sin\theta$	$P_3^3 = -15\sin\theta(1-\cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\ \cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = -\frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = -3\sin\theta\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$



graphs of $r = \left|P_\ell^m(\cos\theta)\right|$ *(in these plots r tells you the magnitude of the function in the direction θ; each figure should be rotated about the z axis).*

Normalisation condition: solution for ϴ:

The volume element in spherical coordinates:

$$d^3\mathbf{r} = r^2 \sin\theta \, dr \, d\theta \, d\phi = r^2 \, dr \, d\Omega, \quad \text{where} \quad d\Omega \equiv \sin\theta \, d\theta \, d\phi,$$

Normalisation condition:

$$\int |\Psi|^2 \, d^3\mathbf{r} = 1, \quad \Rightarrow \quad \int |\psi|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi = \int |R|^2 r^2 \, dr \int |Y|^2 \, d\Omega = 1.$$

It is convenient to normalise *R* and *Y* separately:

$$\int_0^\infty |R|^2 r^2 \, dr = 1$$

$$\int_0^\pi \int_0^{2\pi} |Y|^2 \sin\theta \, d\theta \, d\phi = 1.$$

Normalisation condition: solution for ϴ:

The normalised angular wave functions are called **spherical harmonics**:

$$\boxed{Y_\ell^m(\theta,\phi) = \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\, e^{im\phi}\, P_\ell^m(\cos\theta)\,,}$$

They are orthogonal:

$$\int_0^\pi \int_0^{2\pi} \left[Y_\ell^m(\theta,\phi)\right]^* \left[Y_{\ell'}^{m'}(\theta,\phi)\right] \sin\theta\, d\theta\, d\phi = \delta_{\ell\ell'}\delta_{mm'}$$

Spherical Harmonics:

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta\,(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

The Radial Equation

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

The angular part of the wave function, $Y(\theta,\phi)$, is the same for *all* spherically symmetric potentials.

The actual *shape* of the potential, $V(r)$, affects only the *radial* part of the wave function, $R(r)$.

Variable change:

$$u(r) \equiv rR(r) \quad \Rightarrow \quad \begin{aligned} R &= u/r, \\ dR/dr &= \left[r\,(du/dr) - u\right]/r^2, \\ (d/dr)\left[r^2\,(dR/dr)\right] &= r d^2u/dr^2, \end{aligned}$$

We get the **radial equation:**

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

The Radial Equation

We get the **radial equation:**

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

It is *identical in form* to the one-dimensional Schrödinger, where:

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

is the **effective potential,** which contains a **centrifugal term**: $\left(\hbar^2/2m\right)\left[\ell(\ell+1)/r^2\right]$

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

The normalisation conditions is: $\int_0^\infty |u|^2\, dr = 1.$

which is potential *V(r)* specific.