Quantum Physics 1

Class 19
Three-dimensional Schrodinger Equation

The Schrodinger Equation

Here's what we have been working with:

$$\hat{H}\psi = \hat{E}\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V(x,t)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Here's what the 3D equation is:

$$\hat{H}\psi = \hat{E}\psi$$

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi + V(\vec{r},t)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Expressing basic quantities in 3D Cartesian Coordinates

- Volume $d\tau = dx\ \ dy\ \ dz$
- Probability of finding a particle in $d\tau$ at time t

$$P(x, y, z, t) = |\Psi(x, y, z, t)|^2 dx\ \ dy\ \ dz$$

- Normalization condition

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\, |\Psi(x, y, z, t)|^2 = 1$$

- Stationary state wave function

$$\Psi(x, y, z, t) = \psi(x, y, z) e^{-\frac{iEt}{\hbar}}$$

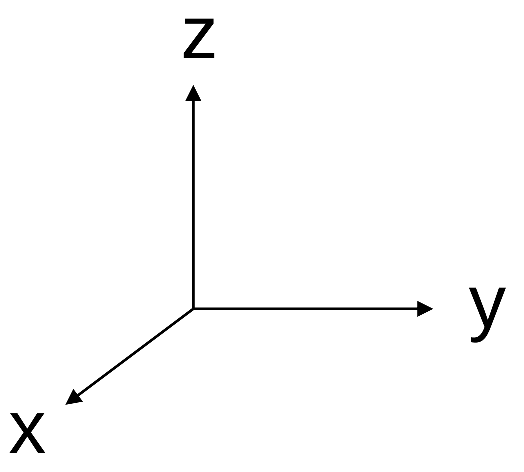
A quick review of coordinate systems

Cartesian coordinates: $\hat{\imath}, \hat{\jmath}, \hat{k}$ form an orthogonal (rectangular) system with each axis at right angles to the other two.

- Line element: $d\vec{l} = dx\hat{\imath} + dy\hat{\jmath} + dz\hat{k}$
- Volume element: $dV = dxdydz$

$$\vec{\nabla} = \hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

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



Cylindrical

Converting to Cartesian coordinates:

$$x = \rho\cos\theta\,, \quad y = \rho\sin\theta\,, \quad z = z$$
$$\rho = (x^2 + y^2)^{1/2}, \quad \tan\theta = y/x$$

- Line element: $d\vec{l} = d\rho\hat{u}_\rho + \rho d\theta\hat{u}_\theta + dz\hat{u}_z$
- Length ds: $ds^2 = dr^2 + r^2 d\theta^2 + dz^2$
- Volume element: $dV = \rho d\rho d\theta dz$

$\hat{\rho}, \hat{\theta}, \hat{z}$

$$\vec{\nabla} = \hat{u}_\rho\frac{\partial}{\partial\rho} + \hat{u}_\theta\frac{1}{\rho}\frac{\partial}{\partial\theta} + \hat{u}_z\frac{\partial}{\partial z}$$
$$\nabla^2 = \frac{1}{\rho}\frac{\partial}{\partial\rho}\rho\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\theta^2} + \frac{\partial^2}{\partial z^2}$$

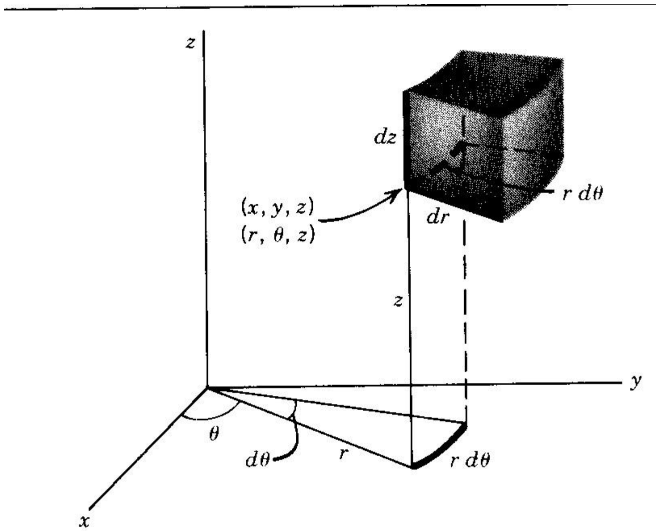


FIGURE 4.4

Spherical

$$x = r\sin\theta\cos\varphi\,; \nearrow\ y = r\sin\theta\sin\varphi\,; \nearrow\ z = r\cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2}; \nearrow \tan\varphi = y/x; \nearrow \tan\theta = \frac{\sqrt{x^2 + y^2}}{z}$$

$$d\vec{l} = dr\hat{r} + rd\theta\hat{\theta} + r\sin\theta\, d\varphi\hat{\varphi}$$

$$dV = r^2\sin\theta\, drd\theta d\varphi$$

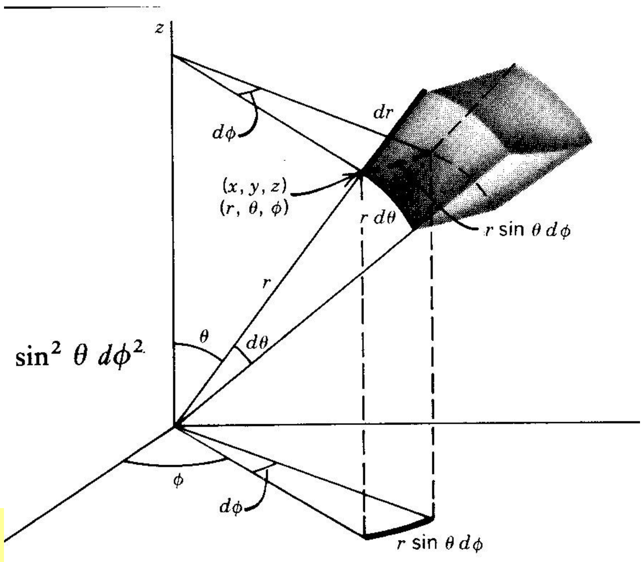


FIGURE 4.5

$$\vec{\nabla} = \hat{u}_r\frac{\partial}{\partial r} + \hat{u}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{u}_\varphi\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}$$

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

A particle in a rectangular 2-D box

$$V(x,y,z) = \begin{cases} 0 & 0 < x < L_x \\ 0 & 0 < y < L_y \\ \end{cases} \quad \text{and infinite otherwise}$$

- We will try a solution using separation of variables.
- We will find that two dimensions leads to two quantum numbers to identify the energy.
- Generally, each dimension or degree of freedom in a problem leads to another distinct quantum number.

Solution by separation of variables

Due to the symmetry of the problem, we choose to solve it in Cartesian coordinates.

$\Psi(x, y, z, t) = \psi(x, y, z)T(t)$

With time independent potential V(x,y,z) we get the TISE again:

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

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

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

Now we assume that a product solution exists:

$\psi(x,y) = X(x)Y(y)$

$$-\frac{\hbar^2}{2m}\left(Y\frac{\partial^2 X}{\partial x^2} + X\frac{\partial^2 Y}{\partial y^2}\right)\psi = EXY$$

Dividing by XY:

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right) - \frac{2m}{\hbar^2}E = 0$$

Pulling all terms in y to one side:

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) - \frac{2m}{\hbar^2}E = -\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}$$

which can only be true if each side is separately equal to the same constant:

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) - \frac{2m}{\hbar^2}E = -\frac{2m}{\hbar^2}E_y$$

$$-\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -\frac{2m}{\hbar^2}E_y$$

$$+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{2m}{\hbar^2}\left(E_y\right)=0$$

For the described rectangular box the solutions are:

$$Y = A\sin k_y\, y + B\cos k_y\, y$$

The y=0 condition gives: B=0

The y=L_y condition gives

$$Z(L_y) = A\sin k_y\, L_y = 0$$

which has non−trivial solutions if

$$k_y = \frac{n_y\pi}{L_y} \text{ with } E_y = \frac{\hbar^2 {k_y}^2}{2m}$$

so: $E_y = \dfrac{\hbar^2 {n_y}^2\pi^2}{2mL_y^2}$

$$-\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\right)-\frac{2m}{\hbar^2}E+\frac{2m}{\hbar^2}E_y \;\; and\ setting\ E_x = E - E_y$$

$$\equiv \left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right)+\frac{2m}{\hbar^2}E_x = 0$$

$$\frac{\partial^2 X}{\partial x^2}+\frac{2m}{\hbar^2}E_x X = 0$$

which has solutions:

$X = A\sin k_x\, x + B\cos k_x\, x$

The x=0 condition gives: B=0

The Falstad applet

The x=L_x condition gives

$X(L_x) = A\sin k_x\, L_x = 0$

which has non−trivial solutions if

$$k_x = \frac{n_x \pi}{L_x} \text{ with } E_x = \frac{\hbar^2 {k_x}^2}{2m}$$

$$E = E_x + E_y = \frac{\hbar^2}{2m}\left({k_x}^2 + {k_y}^2\right) = \frac{\hbar^2 \pi^2}{2m}\left(\frac{{n_x}^2}{L_x^2}+\frac{{n_y}^2}{L_y^2}\right)$$

The Rectangular 3D Box – Quantum well

The 3-D Rectangular Box

$$V(x,y,z) = \begin{cases} 0 & 0 < x < L_x \\ 0 & 0 < y < L_y \\ 0 & 0 < z < L_z \end{cases} \quad \text{and infinite otherwise}$$

Since we are seeking energy eigenfunctions, we assume that the solutions are of the form: $\Psi(\vec{r}$

Now we assume that a product solution exists:

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

$$-\frac{\hbar^2}{2m}\left(ZY\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2}\right)\psi + VXYZ = EXYZ$$

Dividing by XYZ and setting V=0:

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right) + \frac{2m}{\hbar^2}E = 0$$

Pulling all terms in z to one side:

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right) + \frac{2m}{\hbar^2}E = -\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}$$

which can only be true if each side is separately equal to the same constant:

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right) + \frac{2m}{\hbar^2}E = \frac{2m}{\hbar^2}E_z$$

$$-\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = \frac{2m}{\hbar^2}E_z$$

$$+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+\frac{2m}{\hbar^2}(E_z-V_z)=0 \textit{ where } \mathrm{k}_z\equiv\sqrt{\frac{2m}{\hbar^2}(E_z)}$$

For the described rectangular box the solutions are:

$$Z=A\sin k_z z+B\cos k_z z$$

The z=0 condition gives: B=0

The z=L_z condition gives

$$Z(L_z)=A\sin k_z L_z=0$$

which has non−trival solutions if

$$k_z=\frac{n_z\pi}{L_z} \text{ so } E_z=\frac{\hbar^2{k_z}^2}{2m}=\frac{\hbar^2{n_z}^2\pi^2}{2mL_z^2}$$

Or we could assume solutions of the exponential form:

$$Z=Ce^{ik_z z}+De^{-ik_z z}$$

The z=0 boundary condition gives:

$C=-D$ and thus

$$Z=C\left(e^{ik_z z}-e^{-ik_z z}\right)=C'\sin(k_z L_z)\ \ldots$$

Returning to the x and y equation, let′s perform the same separation:
We arbitrarily leave the E_z term on the x side of the equation and set the two sides equal to another constant, E_y

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) + \frac{2m}{\hbar^2}E - \frac{2m}{\hbar^2}E_z = -\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = \frac{2m}{\hbar^2}E_y$$

Solving the y-side: $\frac{\partial^2 Y}{\partial y^2} + \frac{2m}{\hbar^2}E_y Y = 0$ which has solutions
$Y = A\sin k_y\, y + B\cos k_y\, y$

The y=0 condition gives: B=0
The y=L_y condition gives $Z(L_z) = A\sin k_y\, L_y = 0$
which has non−trival solutions if:
$k_y = \frac{n_y \pi}{L_y}$ with $E_y = \frac{\hbar^2 {k_y}^2}{2m} = \frac{\hbar^2 {n_y}^2 \pi^2}{2mL_y^2}$

$$\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right) + \frac{2m}{\hbar^2}E - \frac{2m}{\hbar^2}E_z - \frac{2m}{\hbar^2}E_y \equiv \left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \right) - \frac{2m}{\hbar^2}E_x = 0$$

$$\frac{\partial^2 X}{\partial x^2} + \frac{2m}{\hbar^2}(E_x)X = 0$$

which has solutions:

$X = A\sin k_x x + B\cos k_x x$

The x=0 condition gives: B=0

The x=L_x condition gives

$X(L_x) = A\sin k_x L_x = 0$

which has non−trivial solutions if

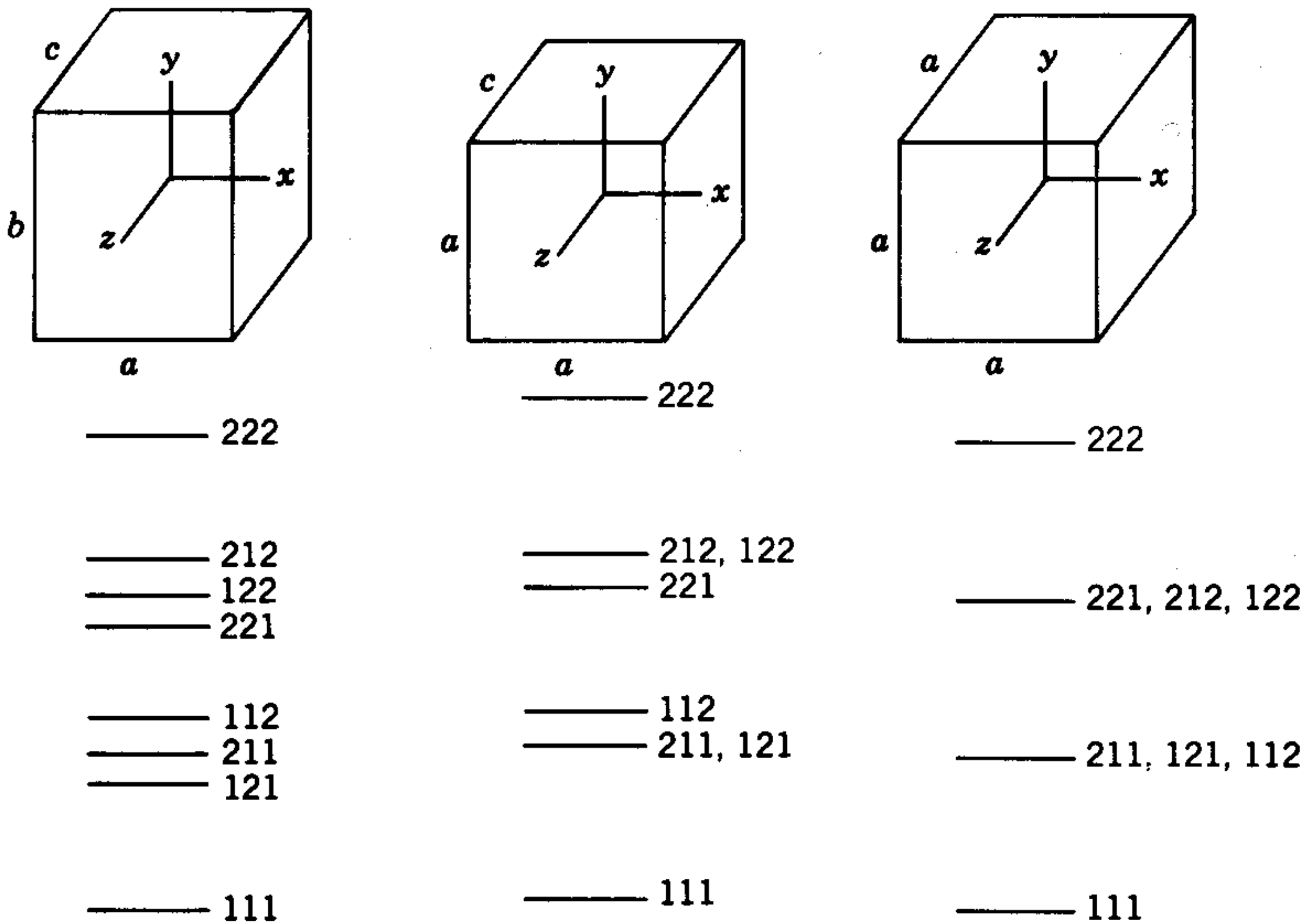
$$k_x = \frac{n_x\pi}{L_x} \text{ with } E_x = \frac{\hbar^2 {k_x}^2}{2m}$$

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}\left({k_x}^2 + {k_y}^2 + {k_z}^2\right)$$

$$= \frac{\hbar^2\pi^2}{2m}\left(\frac{{n_x}^2}{L_x^2} + \frac{{n_y}^2}{L_y^2} + \frac{{n_z}^2}{L_z^2}\right)$$

Figure 5-27

Rectangular boxes for the confinement of a particle. The energy levels are indicated below by the quantum numbers $n_1 n_2 n_3$. The states pass through different stages of degeneracy as the box assumes higher degrees of symmetry.



Spherical symmetry

Solutions for Central Potentials

Let's address the case where the potential only depends on distance from the center.

The 3D time−independent Schrodinger Eq: $\widehat{H}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = E\Psi$

In spherical coordinates*:*

$$\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}\right) + (E-V)\Psi = 0$$

Assuming that the solution can be expressed as a product: $\Psi(\mathrm{r},\theta,\phi)=\mathrm{R}(\mathrm{r})\Theta(\theta)\Phi(\phi)$

$$-\frac{\hbar^2}{2m}\left(\frac{\Theta\Phi}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{\partial d}\right) + (V-E)R\Theta\Phi = 0$$

Assuming: *V*=*V(r)*, dividing through by $\mathrm{R}\Theta\Phi$, and multiplying through by $\sin^2\theta\, \mathrm{r}^2 2\mathrm{m}/\hbar^2$, we can separate the azimuthal term:

$$\sin^2\theta\left(\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{2m}{\hbar^2}\right)(E-V)r^2\right) + \frac{sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m_l^2$$

Which has solutions: $\Phi(\phi) = \mathrm{e}^{\pm \mathrm{i}\mathrm{m}_\mathrm{l}\phi}$.

In order for Φ to be single-valued for any ϕ , m_l must be an integer.

θ solution for central potential

We are now left with the other two variables, r and θ.
Separating the angular terms from the radial terms:

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)-r^2\frac{2m(E-V(r))}{\hbar^2}=+\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta}{\partial\theta}\right]=l(l+1)$$

The angular part of Laplace′s equation is called the Legendre Equation.

$$+\frac{m_l^2}{\sin^2\theta}-\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta}{\partial\theta}\right]=l(l+1)$$

Making the substitution x=cosθ

$$\frac{d}{d\theta}=\frac{dx}{d\theta}\frac{d}{dx}=-\sin\theta\frac{d}{dx}=-\sqrt{1-x^2}\frac{d}{dx},$$ so

In standard form, this is known as the Legendre Equation:

$$\frac{d}{dx}\left[(1-x^2)\frac{d\Theta_{lm}}{dx}\right]+(l(l+1)-\frac{m_l^2}{1-x^2})\Theta_{lm}=0$$

And the solutions are the Associated Legendre Polynomials

θ solution for central potential 2

We will start by solving the special case when $m=0$.

$$\frac{d}{dx}\left[(1-x^2)\frac{dP_l}{dx}\right]+(l(l+1))P_l=0$$

To find the solution we use the power series method,

assume a solution of the form, $y(x)=\sum_{n=0}^{\infty}a_n x^n$

and substitution into gives

$$\sum_{n=2}^{\infty}a_n n(n-1)x^{n-2}-\sum_{n=2}^{\infty}a_n n(n-1)x^n-2\sum_{n=1}^{\infty}a_n n x^n+l(l+1)\sum_{n=0}^{\infty}a_n x^n=0$$

from which we get the recursion relation,

$$a_{n+2}=\frac{(n-l)(n+l+1)}{(n+1)(n+2)}a_n$$

θ solutions for central potential

- Note that the recursion relation only connects terms which differ by two powers in x. This means that the series beaks into two independent series – one even and one odd.
- For the even series there is one arbitrary constant a_0 from which all others are deduced.
- The odd series starts with the arbitrary constant a_1.
- If either series is actually allowed to go to infinity, the wavefunction will sum to infinity unless *l* is only allowed to have a positive integer value. This causes the recursion relation to terminate at the *l*th term.

θ solution for central potential 3

We can deduce the solution for n=0 and use with the recursion relation.

$$P_n(x) = \sum_{j=0}^{N} (-1)^{j} \frac{(2n-2j)!\, x^{n-2j}}{2^n l!\,(n-2j)!\,(n-1)!}$$

where N=n/2 for n even and N=(n−1)/2 for n odd.

A second set of possible solutions yields unphysical results.

The first few Legendre polynomials (P_n) are:

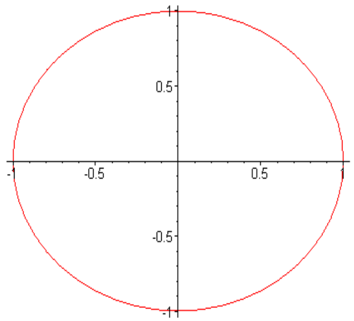
$P_0(x) = 1, \quad P_1(x) = x, \quad P_2(x) = (3x^2-1)/2$

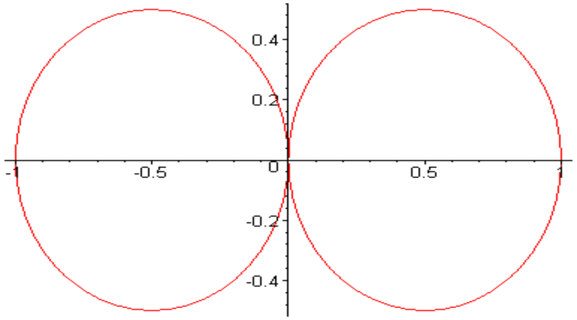
or $P_0 = 1, \quad P_1(\theta) = \cos\theta\,, \quad P_2(\theta) = (3\cos^2\theta - 1)/2$

θ solution for central potential 4

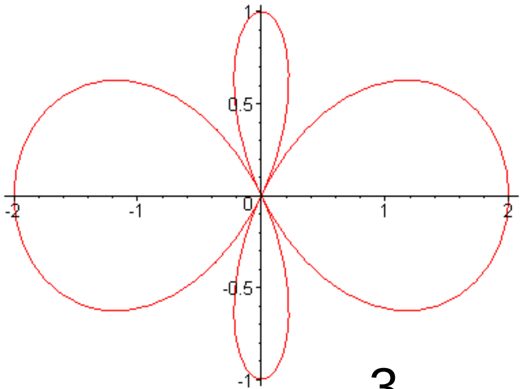
- Example plots of the first few Legendre functions (Legendre_plots.mws)

1





2



3

Properties of Legendre Polynomials

$$P_l(x) = \sum_{j=0}^{N} (-1)^j \frac{(2l-2j)!\, x^{l-2j}}{2^l l!\,(l-2j)!\,(l-1)!}$$

$$where\ N = \frac{l}{2} for\ l\ even\ and\ N = \frac{l-1}{2} for\ n\ odd.$$

The first few Legendre polynomials (P_l) are:

$P_0(x) = 1, P_1(x) = x, P_2(x) = (3x^2 - 1)/2$

or $P_0 = 1, P_1(\theta) = \cos\theta\,, P_2(\theta) = (3\cos^2\theta - 1)/2$

Legendre Polynomials form a complete, orthogonal set of functions on the region $-1 < x < 1$.

Normalization and orthogonality of Legendre Polynomials:

$$\int_{-1}^{1} [P_n(x) P_m(x)]dx = \delta_{nm} \frac{2}{2n+1}$$

θ solution for central potential 5

Orthogonality and normalization
of Legendre Polynomials

$$\int_{-1}^{1}[P_n(x)P_m(x)]dx = \delta_{nm}\frac{2}{2n+1}$$

Orthogonality means that we can express the angular part of any wavefunction using a sum of Legendre polynomials.

θ solution for central potential 6

We will not solve the m $\neq$ 0 case now, but we will state the relation between the Legendre
functions (m=0) and the full solutions (the associated Legendre functions).

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

from which we can find

$$\Theta_{00} = 1,$$

$$\Theta_{10} = x, \quad \Theta_1^{\pm 1} = (1 - x^2)^{1/2},$$

$$\Theta_2^0 = 1 - 3x^2, \quad \Theta_2^{\pm 1} = (1 - x^2)^{1/2} x$$