Spherically Symmetric Problem

Next, we review the quantum mechanical problem of a single particle moving in a 3D spherically symmetric time-independent potential $V(\mathbf{r})$. In 3D, the momentum operator changes to a vector operator $\vec{p} \equiv \mathbf{p} = -i\hbar\vec{\nabla} \equiv -i\hbar\nabla$, where $\vec{\nabla}$ is 3D gradient vector, which in Cartesian coordinates is $\vec{\nabla} = \vec{e}_x\partial_x + \vec{e}_y\partial_y + \vec{e}_z\partial_z$ (vector quantities are interchangeably denoted either by bold font, or by an arrow on top of a character). Then, the time-dependent and time-independent Schrödinger equations in 3D become respectively (see Eqs. (1) and (3) in live script *Particle in Box*)

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \qquad (14)$$

and

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi, \qquad (15)$$

where $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\varphi(t)$ and $\nabla^2 = \vec{\nabla}\cdot\vec{\nabla}$ is 3D Laplacian, which in Cartesian coordinates is: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

The potential energy $V(\mathbf{r})$ and wave function $\psi(\mathbf{r})$ are now functions of 3D position vector $\mathbf{r} = \mathbf{r}(x, y, z)$, thus, the normalization of wave function in 3D is

$$\int |\psi(\mathbf{r})|^2 d^3\mathbf{r} = 1, \qquad (16)$$

where infinitesimal volume element in 3D space is denoted by $d^3\mathbf{r}$ and in Cartesian coordinates it is $d^3\mathbf{r} \to |d\mathbf{r}_x \wedge d\mathbf{r}_y \wedge d\mathbf{r}_z| = dxdydz|\vec{e}_x \wedge \vec{e}_y \wedge \vec{e}_z| = dxdydz$, where we used $d\mathbf{r}_x = \mathbf{r}(x + dx, y, z) - \mathbf{r}(x, y, z) = \vec{e}_x dx$, with $\vec{e}_x = \frac{\partial\mathbf{r}}{\partial x}$, etc.

To utilize the symmetry in atoms with centrally symmetric potentials, we introduce **spherical coordinates** $\mathbf{r} = \mathbf{r}(r, \theta, \phi)$, as sketched in Fig. 1, where $x = r\sin\theta\cos\phi, y = r\sin\theta\sin\phi, z = r\cos\theta$ and θ is a polar angle, while ϕ is called azimuthal angle.

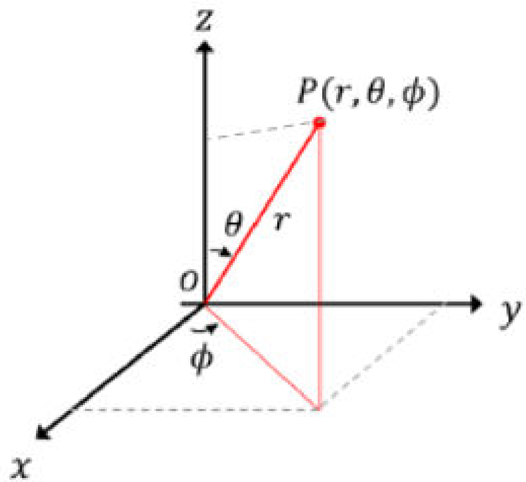


Figure 1: Illustration of spherical and Cartesian coordinates of point P.

Cartesian coordinates are global, i.e. $\overrightarrow{e}_j$ (for $j = x, y, z$) are constant, space independent, unit vectors: $\partial_x \overrightarrow{e}_j = \partial_y \overrightarrow{e}_j = \partial_z \overrightarrow{e}_j = 0$. Such relations in general do not hold in spherical coordinates e.g. $\partial_\theta \overrightarrow{e}_r = \overrightarrow{e}_\theta \neq 0$, since $\overrightarrow{e}_r(r, \theta + \Delta\theta, \phi)$ points in the direction different from $\overrightarrow{e}_r(r, \theta, \phi)$. Even though that $\partial_r \overrightarrow{e}_\alpha = 0$ and $\overrightarrow{e}_\alpha$ in spherical coordinates (for $\alpha = r, \theta, \phi$) are also orthogonal set of unit length vectors, their direction is not constant and changes from point to point in general.

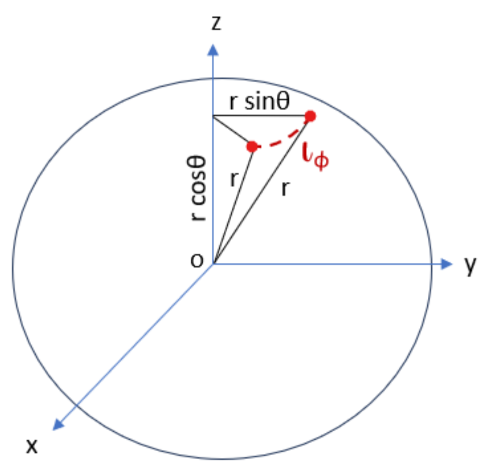


Figure 2: Path $\ell_\phi = r \sin\theta \Delta\phi$ on a sphere, fox fixed r and θ and varying $\phi \to \phi + \Delta\phi$.

Red dots and a dashed path are located on a sphere with radius r, at same value of θ.

If we fix r and θ and just vary ϕ, as shown in Fig. 2 we get:

$$\Delta\mathbf{r}_\phi = \mathbf{r}(r, \theta, \phi + \Delta\phi) - \mathbf{r}(r, \theta, \phi) = r \sin\theta \Delta\phi \overrightarrow{e}_\phi .$$

Analogically we have:

- $d\mathbf{r}_\theta \equiv \dfrac{\partial \mathbf{r}}{\partial \theta} d\theta = \mathbf{r}(r, \theta + d\theta, \phi) - \mathbf{r}(r, \theta, \phi) = r d\theta \vec{e}_\theta$
- $d\mathbf{r}_r = \mathbf{r}(r + dr, \theta, \phi) - \mathbf{r}(r, \theta, \phi) = dr \vec{e}_r.$

Hence the total differential of radius vector $\mathbf{r}$ is:

$$d\mathbf{r} = \frac{\partial \mathbf{r}}{\partial r} dr + \frac{\partial \mathbf{r}}{\partial \theta} d\theta + \frac{\partial \mathbf{r}}{\partial \phi} d\phi = d\mathbf{r}_r + d\mathbf{r}_\theta + d\mathbf{r}_\phi = dr \vec{e}_r + r d\theta \vec{e}_\theta + r \sin\theta d\phi \vec{e}_\phi = dr \vec{e}_r + r\, d\vec{e}_r,$$

where last equality follows from $\mathbf{r} = r\vec{e}_r$ (hence coordinates of a radius vector $\mathbf{r}$ in a local spherical coordinate basis $\vec{e}_r$, $\vec{e}_\theta$, and $\vec{e}_\phi$ are $r_r = (\mathbf{r} \cdot \vec{e}_r) = r$, $r_\theta = r_\phi = 0$) and a chain rule (when applying differential to both sides of this equation) and implies:

- $d\vec{e}_r = \vec{e}_\theta d\theta + \vec{e}_\phi \sin\theta d\phi$, hence: $\dfrac{\partial \vec{e}_r}{\partial \theta} = \vec{e}_\theta$ and $\dfrac{\partial \vec{e}_r}{\partial \phi} = \sin\theta \vec{e}_\phi$.

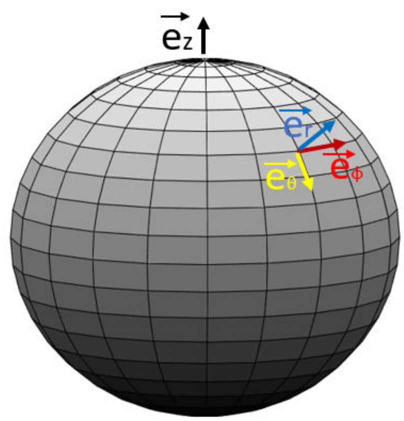


Figure 3: Illustration of unit vectors $\vec{e}_r$- in the direction of radius vector,

$\vec{e}_\theta$ - tangent to meridian, and $\vec{e}_\phi$- tangent to parallel.

From geometrical considerations, since $\dfrac{\partial \vec{e}_\phi}{\partial r} = \dfrac{\partial \vec{e}_\phi}{\partial \theta} = 0$ (see Fig. 3), for differential of $\vec{e}_\phi$ we have:

$$d\vec{e}_\phi = \vec{e}_z \times \vec{e}_\phi d\phi = \vec{e}_z \times (\vec{e}_r \times \vec{e}_\theta) d\phi.$$

Using $\vec{e}_z = \cos\theta \vec{e}_r - \sin\theta \vec{e}_\theta$ (since $(\vec{e}_z \cdot \vec{e}_r) = (\vec{e}_z \cdot \vec{r}/r) = z/r = \cos\theta$ and since $|\vec{e}_z| = 1$, then it follows that $(\vec{e}_z \cdot \vec{e}_\theta) = -\sin\theta$) and opening the triple vector product leads to:

- $d\vec{e}_\phi = (-\vec{e}_r\sin\theta - \vec{e}_\theta\cos\theta)d\phi$, hence: $\dfrac{\partial\vec{e}_\phi}{\partial\phi} = -\vec{e}_r\sin\theta - \vec{e}_\theta\cos\theta$,
- $d\vec{e}_\theta = d(\vec{e}_\phi\times\vec{e}_r) = \vec{e}_\phi\cos\theta d\phi - \vec{e}_r d\theta$, hence: $\dfrac{\partial\vec{e}_\theta}{\partial\theta} = -\vec{e}_r$ and $\dfrac{\partial\vec{e}_\theta}{\partial\phi} = \cos\theta\,\vec{e}_\phi$.

Next, we note that differential of any scalar function can be written as:

$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz = \frac{\partial f}{\partial r}dr + \frac{\partial f}{\partial\theta}d\theta + \frac{\partial f}{\partial\phi}d\phi = \vec{\nabla} f\cdot d\mathbf{r}$.

Hence, for the gradient vector we get (see another derivation in Appendix A)

$$\vec{\nabla} = \vec{e}_x\frac{\partial}{\partial x} + \vec{e}_y\frac{\partial}{\partial y} + \vec{e}_z\frac{\partial}{\partial z} = \vec{e}_r\frac{\partial}{\partial r} + \vec{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \vec{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$$

and consequently the Laplacian in spherical coordinates takes the form

$$\nabla^2 \equiv \vec{\nabla}\cdot\vec{\nabla} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right). \qquad (17)$$

For the 3D volume element in spherical coordinates we get:

$d^3\mathbf{r} \to |d\mathbf{r}_r\wedge d\mathbf{r}_\theta\wedge d\mathbf{r}_\phi| = |dr\,\vec{e}_r\wedge rd\theta\,\vec{e}_\theta\wedge r\sin\theta d\phi\,\vec{e}_\phi| = r^2\sin\theta\, drd\theta d\phi$.

We can confirm the obtained expression of 3D volume element, by computing Jacobian of transformation between the spherical and Cartesian coordinates.

```
syms r phi theta real
```

Define the transformation from spherical to Cartesian coordinates.

```
R = [r*sin(theta)*cos(phi), r*sin(theta)*sin(phi), r*cos(theta)]
```

R = $\left(r\cos(\phi)\sin(\theta) \quad r\sin(\phi)\sin(\theta) \quad r\cos(\theta)\right)$

Find the Jacobian of the coordinate change from spherical coordinates to Cartesian coordinates.

```
J=jacobian(R,[r,phi,theta])
```

J =

$$\begin{pmatrix} \cos(\phi)\sin(\theta) & -r\sin(\phi)\sin(\theta) & r\cos(\phi)\cos(\theta) \\ \sin(\phi)\sin(\theta) & r\cos(\phi)\sin(\theta) & r\cos(\theta)\sin(\phi) \\ \cos(\theta) & 0 & -r\sin(\theta) \end{pmatrix}$$

```
assume(0<=theta & theta<=pi)
simplify(abs(det(J)))
```

ans = $r^2\sin(\theta)$

Note, $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\widehat{\mathbf{L}}^2$ (see Appendix B), where $\widehat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ is the angular momentum vector operator that commutes with the Hamiltonian of the system with central symmetric potential $V(r)$ and hence is a conserved quantity. Dirac, using the commutation relations between angular momentum components $[\widehat{L}^i, \widehat{L}^j] = i\hbar\epsilon_{ijk}\widehat{L}^k$ (with Levi-Civita epsilon) has proved that eigenvalues of $\widehat{\mathbf{L}}^2$ must be necessarily quantized as $\ell(\ell+1)\hbar^2$, where ℓ is an integer or half-integer non-negative number. Since $\widehat{\mathbf{L}}^2$ commutes with $\widehat{\mathbf{L}}$ (and hence with each of its components), we can search for eigenfunctions of $\widehat{\mathbf{L}}^2$ which will be simultaneously eigenfunctions of $\widehat{L}^z$, see Eq. (25) below (hence $\widehat{\mathbf{L}}^2|\ell,m\rangle = \ell(\ell+1)\hbar^2|\ell,m\rangle$ and $\widehat{L}^z|\ell,m\rangle = m\hbar|\ell,m\rangle$). Eigenvalues of $\widehat{L}^z$ (in units of $\hbar$), denoted by m can take on only the following values $m = -\ell, -\ell+1, \ldots \ell$.

In case of a central potential $V(r)$, we represent the wave function as a product of two functions describing radial and angular dependencies, i.e. $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$. The time-independent Schrödinger equation becomes

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]\right\} + \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = 0, \qquad (18)$$

which could be separated into **radial equation** and **angular equation** by introducing the **azimuthal quantum number** ℓ,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E] = \ell(\ell+1) \qquad (19)$$

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -\frac{1}{Y\hbar^2}\widehat{\mathbf{L}}^2 Y = -\ell(\ell+1). \qquad (20)$$

By changing the variable $u(r) = rR(r)$, the radial equation Eq. (19) can be simplified further.

We will show that $\frac{r}{u(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\left(\frac{u(r)}{r}\right) = \frac{r^2}{u(r)}\frac{d^2u(r)}{dr^2}$ using symbolic calculation below [*]:

```
syms u(r)             % define symbolic function
simplify(r/u*diff(r^2*diff(u/r)))
```

ans(r) =

$$\frac{r^2\,\frac{\partial^2}{\partial r^2}\,u(r)}{u(r)}$$

For Eq. (19) in variable $u(r)$ we obtain:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu \qquad (21)$$

which can be rendered as a Schrödinger equation in 1D by extending r to the whole real axes, $r \in (-\infty, \infty)$, and defining the effective potential as

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}, \text{ for } r \geq 0 \qquad (21a)$$

$$V_{\text{eff}}(r) = +\infty \text{, for } r < 0 \qquad (21b).$$

Solution of Eq. (21) depends on quantum number $\ell = 0, 1, 2, \ldots$, hence we denote them as u_ℓ. For different values of ℓ, the effective potential that particle feels is different. Due to Eq. (21b) all finite-energy solutions of Eq. (21) vanish for any ℓ at $r \leq 0$, hence:

$$u(0) = 0. \qquad (21c)$$

For angular equation Eq. (20), again, we assume $Y(\theta, \phi)$ is also separable,

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi). \qquad (22)$$

Plugging this in Eq. (20), and rearranging the equation, we get

$$\left\{\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta\right\} + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = 0. \qquad (23)$$

Eq. (23) can be represented by 2 separate equations by introducing the **magnetic quantum number** m,

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2, \qquad (24)$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2. \qquad (25)$$

```
syms m Phi(phi)
ode1 = laplacian(Phi,phi)/Phi == -m^2
```

ode1(phi) =

$$\frac{\frac{\partial^2}{\partial\phi^2}\,\Phi(\phi)}{\Phi(\phi)} = -m^2$$

```
dsolve(ode1)
```

ans = $C_1\,\mathrm{e}^{-m\,\phi\,\mathrm{i}} + C_2\,\mathrm{e}^{m\,\phi\,\mathrm{i}}$

If there is a time-reversal symmetry in the problem (e.g. when there is no external magnetic field and preferred direction) we can choose wave function, eigen state of time-reversal symmetric Hamiltonian, to be real, hence we can specify $C_1 = \pm C_2$. More popular (and practical) way to specify further the solution of Eq. (25), is to use another condition on wave function, namely that $\Phi(\phi)$ should be also an eigen function of the $\widehat{L}_z$ operator, which is the z component of angular momentum $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ (hence we implicitly assume some preferred direction $\vec{e}_z$). In spherical coordinates, we have

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial \phi} \qquad (26)$$

and

$$\hat{L}_z\Phi = \hbar m\Phi. \qquad (27)$$

Observe, for the real non-zero eigen value $m \neq 0$ (eigen values of Hermitian operators are real), Eq. (27) involves imaginary number i, hence eigen functions of $\hat{L}_z$ operator can not be real if $m \neq 0$.

```
ode2 = ( -1i*diff(Phi,phi) ) == m*Phi
```

ode2(phi) =

$$-\frac{\partial}{\partial \phi}\,\Phi(\phi)\,\mathrm{i} = m\,\Phi(\phi)$$

```
Phi(phi)=dsolve(ode2)
```

Phi(phi) = $C_1\,\mathrm{e}^{m\,\phi\,\mathrm{i}}$

Thus, ignoring the multiplicative constant C_1, which can be absorbed into the overall normalization of the wave function $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$, the solution of Φ could be written in the exponential form:

$$\Phi(\phi) = e^{im\phi}, \qquad (28)$$

where m must be a real number, since it is an eigen value of Hermitian operator $\hat{L}_z$.

By the periodicity of the angular variable ϕ, we have

$$\Phi(\phi) = \Phi(\phi + 2\pi) = \Phi(\phi)e^{i2m\pi}, \qquad (29)$$

```
assume(m,'real')
Phi(phi) = exp(1i*m*phi);
solve(Phi(phi)==Phi(phi+2*pi),m,'ReturnConditions',true)
```

```
ans = struct with fields:
             m: k
    parameters: k
    conditions: in(k, 'integer')
```

so that $e^{i2m\pi} = 1$, from which it follows that m **must be an integer** and hence ℓ **must be non-negative integer** such that $-\ell \leq m \leq \ell$.

By introducing $x = \cos(\theta)$, we can rewrite Eq. (24) for Θ as

$$(1-x^2)\frac{\mathrm{d}^2\Theta(x)}{\mathrm{d}x^2}-2x\frac{\mathrm{d}\Theta}{\mathrm{d}x}+\left(\ell(\ell+1)-\frac{m^2}{1-x^2}\right)\Theta(x)=0$$

and solve it using symbolic computation.

```
syms Theta(x) l m
assume(abs(x) <=1)
assume(l,["integer","positive"])
assume(m,'integer')
assumeAlso(l-abs(m)>=0)
ode3 = (1-x^2)*laplacian(Theta,x)-2*x*diff(Theta,x)+(l*(l+1)+m^2/(x^2-1))*Theta==0
```

ode3(x) =

$$-(x^2-1)\frac{\partial^2}{\partial x^2}\Theta(x)-2x\frac{\partial}{\partial x}\Theta(x)+\Theta(x)\left(l(l+1)+\frac{m^2}{x^2-1}\right)=0$$

```
ySol(x) = dsolve(ode3)
```

ySol(x) =

$$\frac{C_2\,x^{l+m}\,{}_2\mathrm{F}_1\left(-\frac{l}{2}-\frac{m}{2},\frac{1}{2}-\frac{m}{2}-\frac{l}{2};\ \frac{1}{2}-l;\ \frac{1}{x^2}\right)}{\sigma_1}+\frac{C_1\,x^{m-l-1}\,{}_2\mathrm{F}_1\left(\frac{l}{2}-\frac{m}{2}+1,\frac{l}{2}-\frac{m}{2}+\frac{1}{2};\ l+\frac{3}{2};\ \frac{1}{x^2}\right)}{\sigma_1}$$

where

$$\sigma_1=(x^2-1)^{m/2}$$

The first solution ${}_2F_1\left(-\frac{\ell}{2}-\frac{m}{2},\frac{1-\ell-m}{2};\frac{1}{2}-\ell;\frac{1}{x^2}\right)\frac{x^{\ell+m}}{(1-x^2)^{m/2}}$ is everywhere real, finite and continuous for $x\in[-1,1]$ for any integers m and ℓ such that $0\le|m|\le\ell$.

The second solution ${}_2F_1\left(\frac{\ell}{2}-\frac{m}{2}+1,\frac{1+\ell-m}{2};\frac{3}{2}+\ell;\frac{1}{x^2}\right)\frac{x^{m-\ell-1}}{(1-x^2)^{m/2}}$ is in general complex, having nonzero real and imaginary parts, which are either not everywhere finite on interval $x\in[-1,1]$ or not continuous at $x=\pm1$ or $x=0$ points, hence for physically acceptable solutions we put $C_1=0$.

For $|x|\le1$ the hypergeometric function ${}_2F_1\left(-\frac{\ell}{2}-\frac{m}{2},\frac{1-\ell-m}{2};\frac{1}{2}-\ell;\frac{1}{x^2}\right)$ is related with the associated Legendre polynomial $P_\ell^m(x)$ as:

$$P_\ell^m(x)=\frac{2^\ell\,\Gamma(\ell+1/2)}{\sqrt{\pi}\,\Gamma(\ell+1-m)}\,{}_2F_1\left(-\frac{\ell}{2}-\frac{m}{2},\frac{1-\ell-m}{2};\frac{1}{2}-\ell;\frac{1}{x^2}\right)\frac{x^{\ell+m}}{(1-x^2)^{m/2}}.$$

We confirm the above relation between the associated Legendre polynomial and the hypergeometric function using `isAlways()` function and also by plotting together both sides of the above equation.

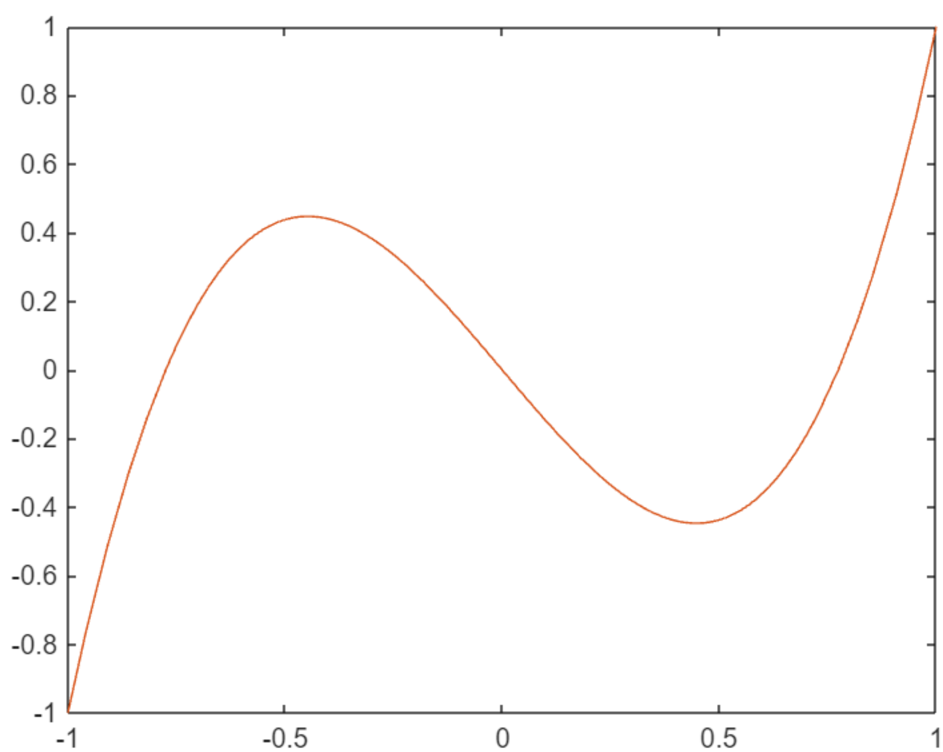
```
syms x
```

```
l=3;
m=0;

isAlways(2^l*gamma(l+1/2)/(sqrt(pi)*gamma(l+1-m))*hypergeom([- l/2 - m/2, 1/2 - m/2
- l/2], 1/2 - l, 1/x^2)*x^(l + m)/(1-x^2)^(m/2)==AssociatedLegendreP(l,m))
```

```
ans = logical
   1
```

```
fplot(2^l*gamma(l+1/2)/(sqrt(pi)*gamma(l+1-m))*hypergeom([- l/2 - m/2, 1/2 - m/2 -
l/2], 1/2 - l, 1/x^2)*x^(l + m)/(1-x^2)^(m/2),[-1,1])
hold on
fplot(AssociatedLegendreP(l,m),[-1,1])    % AssociatedLegendreP function is defined
at the end of script
hold off
```



Hence, we can write:

$$\Theta(\theta) \sim P_\ell^m(\cos\theta), \qquad (30)$$

where P_ℓ^m for $\ell \geq m \geq 0$ satisfy

$$P_\ell^m(x) = (-1)^m(1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x). \qquad (31)$$

For negative values of $\widetilde{m} = -1, -2, \ldots$, expression of $P_\ell^{\widetilde{m}}$ can be obtained by:

$$P_\ell^{\widetilde{m}}(x) = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_\ell^m(x), \qquad (32)$$

where $m = -\widetilde{m} > 0$ and $P_\ell(x) = P_\ell^0(x)$ is the ℓ-th Legendre polynomial that can be written, using Rodrigues' formula, as:

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx}\right)^\ell (x^2 - 1)^\ell. \qquad (33)$$

As already discussed, ℓ and m can only take following values:

$$\ell = 0, 1, 2, \ldots, \quad m = -\ell, -\ell + 1, \ldots, -1, 0, 1, \ldots, \ell - 1, \ell. \qquad (34)$$

Conditions in Eq. (34) follow from the commutation relations between angular momentum components (Dirac's proof that restricts values of both ℓ and m to integer or half-integer values with $\ell \geq 0$ and $|m| \leq \ell$) and Eq. (29) that demands periodicity of the wave function and restricts m (and hence ℓ) to integer values (non-negative integers).

The volume element in spherical coordinates is $d\mathbf{r} = r^2 \sin\theta dr d\theta d\phi$, thus the normalization condition becomes

$$\int |\psi|^2 r^2 \sin\theta dr d\theta d\phi = \int |R|^2 r^2 dr \int |Y|^2 \sin\theta d\theta d\phi = 1. \qquad (35)$$

Usually we normalize radial and angular parts of the wave function separately,

$$\int_0^\infty |R|^2 r^2 dr = 1 \text{ and } \int_0^\pi \int_0^{2\pi} |Y|^2 \sin\theta d\theta d\phi = 1. \qquad (36)$$

The normalized angular wave functions are called spherical harmonics:

$$Y_\ell^m(\theta, \phi) = \sqrt{\frac{(2\ell + 1)}{4\pi} \frac{(\ell - m)!}{(\ell + m)!}} e^{im\phi} P_\ell^m(\cos\theta). \qquad (37)$$

Expressions of $P_\ell^m(\cos\theta)$ for $\ell = 0$ and $\ell = 1$ are: $P_0^0(\cos\theta) = 1$, $P_1^1(\cos\theta) = -\sin\theta$, $P_1^0(\cos\theta) = \cos\theta$, $P_1^{-1}(\cos\theta) = \frac{\sin\theta}{2}$ and we used that $|\sin\theta| = \sin\theta$ for $0 \leq \theta \leq \pi$.

Expressions of $Y_\ell^m(\theta, \phi)$ for $\ell = 0$ and $\ell = 1$ are: $Y_0^0(\theta, \phi) = \frac{1}{2\sqrt{\pi}}$, $Y_1^1(\theta, \phi) = -\frac{\sqrt{3}}{\sqrt{8\pi}} \sin\theta e^{i\phi}$, $Y_1^0(\theta, \phi) = \frac{\sqrt{3}}{2\sqrt{\pi}} \cos\theta$, $Y_1^{-1}(\theta, \phi) = \frac{\sqrt{3}}{\sqrt{8\pi}} \sin\theta e^{-i\phi}$.

Snippet below calculates $P_\ell^m(\cos\theta)$ and $Y_\ell^m(\theta, \phi)$ for arbitrary values of $\ell \geq 0$ and $m = -\ell, \ldots\ell$.

```
syms theta phi real
l = 1;
```

```
assume(0<=theta & theta<=pi);
m_allowed = string((-l:l));
m = double(m_allowed(3));
P_lm=simplify(subs(AssociatedLegendreP(l,m),x,cos(theta)),Steps=50);
simplify(P_lm)
```

ans = $-\sin(\theta)$

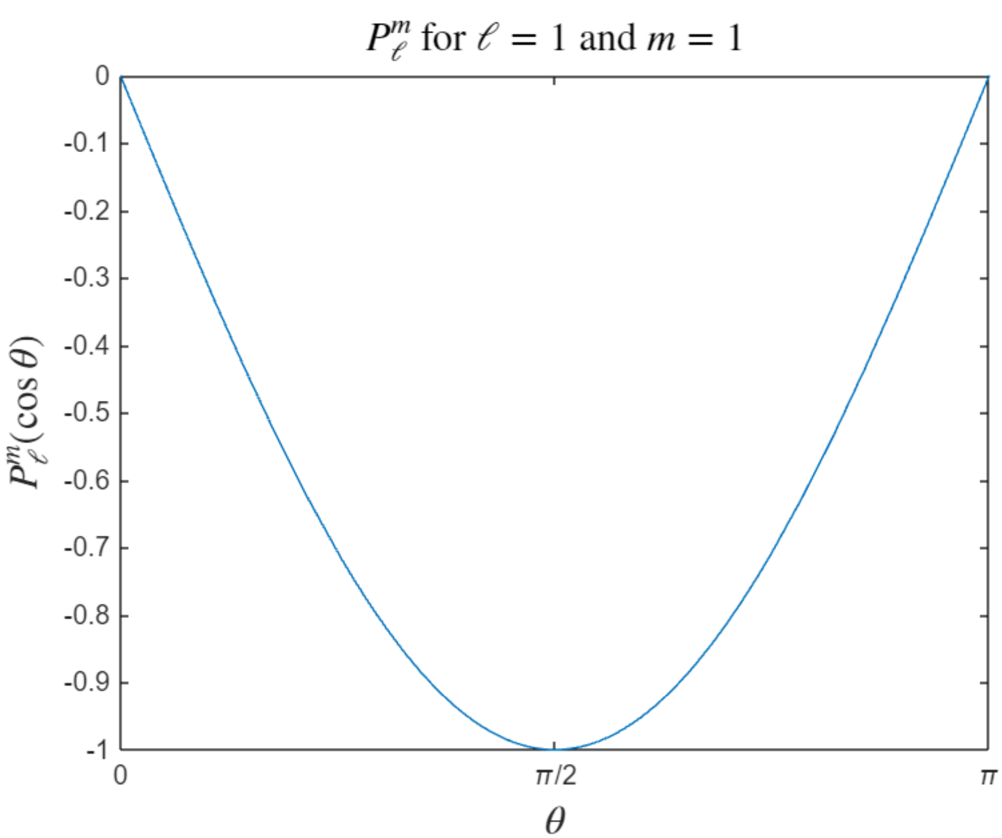
```
% function AssociatedLegendreP(l,m) is defined in the end
Y_lm(theta,phi)=sqrt((2*l+1)*factorial(l-m)/
(4*sym(pi)*factorial(l+m)))*P_lm*exp(1i*m*phi)
```

Y_lm(theta, phi) =

$$-\frac{\sqrt{3}\ \sqrt{8}\ e^{\phi\,i}\sin(\theta)}{8\ \sqrt{\pi}}$$

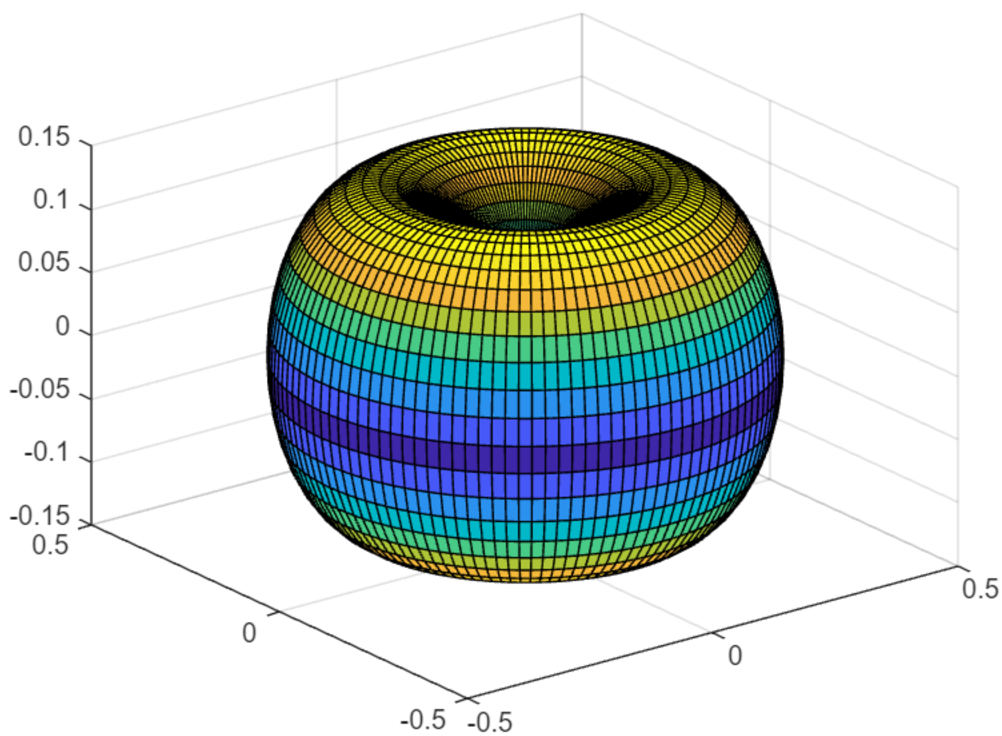
Next we plot associated Legendre function $P_\ell^m(\cos\theta)$ as function of polar angle θ.

```
fplot(theta,P_lm,[0,pi])
xlabel("$\theta $",'Interpreter','latex',Fontsize=15)
xticks([0,pi/2,3.1415])
xticklabels({'0', '\pi/2','\pi'})
ylabel("$P_{\ell}^m(\cos{\theta})$",'Interpreter','latex',Fontsize=15)
title(['$P_{\ell}^m$ for $\ell=$',num2str(l), ' and $m=$',
num2str(m)] ,'Interpreter','latex',Fontsize=15)
```



Next we will visualize absolute value of normalized spherical harmonics.

```
figure;
l = 3;
m_allowed = string((-l:l));
m = double(m_allowed(1));
dalpha = pi/60;
pol = 0:dalpha:pi;
az = 0:dalpha:2*pi;
[phi,theta] = meshgrid(az,pol);
Plm = legendre(l,cos(theta));
%Plm is 3D Tensor, first index of tensor corresponds to different m values:
%m=0,1,2,...l
if l ~= 0
    Plm = reshape(Plm(abs(m)+1,:,:),size(phi));
end
a = (2*l+1)*factorial(l-abs(m));
b = 4*pi*factorial(l+abs(m));
C = sqrt(a/b);
[x,y,z] = sph2cart(phi,pi/2-theta,abs(C*exp(1i*m*phi).*Plm));
surf(x,y,z,abs(z));
```



Exercises

Exercise 1: Show that for function $u(r)$ that does not depend on angular variables θ and ϕ, following relation holds: $\nabla^2\left(\frac{u(r)}{r}\right) = \frac{1}{r}\frac{d^2u(r)}{dr^2} - 4\pi u(0)\delta^3(\mathbf{r})$, where $\delta^3(\mathbf{r})$ is Dirac's 3D delta function.

Hint: $\nabla^2\left(\frac{u(r)}{r}\right) = \lim_{\varepsilon\to 0}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\left(\frac{u(r)}{\sqrt{r^2+\varepsilon^2}}\right) = \frac{1}{r}\frac{d^2u(r)}{dr^2} - 4\pi u(0)\delta^3(\mathbf{r}) + \lim_{\varepsilon\to 0}\frac{2u'(0)\varepsilon^2}{r(r^2+\varepsilon^2)^{3/2}}$, where $4\pi\delta^3(\mathbf{r}) = \lim_{\varepsilon\to 0}\frac{3\varepsilon^2}{(r^2+\varepsilon^2)^{5/2}}$ and the integral over the 3D space for the last term produces $8\pi u'(0)\varepsilon$, hence, in the limit $\varepsilon \to 0$ it vanishes and can be safely ignored. Hence:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\left(\frac{u(r)}{r}\right) = \frac{1}{r}\frac{d^2u(r)}{dr^2} - 4\pi u(0)\delta^3(\mathbf{r}) \qquad (38),$$

and multiplying both sides of Eq. (38) with r^2 leads to: $\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\left(\frac{u(r)}{r}\right) = r\frac{d^2u(r)}{dr^2}$, since $r^2\delta^3(\mathbf{r}) = 0$.

Exercise 2: Prove the following equations and then prove the expression in Eq. (26).

$$x\frac{\partial\phi}{\partial y} - y\frac{\partial\phi}{\partial x} = 1, \quad x\frac{\partial\theta}{\partial y} - y\frac{\partial\theta}{\partial x} = 0, \quad x\frac{\partial r}{\partial y} - y\frac{\partial r}{\partial x} = 0$$

```
syms x y z real
phi = atan2(y,x);
theta = atan2(z,sqrt(x^2 + y^2));
r = sqrt(x^2 + y^2 + z^2);
simplify(x*diff(phi,y)-y*diff(phi,x))
```

ans = 1

```
simplify(x*diff(theta,y)-y*diff(theta,x))
```

ans = 0

```
simplify(x*diff(r,y)-y*diff(r,x))
```

ans = 0

Exercise 3: Using symbolic computation obtain explicit expressions of $Y_\ell^m(\theta,\phi)$ for values of $\ell = 1, 2, 3$ and $-\ell \le m \le \ell$ and show that: $\sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\theta,\phi)Y_\ell^m(\theta,\phi) = \frac{2\ell+1}{4\pi}$.

Exercise 4: By similar steps as presented for spherical coordinates, derive expression of the differential $d\mathbf{r} = d\mathbf{r}_z + d\mathbf{r}_\rho + d\mathbf{r}_\phi$, where $\mathbf{r} = \mathbf{r}(z,\rho,\phi)$, gradient vector $\vec{\nabla}$, Laplacian ∇^2 and 3D volume element $d^3\mathbf{r} \to |d\mathbf{r}_z \wedge d\mathbf{r}_\rho \wedge d\mathbf{r}_\phi|$ in cylindrical coordinates.

Hint: from geometrical considerations derive and use the following relations:

- $d\vec{e}_z = 0$
- $d\vec{e}_\phi = -\vec{e}_\rho d\phi$
- $d\vec{e}_\rho = \vec{e}_\phi d\phi$

Confirm the expression of 3D volume element, using symbolic computation.

```
syms rho phi z real
assume(rho>=0)
```

Define the coordinate transformation from cylindrical coordinates to Cartesian coordinates.

```
R = [rho*cos(phi), rho*sin(phi), z]  %[x, y, z]
```

R = $\begin{pmatrix} \rho\cos(\phi) & \rho\sin(\phi) & z \end{pmatrix}$

Find the Jacobian of the coordinate change from cylindrical to Cartesian coordinates.

```
J=jacobian(R,[rho,phi,z])
```

J =

$$\begin{pmatrix} \cos(\phi) & -\rho\sin(\phi) & 0 \\ \sin(\phi) & \rho\cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

```
simplify(abs(det(J)))
```

ans = ρ

Exercise 5: Calculate divergence and curl (rotor) of a vector field $\mathbf{E}(r,\theta,\phi)$ in spherical coordinates.

Hint: $\mathrm{div}(\mathbf{E}) = \nabla\cdot\mathbf{E}$, where in spherical coordinates

$\nabla = \vec{e}_r\frac{\partial}{\partial r} + \vec{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \vec{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$ and $\mathbf{E} = E_r\vec{e}_r + E_\theta\vec{e}_\theta + E_\phi\vec{e}_\phi$.

A dot product of a gradient vector with $\mathbf{E}$ gives (using $\partial_\theta\vec{e}_r = \vec{e}_\theta$, etc.):

$$\begin{aligned}\nabla\cdot\mathbf{E} &= \left(\vec{e}_r\frac{\partial}{\partial r} + \vec{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \vec{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\right)\cdot\left(E_r\vec{e}_r + E_\theta\vec{e}_\theta + E_\phi\vec{e}_\phi\right) \\ &= \partial_r E_r + \frac{E_r}{r} + \frac{1}{r}\partial_\theta E_\theta + \frac{E_r}{r} + \frac{E_\theta\cos\theta}{r\sin\theta} + \frac{1}{r\sin\theta}\partial_\phi E_\phi \\ &= \partial_r E_r + \frac{2E_r}{r} + \frac{1}{r}\partial_\theta E_\theta + \frac{E_\theta\cos\theta}{r\sin\theta} + \frac{1}{r\sin\theta}\partial_\phi E_\phi\end{aligned}.$$

Hence, divergence of a vector field $\mathbf{E}(r,\theta,\phi)$ in spherical coordinates is:

$$\nabla\cdot\mathbf{E}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2E_r\right)+\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta E_\theta)+\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}E_\phi.$$

Similarly, calculate $\mathbf{curl}(\mathbf{E})=\nabla\times\mathbf{E}$, using $\vec{e}_\theta=\vec{e}_\phi\times\vec{e}_r$, etc.

Appendix A

Here we derive expression of a gradient vector in spherical coordinates.

$$\begin{aligned}
\vec{\nabla} &= \vec{e}_x\frac{\partial}{\partial x}+\vec{e}_y\frac{\partial}{\partial y}+\vec{e}_z\frac{\partial}{\partial z}\\
&= \vec{e}_x\left(\frac{\partial r}{\partial x}\partial_r+\frac{\partial\theta}{\partial x}\partial_\theta+\frac{\partial\phi}{\partial x}\partial_\phi\right)\\
&\quad+\vec{e}_y\left(\frac{\partial r}{\partial y}\partial_r+\frac{\partial\theta}{\partial y}\partial_\theta+\frac{\partial\phi}{\partial y}\partial_\phi\right)\\
&\quad+\vec{e}_z\left(\frac{\partial r}{\partial z}\partial_r+\frac{\partial\theta}{\partial z}\partial_\theta+\frac{\partial\phi}{\partial z}\partial_\phi\right)\\
&= \left(\vec{e}_x\frac{\partial r}{\partial x}+\vec{e}_y\frac{\partial r}{\partial y}+\vec{e}_z\frac{\partial r}{\partial z}\right)\partial_r\\
&\quad+\left(\vec{e}_x\frac{\partial\theta}{\partial x}+\vec{e}_y\frac{\partial\theta}{\partial y}+\vec{e}_z\frac{\partial\theta}{\partial z}\right)\partial_\theta\\
&\quad+\left(\vec{e}_x\frac{\partial\phi}{\partial x}+\vec{e}_y\frac{\partial\phi}{\partial y}+\vec{e}_z\frac{\partial\phi}{\partial z}\right)\partial_\theta\\
&= \vec{\nabla}r\partial_r+\vec{\nabla}\theta\partial_\theta+\vec{\nabla}\phi\partial_\phi
\end{aligned}$$

Hence we obtain that:

$$\vec{\nabla}=\vec{\nabla}r\partial_r+\vec{\nabla}\theta\partial_\theta+\vec{\nabla}\phi\partial_\phi=\vec{e}_r|\vec{\nabla}r|\partial_r+\vec{e}_\theta|\vec{\nabla}\theta|\partial_\theta+\vec{e}_\phi|\vec{\nabla}\phi|\partial_\phi,$$

where the last equality follows from relations in any orthogonal coordinate system: $\vec{\nabla}\alpha=\vec{e}_\alpha|\vec{\nabla}\alpha|$, for $\alpha=r,\theta,\phi$, where $|\vec{A}|=\sqrt{(\vec{A}\cdot\vec{A})}$ is a norm (length) of a vector.

Below we calculate the norms: $|\vec{\nabla}r|,|\vec{\nabla}\theta|,|\vec{\nabla}\phi|$.

```
syms x y z real
r=sqrt(x^2+y^2+z^2);
simplify(norm(gradient(r)))
```

ans = 1

```
theta=acos(z/sqrt(x^2+y^2+z^2));
```

```
simplify(norm(gradient(theta)))
```

ans =

$$\frac{1}{\sqrt{x^2+y^2+z^2}}$$

```
phi=atan(y/x);
simplify(norm(gradient(phi)))
```

ans =

$$\frac{1}{\sqrt{x^2+y^2}}$$

Using that $|\vec{\nabla}\theta| = \frac{1}{\sqrt{x^2+y^2+z^2}} = \frac{1}{r}$ and $|\vec{\nabla}\phi| = \frac{1}{\sqrt{x^2+y^2}} = \frac{1}{r\sin\theta}$, we obtain that

$\vec{\nabla} = \vec{e}_r\frac{\partial}{\partial r} + \vec{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \vec{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$.

Unit vectors of local spherical coordinate system are: $\vec{e}_r = \frac{\vec{\nabla}r}{|\vec{\nabla}r|} = \vec{\nabla}r$, $\vec{e}_\theta = \frac{\vec{\nabla}\theta}{|\vec{\nabla}\theta|}$, and $\vec{e}_\phi = \frac{\vec{\nabla}\phi}{|\vec{\nabla}\phi|}$.

Using expression of gradient in Cartesian coordinates $\vec{\nabla} = \vec{e}_x\frac{\partial}{\partial x} + \vec{e}_y\frac{\partial}{\partial y} + \vec{e}_z\frac{\partial}{\partial z}$ we obtain:

- $\vec{e}_r = \vec{\nabla}r = \frac{\partial r}{\partial x}\vec{e}_x + \frac{\partial r}{\partial y}\vec{e}_y + \frac{\partial r}{\partial z}\vec{e}_z$
- $\vec{e}_\theta = \frac{1}{|\vec{\nabla}\theta|}\left(\frac{\partial\theta}{\partial x}\vec{e}_x + \frac{\partial\theta}{\partial y}\vec{e}_y + \frac{\partial\theta}{\partial z}\vec{e}_z\right)$
- $\vec{e}_\phi = \frac{1}{|\vec{\nabla}\phi|}\left(\frac{\partial\phi}{\partial x}\vec{e}_x + \frac{\partial\phi}{\partial y}\vec{e}_y + \frac{\partial\phi}{\partial z}\vec{e}_z\right)$

Confirming that $(\vec{e}_r\cdot\vec{e}_\theta) = 0$

```
simplify(diff(r,x)*diff(theta,x)+diff(r,y)*diff(theta,y)+diff(r,z)*diff(theta,z))
```

ans = 0

Confirming that $(\vec{e}_r\cdot\vec{e}_\phi) = 0$

```
simplify(diff(r,x)*diff(phi,x)+diff(r,y)*diff(phi,y)+diff(r,z)*diff(phi,z))
```

ans = 0

Confirming that $(\vec{e}_\theta\cdot\vec{e}_\phi) = 0$

```
simplify(diff(theta,x)*diff(phi,x)+diff(theta,y)*diff(phi,y)
+diff(theta,z)*diff(phi,z))
```

ans = 0

Note, when we specify a point in 3D by three numbers (r,θ,ϕ), which we call spherical coordinates of a point $\mathbf{r}=r\sin\theta\cos\phi\,\vec{e}_x+r\sin\theta\sin\phi\,\vec{e}_y+r\cos\theta\,\vec{e}_z$, these are not coordinates of the radius vector $\mathbf{r}$ in local spherical coordinate systems. Coordinates of $\mathbf{r}$ in local spherical coordinate system $\vec{e}_r,\ \vec{e}_\theta,\ \vec{e}_\phi$ are $(r,0,0)$.

Appendix B

Here we show that $\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{1}{\hbar^2 r^2}\hat{\mathbf{L}}^2$, where

$$\hat{\mathbf{L}}=\hat{\mathbf{r}}\times\hat{\mathbf{p}}=-\hat{\mathbf{p}}\times\hat{\mathbf{r}}.$$

$$\begin{aligned}
&\hat{\mathbf{r}}=\hat{r}\mathbf{e}_r=r\mathbf{e}_r,\quad \mathbf{p}=-i\hbar\nabla=\mathbf{e}_r\hat{p}_r+\mathbf{e}_\theta\hat{p}_\theta+\mathbf{e}_\phi\hat{p}_\phi\\
&\hat{\mathbf{L}}=r\mathbf{e}_r\times\mathbf{e}_\theta\hat{p}_\theta+\mathbf{e}_r\times\mathbf{e}_\phi\hat{p}_\phi=r\mathbf{e}_\phi\cdot\hat{p}_\theta-r\mathbf{e}_\theta\cdot\hat{p}_\phi\\
&\hat{p}_r=-i\hbar\frac{\partial}{\partial r}\\
&\hat{p}_\theta=-i\hbar\frac{1}{r}\frac{\partial}{\partial\theta}\\
&\hat{p}_\phi=-i\hbar\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\\
&\hat{\mathbf{L}}^2=-\hbar^2\left(r\mathbf{e}_\phi\frac{1}{r}\frac{\partial}{\partial\theta}-r\mathbf{e}_\theta\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}\right).\left(\mathbf{e}_\phi\frac{\partial}{\partial\theta}-\mathbf{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)\\
&\quad=-\hbar^2\left(\frac{\partial^2}{\partial\theta^2}+\frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)=-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)
\end{aligned}$$

Since $\hat{\mathbf{L}}=-i\hbar\left(\mathbf{e}_\phi\frac{\partial}{\partial\theta}-\mathbf{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$ then $\hat{L}^z=(\hat{\mathbf{L}}\cdot\mathbf{e}_z)=i\hbar(\mathbf{e}_\theta\cdot\mathbf{e}_z)\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}=-i\hbar\frac{\partial}{\partial\phi}$. We used that $(\mathbf{e}_\phi\cdot\mathbf{e}_z)=0$ and $(\mathbf{e}_\theta\cdot\mathbf{e}_z)=-\sin\theta$ (see here) .

Helper function for defining the associated Legendre function P_ℓ^m symbolically

```
function y = AssociatedLegendreP(l,m)
    arguments
        l (1,1) {mustBeInteger,mustBeNonnegative}
        m (1,1) {mustBeInteger}
    end
    if m^2>l^2
        error('|m| can not exceed l')
    end
```

```
    syms x;
    if m<0
        y = factorial(l+m)/factorial(l-m)*(1 - x^2)^(-m/2)*diff(legendreP(l,x),x,-
m);
    else
        y = (-1)^m*(1 - x^2)^(m/2)*diff(legendreP(l,x),x,m);
    end
end
```