DOING PHYSICS WITH PYTHON

QUANTUM MECHANICS

CENTRAL FORCES

ANGULAR MOMENTUM and SPHERICAL HARMONICS

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Please email any corrections, suggestions, improvements, etc

DOWNLOAD DIRECTORY FOR PYTHON SCRIPTS

qm061.py
Polar plots of the azimuthal wavefunction and its probability density for different values of l and m_l.

qm061A.py
Angular dependent wavefunctions – spherical harmonics: Plots for $Y_{l,m_l}(\theta,\phi)$ and $Y_{l,m_l}^{*}(\theta,\phi)\,Y_{l,m_l}(\theta,\phi)$.

qm061C.py   [3D] surface plots of the spherical harmonics.

qm061S.py   Spherical harmonics plotted on a unit sphere.

qm061R.py   Spherical harmonics polar plots

GitHub

Google Drive

INTRODUCTION

It is often better to use the **spherical coordinate system** rather than the Carestian coordinate system in modelling quantum systems. For example, an electron is attracted to the nucleus by the Coulomb force between opposite charges. This is known as a **central force**, one that is directed toward a fixed point.

The spherical coordinates about an Origin O are (r, θ, ϕ)

   r radius line

   θ polar angle [rad]

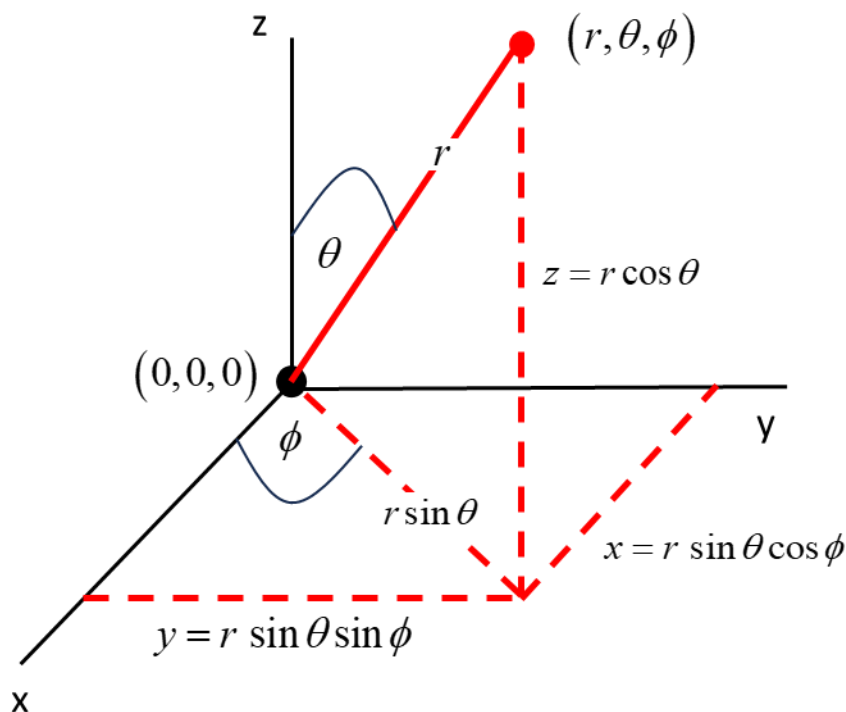 ϕ azimuthal angle [rad]

Fig. 1. Spherical coordinate system.

Just like energy for a bound particle is quantized, the angular momentum $\vec{L}$ is also quantized. However, unlike energy, the angular momentum is a vector which has three components. For physically accepted wavefunctions for the angular momentum, not all angular momentum components can be known simultaneously. This is because the uncertainty principle applies to angular momentum just as it does to the momentum. The **uncertainty principle for angular momentum** is

It is impossible to specify simultaneously any two components of angular momentum – if one component of the angular momentum $\vec{L}$ is sharp, then the remaining two components must be *fuzzy*.

Thus, we can have $\vec{L}$ and L_z sharp (i.e. quantized) and the wavefunctions for $\vec{L}$ and L_z are the **spherical harmonics**. The time-independent state wavefunctions are given by

$$\psi(\vec{r}) = \psi(r,\theta,\phi) = R(r)\, \Theta(\theta)\, \Phi(\phi)$$

The time-independent Schrödinger Equation for the eigenvalues E and eigenfunction $\psi(\vec{r})$

$$\hat{H}\,\psi(\vec{r}) = E\,\psi(\vec{r})$$

where the Hamiltonian operator is

$$\hat{H} = \frac{-\hbar^2}{2m_\mu}\nabla^2 + U(\vec{r})$$

where ∇^2 is the Laplacian operator in spherical coordinates is

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

We can rewrite the Schrodinger equation as three separate equations:

- Radial equation $R(r)$

- Polar equation $\Theta(\theta)$

- Azimuthal equation $\Phi(\phi)$

and solve each of these equations independently.

Radial wavefunction $R(r)$

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

The radial wave equation determines the radial part of the wavefunction $\psi(r,\theta,\phi)$ and the allowed particle energies E. This radial wave equation is valid for any central force. The radial wavefunction $R(r)$ for the state (n,l) is normalized

$$\int_0^\infty \left|R_{nl}(r)\right|^2 r^2\,dr = 1$$

where n is the principal quantum number and l is the orbital quantum number.

Azimuthal equation $\Phi(\phi)$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m_l^2 \qquad m_l \text{ is the separation constant}$$

The solution for the azimuthal wavefunction $\Phi(\phi)$ is

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}\exp\left(i\,m_l\,\phi\right) \qquad \text{normalized}$$

where $0 \le \phi \le 2\pi \ \left(-\pi \le \phi \le \pi\right)$.

A complete rotation through 2π rad must leave the quantum system in the same state, thus, for physically acceptable solution, m_l can only have values

$$m_l = 0, \ \pm 1, \pm 2, \pm 3, \ \ldots$$

m_l is known as the **magnetic quantum number**.

The probability density is

$$\Phi^*(\phi)\,\Phi(\phi) = \frac{1}{2\pi} \qquad \text{independent of } \phi$$

and the probability of finding the azimuthal orientation of the molecule in the region from 0 to 2π is

$$probability\left(0 \le \phi \le 2\pi\right) = \int_0^{2\pi}\frac{1}{2\pi}\,d\phi = 1$$

So, we never can know the orientation of the molecule, we only know that there is an equal probability of finding the azimuthal angle ϕ when measured.

The azimuthal wavefunction can be expressed in terms of its real and imaginary parts

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \exp\left(i\, m_l\, \phi\right) = \frac{1}{\sqrt{2\pi}}\left[\cos\left(m_l\, \phi\right) + i\, \sin\left(m_l\, \phi\right)\right]$$

We can visualize the azimuthal wavefunctions using xy plots and polar plots (figures 2A and 2B).

We can now find the eigenfunctions and eigenvalues of the operator for the z-component of the angular momentum $\hat{L}_z$

$$\hat{L}_z \equiv -i\,\hbar\,\frac{\partial}{\partial \phi}$$

$$-i\,\hbar\,\frac{\partial}{\partial \phi}\left(e^{im_l\phi}\right) = m_l\,\hbar$$

So, $\Phi = e^{im_l\phi}$ are the eigenfunctions of the operator $\hat{L}_z$ and their corresponding eigenvalues are $L_z = m_l\,\hbar$.

The real part of $\Phi(\phi)$ is a cosine function and the imaginary part is a sine function. m_l gives the number of complete cycles of the azimuthal wavefunction within the range 0 to 2π for ϕ (figure 2).
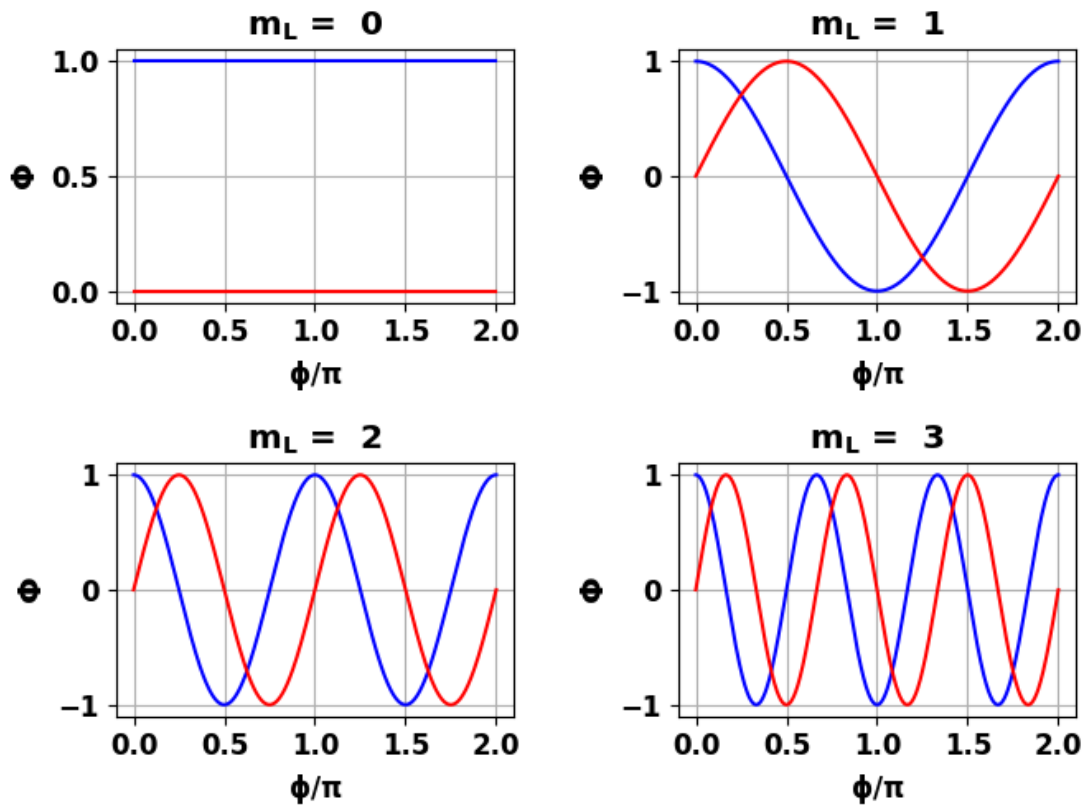
Fig. 2A. Azimuthal wavefunction $\Phi(\phi)$ (not normalized): real part a cosine function (blue) and imaginary part a sine function (red). The azimuthal function is single valued at $\phi = 0$ and $\phi = 2\pi$ rad. m_l gives the number of cycles in the azimuthal wavefunction for $0 \leq \phi \leq 2\pi$.   **qp061.py**
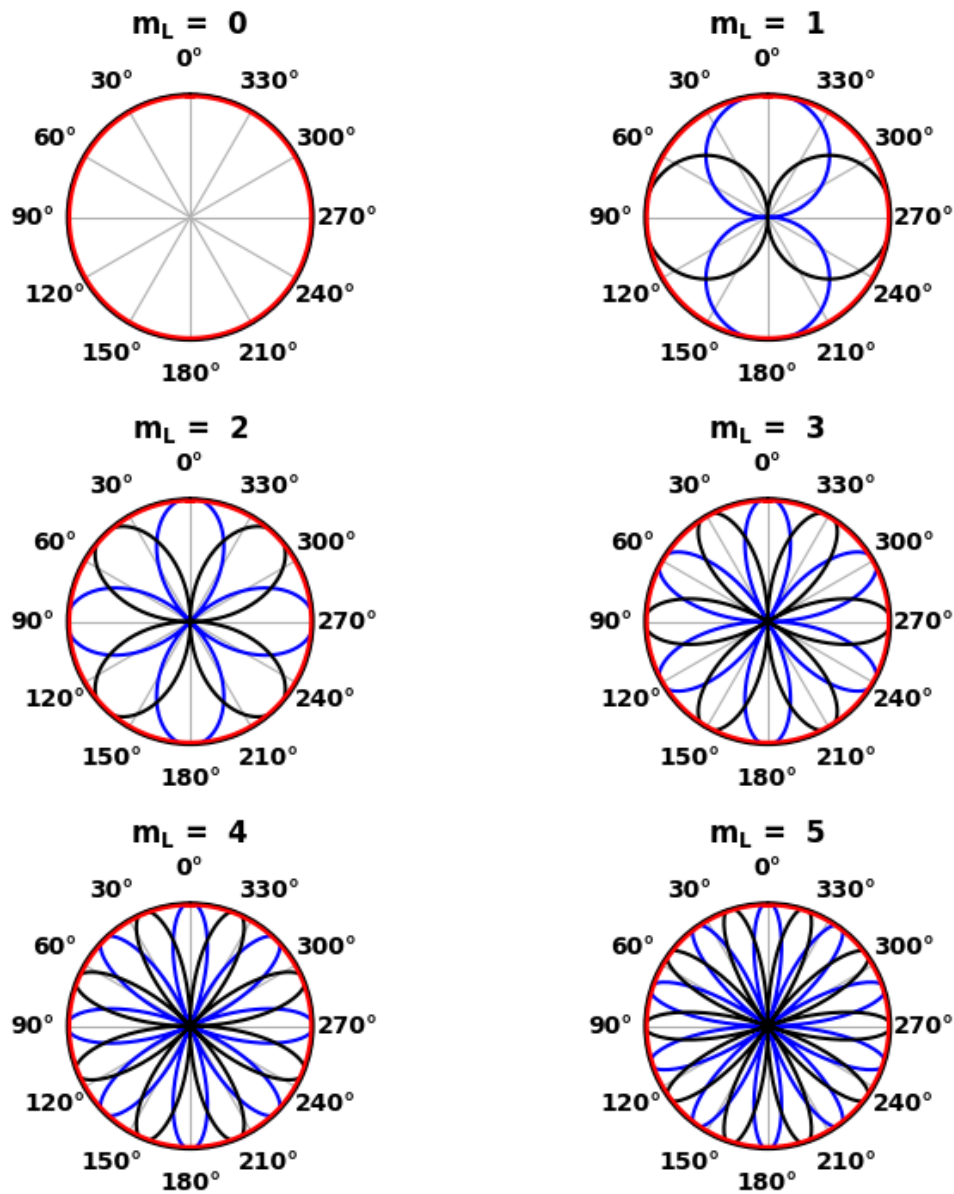
Fig. 2B. Polar plots of the real parts (blue), imaginary parts (**black**) of the **azimuthal wavefunction** and the probability density function (red). Note: the probability density is independent of the azimuthal angle ϕ. The Z-axis is along the line 0°-180°. **qm061.py**

Polar equation $\Theta(\theta)$

$$\frac{d^2\Theta}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta} + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0$$

where $l(l+1)$ is a separation constant.

Th solutions $\Phi_{l,m}(\theta)$ of this ODE are called the **associated Legendre functions** which are functions of sine and cosine terms. Solutions are only physical acceptable if l and m_l have the values

$$l\pm = 0, 1, 2, 3,... \qquad m_l = 0, \pm1, \pm2, \pm3, \ldots, \pm l$$

l is called the **orbital quantum number** and m_l the **magnetic quantum number**. (Note: chemists often use J not l, $J \equiv l$)

The wavefunction for the angular dependence can be expressed in terms of **spherical harmonics** where

$$Y_{l,m_l}(\theta,\phi) = \Theta_{l,m_l}(\theta)\,\Phi_{ml}(\phi)$$

The separation constants l and m_l relate to the allowed values of the angular momentum and its z component.

$$\left|\vec{L}\right| = \sqrt{l(l+1)}\,\hbar \quad l = 0, 1, 2, 3, ...$$

$$L_z = m_l\,\hbar \quad m_l = 0, \pm1, \pm2, \pm3, \ldots, \pm l)$$

The solution of the polar equation in Θ are known as **the associated Legendre functions** $P_{l,m_l}(\cos\theta)$

$$\Theta(\theta) \equiv P_{l,m_l}(\cos\theta)$$

The full angular dependence described by the spherical harmonics for the central force wavefunction now becomes

$$Y_{l,m_l}(\theta,\phi) = P_{l,m_l}(\theta)\ \Phi_{ml}(\phi)$$

and for a normalized function

$$\int_0^{2\pi}\int_0^{\pi} Y_{l,m_l}{}^*(\theta,\phi)\ Y_{l,m_l}(\theta,\phi)\sin\theta\,d\theta\,d\phi = 1$$

Note: The probability density function *probD* is independent of the azimuthal angle since

$$e^{im_l\phi}\ e^{-im_l\phi} = e^0 = 1$$

$$probD(\theta) = Y_{l,m_l}{}^*(\theta,\phi)\ Y_{l,m_l}(\theta,\phi) = P_{l,m_l}{}^*(\theta)\ P_{l,m_l}(\theta)$$

The spherical harmonics can be computed in Python using the Code

```
import scipy.special
from scipy.special import sph_harm
Y = sph_harm(mL,L,phi,theta).real
```

From the spherical harmonics function we can get the associated Legendre function by setting $\phi = 0$.

qm061A.py   *Note: for clarity l is used for L in the Code.*

Input cell

```
#%%  INPUTS >>>>>
L = 3            # ORBITAL QUANTUM NUMBER
mL = 0           # MAGNETIC QUANTUM NUMBER
N = 599          # number of grid points
phi = 0          # azimuthal angle  [rad]
                 # if phi = 0 --> Legendre function
```

Setup cell

```
#%%  SETUP

theta = linspace(0,pi,N)             # polar angle  [ra]

Y = sph_harm(abs(mL),L,phi,theta).real    # spherical harmonics

probD = Y*Y                          # probability density

fn = 2*pi*Y*Y*sin(theta)             # check normalization

prob = simps(fn,theta)               # probability = 1

print('check probability = 1:  prob = %2.3f' % prob)
```

The variable prob gives the probability of finding the orientation of

the angular momentum $\hat{L}$ in space.

The variable probD is the probability density for the angular

momentum $\hat{L}$ having a polar angle θ

$$probD(\theta) = Y_{l,m_l}{}^*(\theta,\phi)\, Y_{l,m_l}(\theta,\phi) \quad \text{independent of } \phi$$

$$probD(\theta) = P_{l,m_l}{}^*(\theta)\, P_{l,m_l}(\theta)$$

$$\vec{L}(\theta,\phi) = l(l+1)\hbar$$
$$L_z = ml\,\hbar \quad L_x = ? \quad L_y = ?$$

$$Y_{l,m_l}{}^{*}(\theta,\phi)\, Y_{l,m_l}(\theta,\phi) = P_{l,m_l}{}^{*}(\theta)\, P_{l,m_l}(\theta)$$

orientation angles with max probability

L = 3 m_L = 2 ϕ / π = 0.00
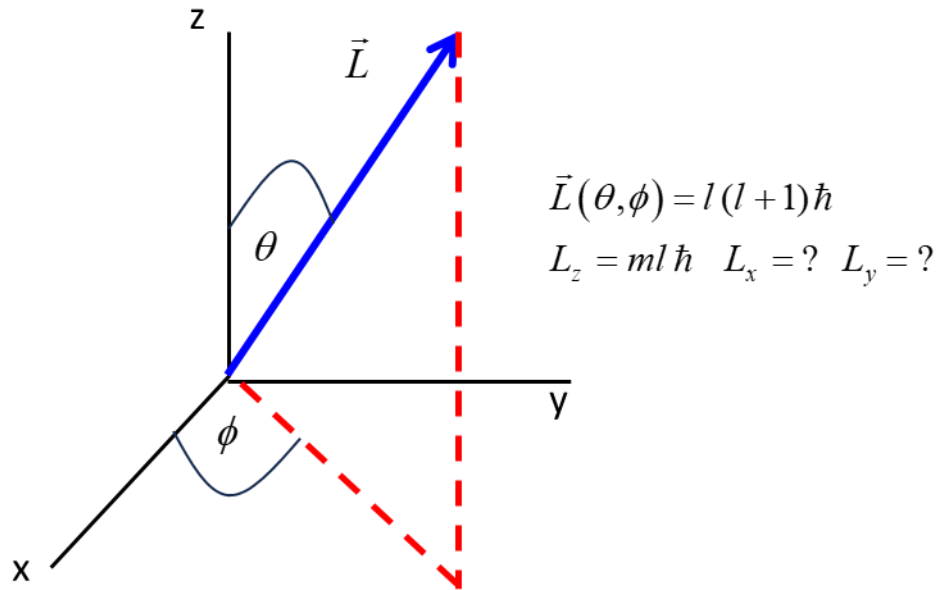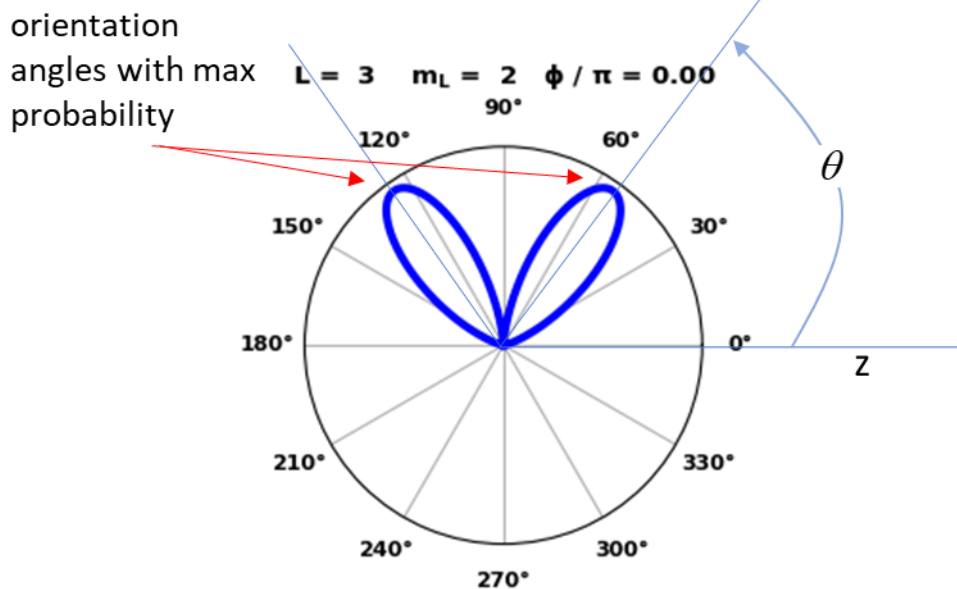
Fig. 3. The orientation of the angular momentum vector $\vec{L}$ is specified by its polar angle θ and azimuthal angle ϕ. The orientation probability density depends only upon θ. The magnitudes of the angular momentum and its z-component are quantized, but we have no knowledge of the x-component and the y-component. There is zero probability of the angular momentum being aligned along the Z-axis.

The following figures (figure 4) show plots for $Y_{l,m_l}(\theta,\phi)$ and

$Y_{l,m_l}{}^{*}(\theta,\phi)\, Y_{l,m_l}(\theta,\phi)$. When $\phi = 0$ then you get plots of the Associated

Legendre functions as

$$\phi = 0 \quad \Phi_{m_l}(0) = e^{-i m_l \phi} = 1 \quad Y_{l,m_l}(\theta,0) = P_{l,m_l}(\theta)$$

14
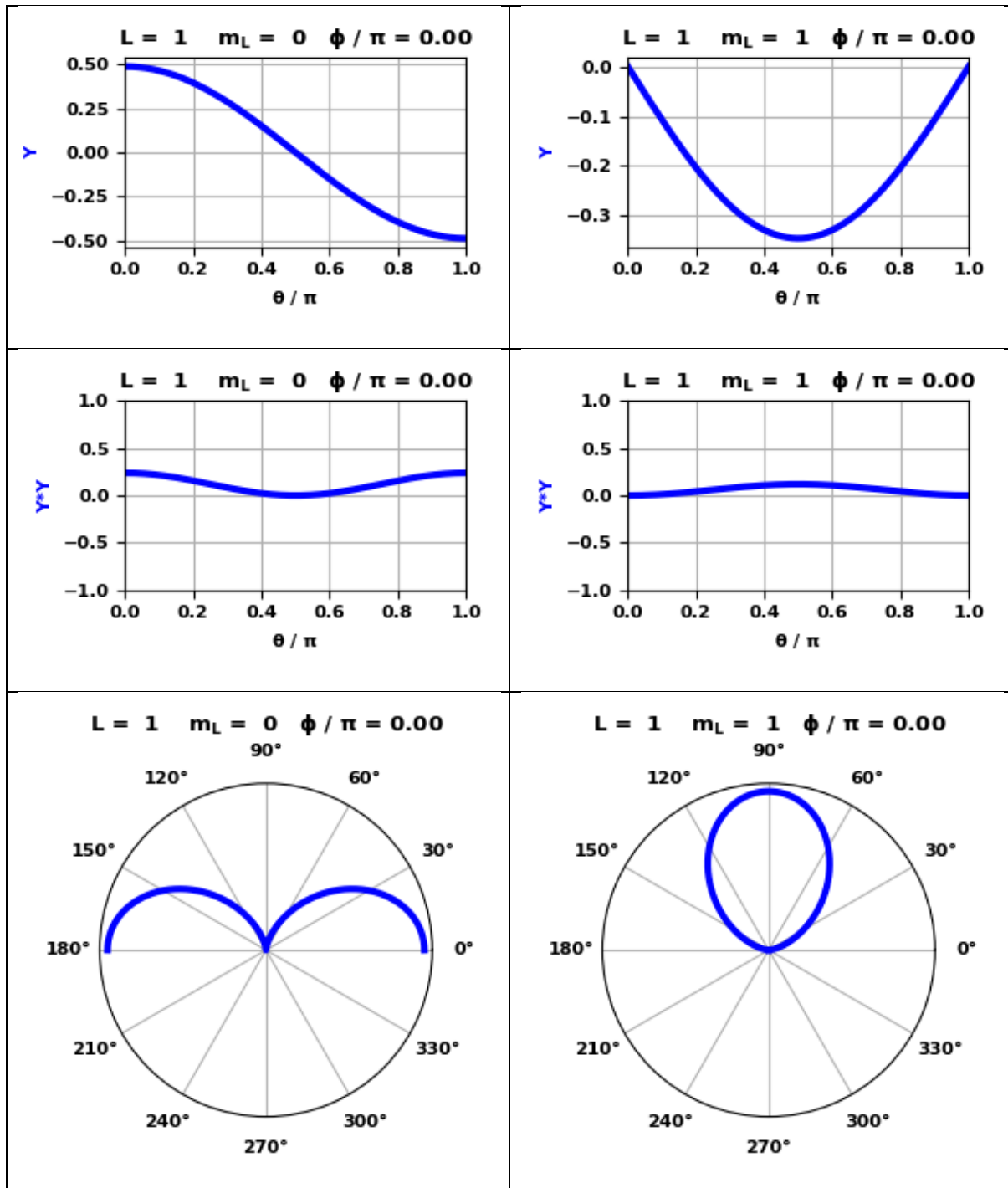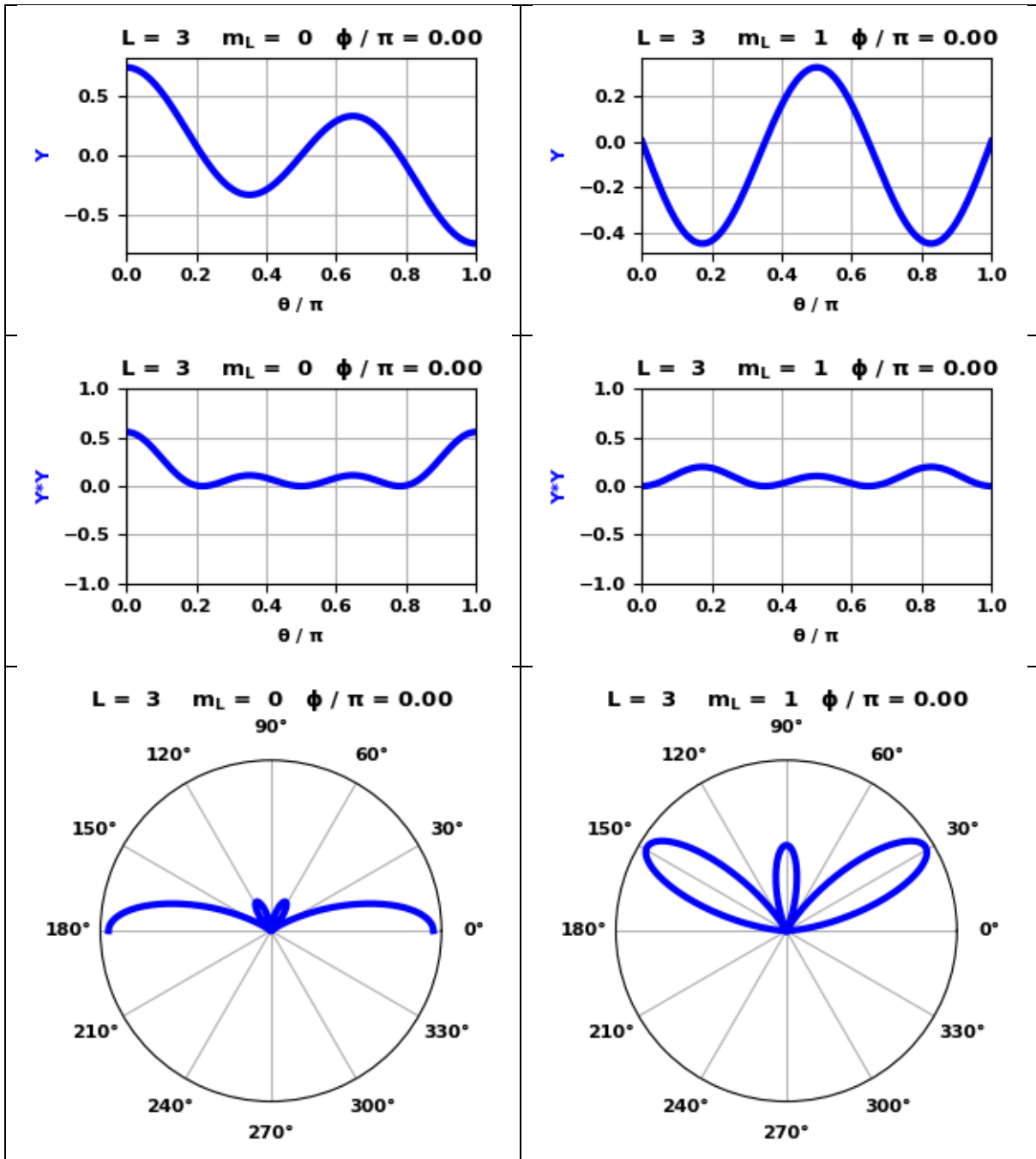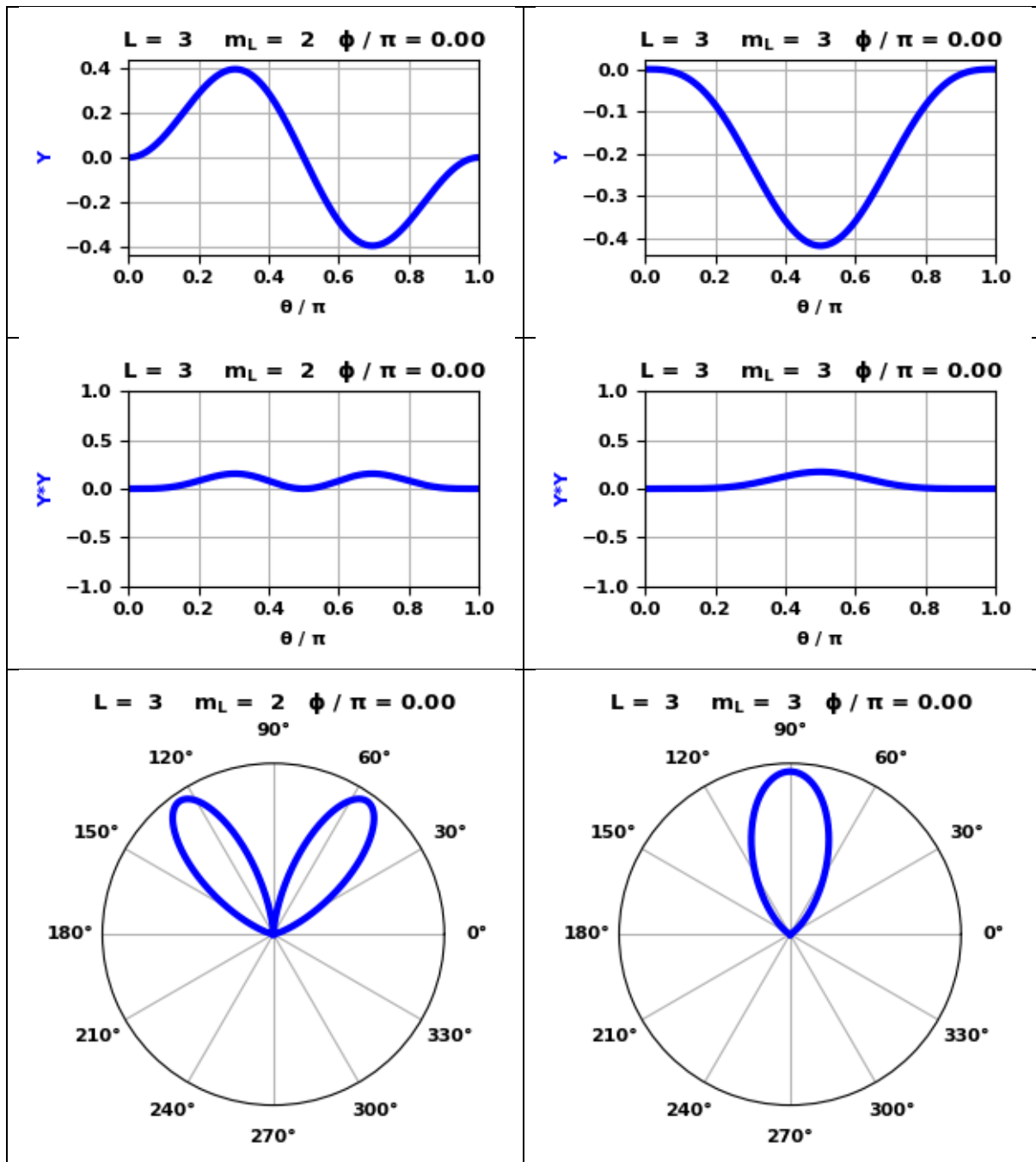
Fig. 4. Plots for $Y_{l,m_l}(\theta,\phi)$ and $Y_{l,m_l}^{*}(\theta,\phi)\, Y_{l,m_l}(\theta,\phi)$. In the polar format $\left|Y(\theta,\phi)\right|^2$, if you rotate the curve around the $180^{\circ} - 0^{\circ}$ axis, you can visualize the [3D] pattern for the spherical harmonics. **qm061A.py**

The Code **qm061C.py** can be used to graph [3D] surface plots of the spherical harmonics $Y_{l,m_l}(\theta,\phi)$ (figure 5).

l = 0 m_l = 0
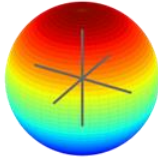
l = 1 m_l = −1   l = 1 m_l = 0   l = 1 m_l = 1   l = 2 m_l = −2
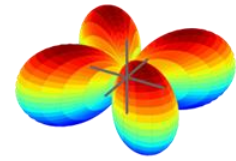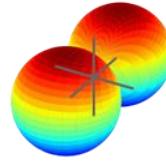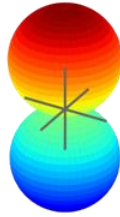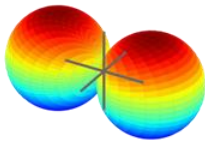
l = 2 m_l = −1   l = 2 m_l = 0   l = 2 m_l = 1   l = 2 m_l = 2
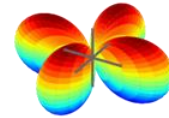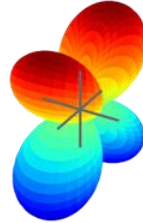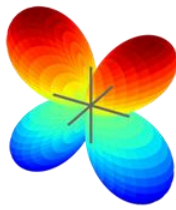
l = 3 m_l = −3   l = 3 m_l = −2   l = 3 m_l = −1   l = 3 m_l = 0
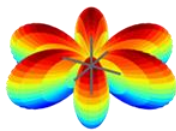
l = 3 m_l = 1   l = 3 m_l = 2   l = 3 m_l = 3   l = 7 m_l = 6

Fig. 5. Spherical harmonics. Note: that all the spherical harmonics are rotationally symmetric about the Z-axis. In the Python figure Window you can rotate the [3D] plots. **qm061C.py**

ANGULAR MOMENTUM: SPACE QUANTIZATION

The magnitude of the orbital angular momentum magnitude $\left|\vec{L}\right|$ and its projection along the z-axis L_z, are both sharp and quantized according to the restrictions imposed by the orbital and magnetic quantum numbers, respectively. Together, l and m_l specify the orientation of the angular momentum vector $\left|\vec{L}\right|$. The direction of $\left|\vec{L}\right|$ being quantized with respect to the Z-axis (arbitrary axis) is referred to as **space quantization**.

$$\left|\vec{L}\right| = \sqrt{l\,(l+1)}\,\hbar \quad l = 0, 1, 2, 3, \ldots$$

$$l = 2 \quad \left|\vec{L}\right| = \sqrt{6}\,\hbar$$

$L_z = +2\hbar$

$L_z = +1\hbar$

$L_z = -0$

$L_z = -1\hbar$

$L_z = -2\hbar$
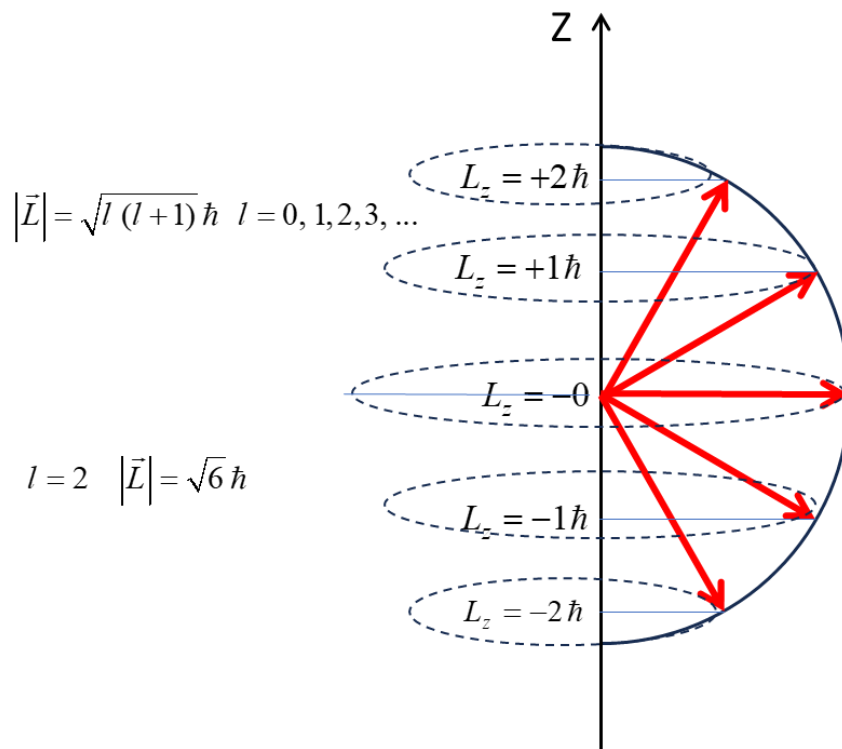
Fig. 6.   Allowed projections of $\vec{L}$ onto the Z-axis for $l = 2$. From a [3D] perspective, $\vec{L}$ lies on the surface of a cone. The fuzzy character of L_x and L_y are shown by allowing $\vec{L}$ to precess about the Z-axis, so that L_x and L_y change continually while L_z maintains the fixed value $L_z = m_l\,\hbar$.

SPHERICAL HARMONICS (further notes)

Reference

Spherical harmonics are powerful mathematical tools, allowing us to represent any function on a sphere. That is, spherical harmonics are basis functions defined on a spherical surface. A function $f(x, y, z)$ defined on the unit sphere can be expressed as

$$f(x, y, z) = \sum_{l=-0}^{\infty} \sum_{m_l=-l}^{l} a_{l,m_l} \, Y_{lm_l}(x, y, z)$$

$$x^2 + y^2 + z^2 = 1$$

l is the degree of the function and can be though of as a "frequency": $l = 1$ gives 1 cycle, $l = 2$ gives 2 cycles, ... as shown in figure 7.

l = 2   m_l = − 2
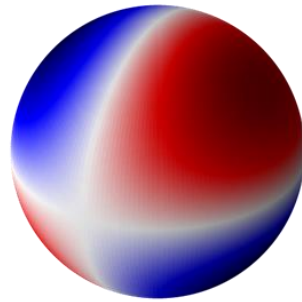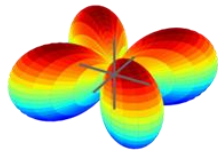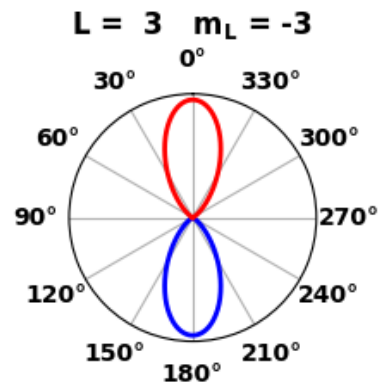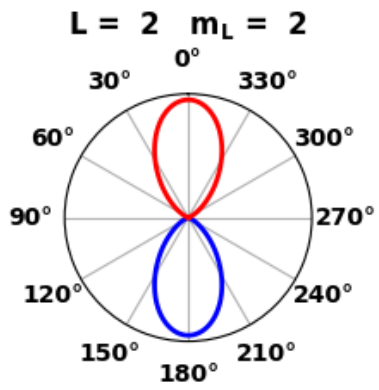
l = 2   m_l = − 1
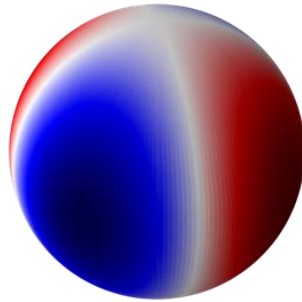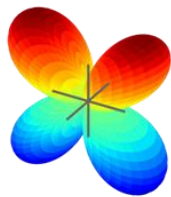
l = 2   m_l = 0
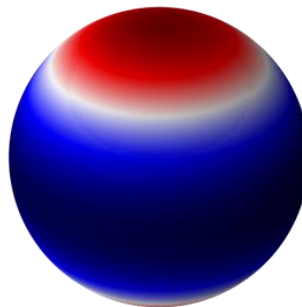
l = 2   m_l = 1
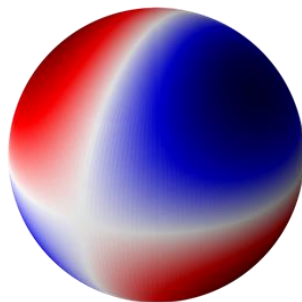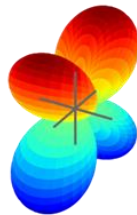
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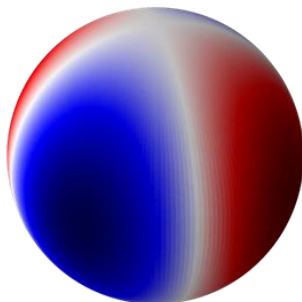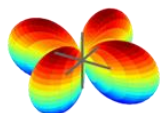
Fig. 7. Visualization of the spherical harmonics for $l = 2$.

L = 0   m_L = 0

L = 1   m_L = -1

L = 1   m_L = 0

L = 1   m_L = 1

L = 2   m_L = -2

L = 2   m_L = -1

20

L = 2   m_L = 0

L = 2   m_L = 1

L = 2   m_L = 2

L = 3   m_L = -3

L = 3   m_L = -2
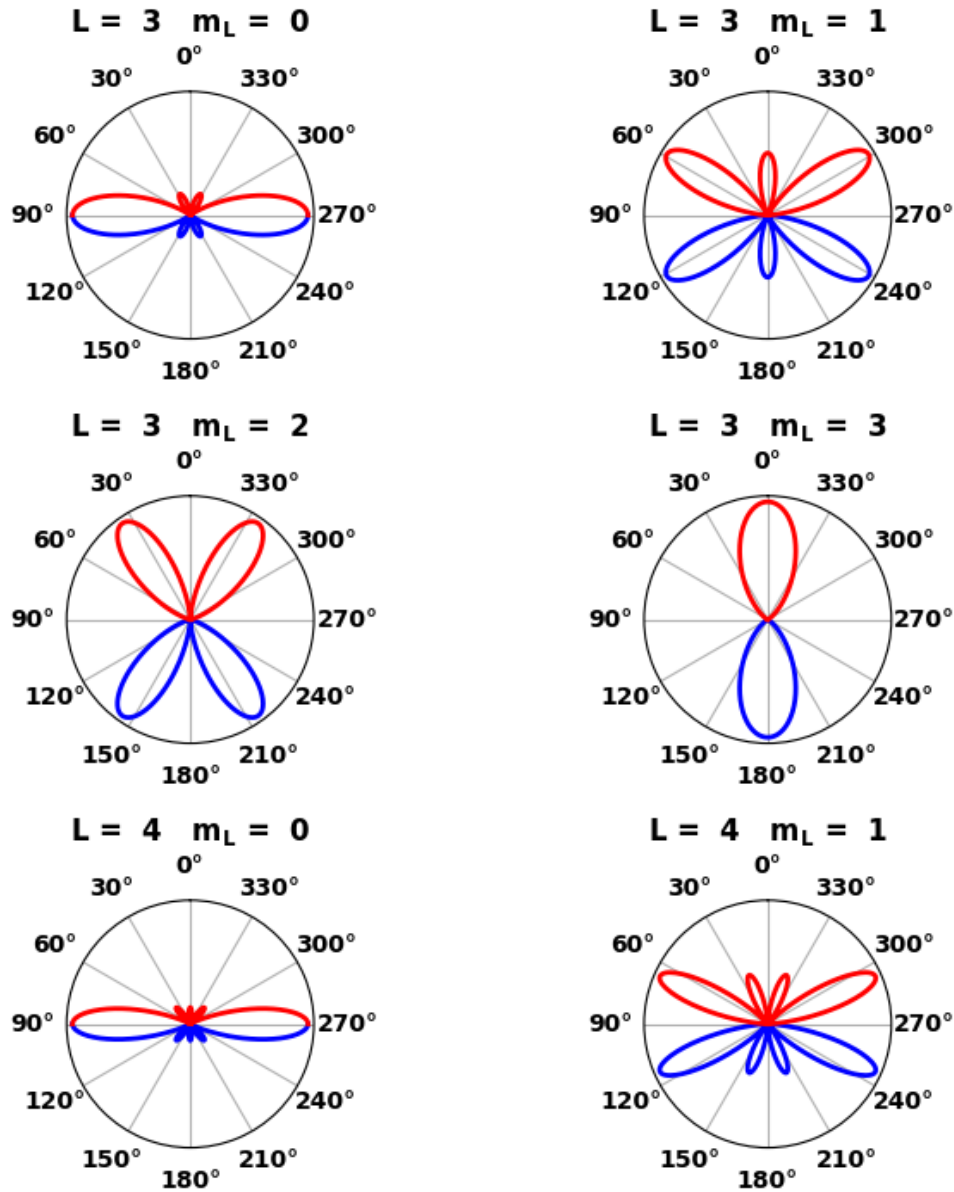
L = 3   m_L = -1
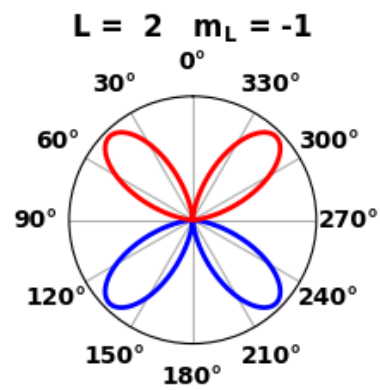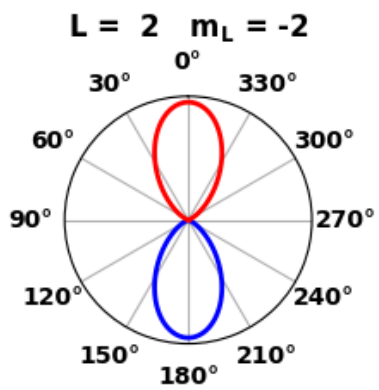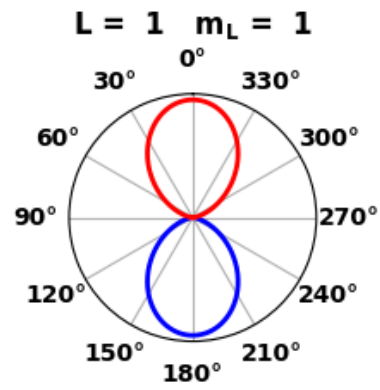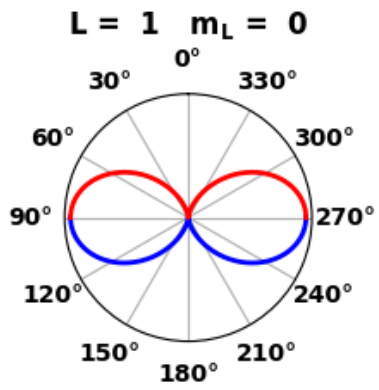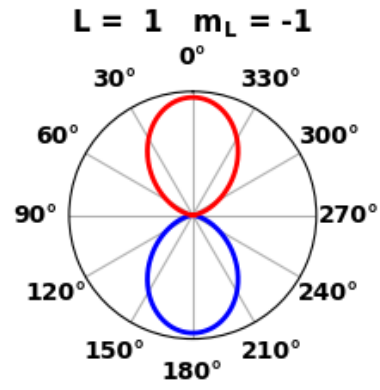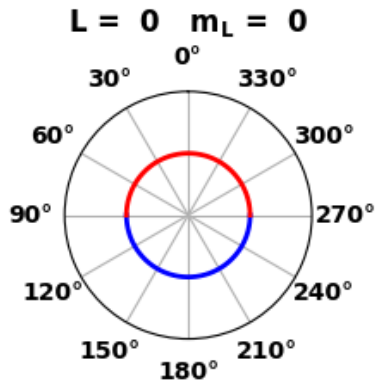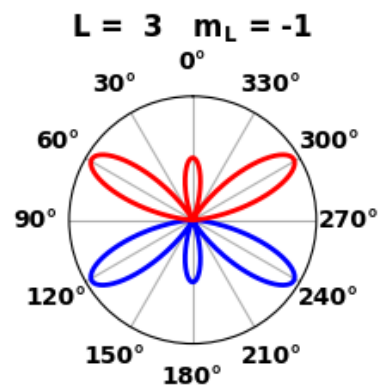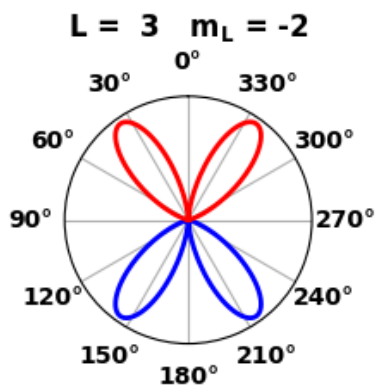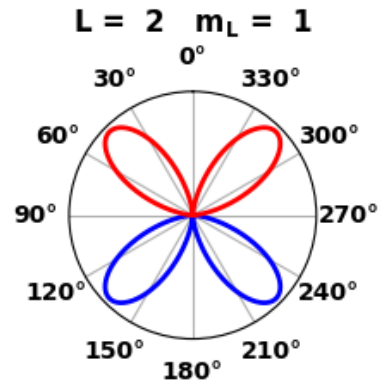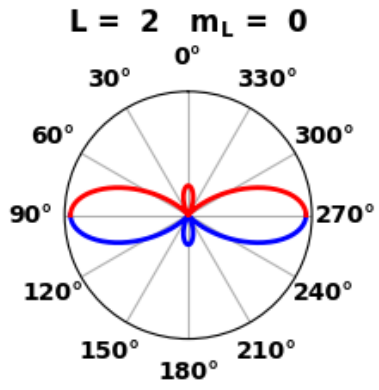
Fig. 8. Polar plots of the probability density for the alignment of the angular momentum. The Z-axis is along the $0°$-$180°$ lines. The probability density is indpendent of the azimuthal angle. Blue and red indicate opposite signs of the wavefunction. The distance from the Origin to the coloured curves is proportional to the probaility density

$$probD(\theta) = Y_{l,m_l}^{*}(\theta,\phi)\, Y_{l,m_l}(\theta,\phi).$$