1 Properties of Spherical Harmonics

1.1 Repetition

In the lecture the spherical harmonics $Y_{\ell,m}(\theta,\phi)$ were introduced as the eigenfunctions of angular momentum operators $\hat{l}_z$ and $\hat{l}^2$ in spherical coordinates. We found that

$$\hat{l}_z Y_{\ell,m}(\theta,\phi) = \hbar m Y_{\ell,m}(\theta,\phi) \qquad [1.1]$$

and

$$\hat{l}^2 Y_{\ell,m}(\theta,\phi) = \hbar\ell(\ell+1) Y_{\ell,m}(\theta,\phi) \; . \qquad [1.2]$$

The spherical harmonics can be defined as

$$Y_{\ell,m}(\theta,\phi) = N_{\ell,m} \cdot P_\ell^{|m|}(\cos\theta) \cdot e^{im\phi} \qquad [1.3]$$

where ℓ is the quantum number of the orbital angular momentum and m the magnetic quantum number. There are analytical definitions for the normalization factor $N_{\ell,m}$ and the associated Legendre Polynomials $P_\ell^m(\cos\theta)$ that allow the calculations of the spherical harmonics.

The spherical harmonics for $\ell = 0, 1,$ and 2 are given by

$$Y_{0,0}(\theta,\phi) = \frac{1}{\sqrt{4\pi}} \qquad [1.4]$$

$$\begin{aligned} Y_{1,0}(\theta,\phi) &= \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta \\ Y_{1,\pm 1}(\theta,\phi) &= \mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\phi} \end{aligned} \qquad [1.5]$$

$$Y_{2,0}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$
$$Y_{2,\pm1}(\theta,\phi) = \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{\pm i\phi} \quad [1.6]$$
$$Y_{2,\pm2}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\phi}$$

Note, that the sign of the functions $Y_{1,\pm1}(\theta,\phi)$ and $Y_{2,\pm1}(\theta,\phi)$ is defined differently than in the script of the lecture. The definition here is in agreement with most of the literature on spherical harmonics.

1.2 Graphical Representation of Spherical Harmonics

The spherical harmonics are often represented graphically since their linear combinations correspond to the angular functions of orbitals. Figure 1.1a shows a plot of the spherical harmonics where the phase is color coded. One can clearly see that $|Y_{\ell,m}(\theta,\phi)|$ is symmetric for a rotation about the z axis. The linear combinations $1/\sqrt{2}(Y_{\ell,m}(\theta,\phi) + (-1)^m Y_{\ell,-m}(\theta,\phi)) = \sqrt{2}|Y_{\ell,m}(\theta,\phi)|\cos(m\phi)$, $Y_{\ell,0}(\theta,\phi)$ and $-i/\sqrt{2}(Y_{\ell,m}(\theta,\phi) - (-1)^m Y_{\ell,-m}(\theta,\phi)) = \sqrt{2}|Y_{\ell,m}(\theta,\phi)|\sin(m\phi)$ are always real and have the form of typical atomic orbitals that are often shown.

1.3 Properties of Spherical Harmonics

There are some important properties of spherical harmonics that simplify working with them.

1.3.1 Orthogonality and Normalization

The spherical harmonics are normalized and orthogonal, i.e.,

$$\int_0^{2\pi}\int_0^{\pi} Y_{\ell_1,m_1}(\theta,\phi)Y^*_{\ell_2,m_2}(\theta,\phi)\sin\theta(d\theta)d\phi = \delta_{m_1,m_2}\delta_{\ell_1,\ell_2} \quad [1.7]$$

where the Kronecker delta is defined as

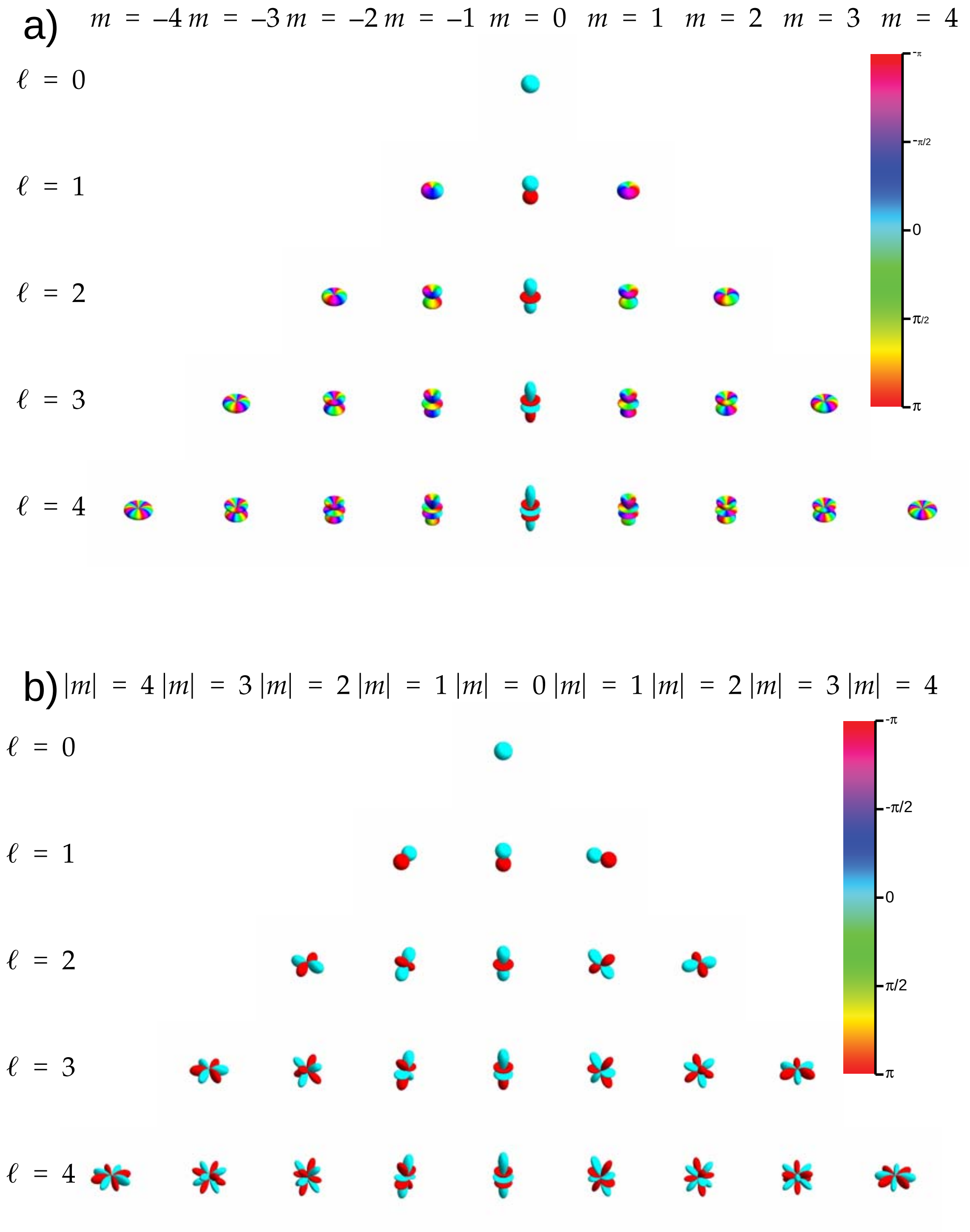

Figure 1.1: Graphical Representation of the Spherical Harmonics
a) Plot of the spherical harmonics $Y_{\ell,m}(\theta,\phi)$ where the phase of the function is color coded. Note that $|Y_{\ell,m}(\theta,\phi)|$ is always axially symmetric with respect to a rotation about the z axis since it depends only on the angle θ. The phase of the function changes with a periodicity of m. b) The linear combinations $1/\sqrt{2}(Y_{\ell,m}(\theta,\phi)+(-1)^m Y_{\ell,-m}(\theta,\phi)) = \sqrt{2}|Y_{\ell,m}(\theta,\phi)|\cos(m\phi)$, $Y_{\ell,0}(\theta,\phi)$, and $-i/\sqrt{2}(Y_{\ell,m}(\theta,\phi)-(-1)^m Y_{\ell,-m}(\theta,\phi)) = \sqrt{2}|Y_{\ell,m}(\theta,\phi)|\sin(m\phi)$ are all real and show only a phase of 0 (positive) and π (negative) and correspond to the typical orbital shapes.

$$\delta_{a,b} = \begin{cases} 0 & a \neq b \\ 1 & a = b \end{cases} . \quad [1.8]$$

They form a complete basis set of the Hilbert space of square-integrable functions, i.e., every such function can be expressed as a linear combination of spherical harmonics

$$f(\theta, \phi) = \sum_{\ell = 0}^{\infty} \sum_{m = -\ell}^{\ell} f_{\ell, m} Y_{\ell, m}(\theta, \phi) . \quad [1.9]$$

The coefficients $f_{\ell, m}$ can be calculated as

$$f_{\ell, m} = \int_0^{2\pi} \int_0^{\pi} f(\theta, \phi) Y^*_{\ell, m}(\theta, \phi) \sin\theta (d\theta) d\phi . \quad [1.10]$$

1.3.2 Product of Two Spherical Harmonics

Since the spherical harmonics form a orthonormal basis set, the product of two spherical harmonics can again be expressed in spherical harmonics. Let us first look at a simple example

$$Y_{1, 0}(\theta, \phi) \cdot Y_{1, 0}(\theta, \phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta \cdot \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta = \frac{3}{4\pi}\cos^2\theta . \quad [1.11]$$

Comparing this to the spherical harmonics of Eqs. [1.4]-[1.6] it is immediately clear that we need the functions $Y_{2, 0}(\theta, \phi)$ and $Y_{0, 0}(\theta, \phi)$ to express the product. We can make an Ansatz

$$Y_{1, 0}(\theta, \phi) \cdot Y_{1, 0}(\theta, \phi) = c_{0, 0} Y_{0, 0}(\theta, \phi) + c_{2, 0} Y_{2, 0}(\theta, \phi) \quad [1.12]$$

which leads to

$$\begin{aligned} \frac{3}{4\pi}\cos^2\theta &= c_{0, 0}\frac{1}{\sqrt{4\pi}} + c_{2, 0}\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1) \\ &= c_{0, 0}\frac{1}{\sqrt{4\pi}} - c_{2, 0}\frac{1}{4}\sqrt{\frac{5}{\pi}} + c_{2, 0}\frac{3}{4}\sqrt{\frac{5}{\pi}}\cos^2\theta \end{aligned} . \quad [1.13]$$

From this it is immediately clear that

$$c_{2,0} = \frac{3}{4\pi} \cdot \frac{4}{3}\sqrt{\frac{\pi}{5}} = \frac{1}{\sqrt{5\pi}} \qquad [1.14]$$

and

$$c_{0,0} = \frac{1}{\sqrt{5\pi}}\frac{1}{4}\sqrt{\frac{5}{\pi}} \cdot \sqrt{4\pi} = \frac{1}{\sqrt{4\pi}} . \qquad [1.15]$$

For a general product this is of course more complicated but there are a few simple rules for the general product $Y_{\ell_1, m_1}(\theta, \phi) \cdot Y_{\ell_2, m_2}(\theta, \phi)$. Since the dependence on ϕ is always given by $\exp(im\phi)$, it is immediately clear that the product function has to have the magnetic quantum number $M = m_1 + m_2$. Using similar arguments, the orbital angular quantum number can be limited to the range $|\ell_1 - \ell_2| \le L \le |\ell_1 + \ell_2|$. In principle, it is not important to know these restrictions since the Clebsch-Gordan coefficients (or the Wigner 3j symbols) will do the selection automatically.

The product can in general be written as the following linear combination

$$\begin{aligned} Y_{\ell_1, m_1}(\theta, \phi) \cdot Y_{\ell_2, m_2}(\theta, \phi) &= \sum_{L, M} \sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)(2L + 1)}{4\pi}} \\ &\quad \times \begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & M \end{pmatrix} Y^*_{L, M}(\theta, \phi) \begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \qquad [1.16]$$

where the Wigner 3j symbols are related to the Racah or Clebsch-Gordan coefficients by

$$\begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & M \end{pmatrix} = (-1)^{\ell_1 - \ell_2 - M} \frac{1}{\sqrt{(2L + 1)}} c(\ell_1, m_1, \ell_2, m_2, L, -M) . \qquad [1.17]$$

The Wigner 3j symbols or the Clebsch-Gordan coefficients can be found in tables in books about angular momentum or calculated using programs like Matlab, Macsyma, or Mathematica. Written with Clebsch-Gordan coefficients we obtain for Eq. [1.16]

$$Y_{\ell_1, m_1}(\theta, \phi) \cdot Y_{\ell_2, m_2}(\theta, \phi) = \sum_{L, M} \sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi(2L + 1)}} Y_{L, M}(\theta, \phi) \times c(\ell_1, m_1, \ell_2, m_2, L, M) c(\ell_1, 0, \ell_2, 0, L, 0) \quad . \tag{1.18}$$

To calculate the coefficients for the above example, we need the Wigner 3j symbols for

$$\begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} = -\frac{1}{\sqrt{3}} \qquad \begin{pmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} = 0 \qquad \begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} = \sqrt{\frac{2}{15}} \tag{1.19}$$

and obtain

$$\begin{aligned} Y_{1, 0}(\theta, \phi) \cdot Y_{1, 0}(\theta, \phi) &= \sum_{L = 0}^{2} 3 \sqrt{\frac{(2L + 1)}{4\pi}} \begin{pmatrix} 1 & 1 & L \\ 0 & 0 & 0 \end{pmatrix}^2 Y_{L, 0}(\theta, \phi) \\ &= \frac{1}{\sqrt{4\pi}} Y_{0, 0}(\theta, \phi) + 0 Y_{1, 0}(\theta, \phi) + \frac{1}{\sqrt{5\pi}} Y_{2, 0}(\theta, \phi) \end{aligned} \quad . \tag{1.20}$$

In the same way more complex products can be calculated and decomposed in the spherical harmonics. This is an iterative way to calculate the functional form of higher-order spherical harmonics from the lower-order ones. We will discuss this in more detail in an exercise.

1.3.3 Addition Theorem of Spherical Harmonics

The spherical harmonics obey an addition theorem that can often be used to simplify expressions

$$\sum_{m = -\ell}^{\ell} Y_{\ell, m}(\theta_1, \phi_1) Y^*_{\ell, m}(\theta_2, \phi_2) = \frac{2\ell + 1}{4\pi} P_\ell(\cos\omega) \tag{1.21}$$

where ω omega describes the angle between two unit vectors oriented at the polar coordinates (θ_1, ϕ_1) and (θ_2, ϕ_2) with

$$\cos\omega = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \ . \tag{1.22}$$

1.3.4 Integrals Over Spherical Harmonics

The integration over the product of three spherical harmonics can be simplified using the product rule of Eq. [1.16] and the orthogonality of Eq. [1.7]. This leads to

$$\begin{aligned}
&\int_0^{2\pi}\int_0^{\pi} Y_{\ell_1, m_1}(\theta, \phi) Y_{\ell_2, m_2}(\theta, \phi) Y_{\ell_3, m_3}(\theta, \phi) \sin\theta (d\theta) d\phi \\
&\qquad = \sum_{L, M} \sqrt{\frac{(2\ell_1+1)(2\ell_2+1)(2L+1)}{4\pi}} \begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & m_2 & M \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix} \\
&\qquad\quad \times \int_0^{2\pi}\int_0^{\pi} Y^*_{L, M}(\theta, \phi) Y_{\ell_3, m_3}(\theta, \phi) \sin\theta (d\theta) d\phi \\
&\qquad = \sqrt{\frac{(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)}{4\pi}} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix}
\end{aligned} \qquad [1.23]$$

a simple expression involving only a normalization constant and two Wigner 3j symbols.

1.4 Literature

(1) D. M. Brink, G. R. Satchler, Angular Momentum, third edition, Clarendon Press, 1993.

(2) A. R. Edmonds, Angular Momentum in Quantum Mechanics, Princeton University Press, 1960.

(3) M. E. Rose, Elementary Theory of Angular Momentum, John Wiley & Sons Inc., New York, 1957.