

## 3D Rigid Rotor

We can now extend the Rigid Rotor problem to a rotation in 3D, corresponding to motion on the surface of a sphere of radius  $R$ . The Hamiltonian operator in this case is derived from the Laplacian in spherical polar coordinates given as

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

For constant radius the first two terms are zero and we have

$$\hat{H}(\theta, \phi) = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2mR^2} \left( \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right)$$

We also note that

$$\hat{H} = \frac{\hat{L}^2}{2I}$$

where the operator for squared angular momentum is given by

$$\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right)$$

The Schrödinger equation is given by

$$-\frac{\hbar^2}{2mR^2} \left( \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi(\theta, \phi)}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \psi(\theta, \phi)}{\partial \theta} \right) = E\psi(\theta, \phi)$$

The wavefunctions are quantized in 2 directions corresponding to  $\theta$  and  $\phi$ . It is possible to derive the solutions, but we will not do it here. The solutions are denoted by  $Y_{l,m_l}(\theta, \phi)$  and are called spherical harmonics. The quantum

numbers take values  $l = 0, 1, 2, 3, \dots$  and  $m_l = 0, \pm 1, \pm 2, \dots \pm l$ . The energy depends only on  $l$  and is given by

$$E = l(l + 1) \frac{\hbar^2}{2I}$$

The first few spherical harmonics are given by

$$Y_{0,0} = \sqrt{\frac{1}{4\pi}}$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos(\theta)$$

$$Y_{1,\pm 1} = \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{\pm i\phi}$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{2,\pm 1} = \sqrt{\frac{15}{8\pi}} \cos \theta \sin \theta e^{\pm i\phi}$$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$$

These spherical harmonics are related to atomic orbitals in the H-atom. Notice that the  $\phi$  term in the wavefunction is the same as the 1D rigid rotor wavefunction. This implies that the spherical harmonics are eigenfunctions of the  $\hat{L}_z$  and  $\hat{L}^2$  such that

$$\hat{L}^2 Y_{l,m_l}(\theta, \phi) = l(l + 1) \hbar^2 Y_{l,m_l}(\theta, \phi)$$

$$\hat{L}_z Y_{l,m_l}(\theta, \phi) = m_l \hbar Y_{l,m_l}(\theta, \phi)$$

Thus the angular momentum vector shows quantization. The spherical harmonics are not eigenfunctions of  $\hat{L}_x$  and  $\hat{L}_y$ . It is just for convenience that we chose the z-direction the way we did. There is nothing magical about this direction.

The polar plots of the spherical harmonics give the angular distribution of the particle. We will discuss this when we discuss the Hydrogen atom solutions. Notice that for  $l = 0$ , the only possibility is  $m_l = 0$ . The corresponding

function  $Y_{0,0}$  is independent of  $\theta$  and  $\phi$  and this spherically symmetric. For  $l = 1$ ,  $m_l = 0$ , the function is proportional to  $\cos(\theta)$ . This implies that the function is maximum along  $\theta = 0$  or the Z-axis. The functions for  $l = 1$ ,  $m_l = \pm 1$  have maxima in the x-y plane. Since the wavefunctions  $Y_{1,1}$  and  $Y_{1,-1}$  are complex and difficult to visualize, we construct two linear combinations

$$Y_{1,x} = \frac{1}{\sqrt{2}} (Y_{1,1} + Y_{1,-1}) \propto \sin \theta \cos \phi$$

$$Y_{1,y} = \frac{1}{\sqrt{2}} (Y_{1,1} - Y_{1,-1}) \propto \sin \theta \sin \phi$$

These functions are maximum along the  $X$  and  $Y$  axes. The wavefunctions  $Y_{1,0}$ ,  $Y_{1,x}$  and  $Y_{1,y}$  are the angular parts of the  $p_z$ ,  $p_x$  and  $p_y$  orbitals of a Hydrogen atom.

Similarly, the functions for  $Y_{2,m_l}$  can be written as  $Y_{2,0}$ ,  $1/\sqrt{2}(Y_{2,1} + Y_{2,-1})$ ,  $1/\sqrt{2}(Y_{2,1} - Y_{2,-1})$ ,  $1/\sqrt{2}(Y_{2,2} + Y_{2,-2})$ ,  $1/\sqrt{2}(Y_{2,2} - Y_{2,-2})$ , so that they are real and these correspond to the orbitals  $d_{z^2}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$  and  $d_{x^2-y^2}$  and they are proportional to the described powers.

## 1 Spin Angular Momentum

The relations

$$\hat{L}^2 Y_{l,m_l} = \hbar^2 l(l+1) Y_{l,m_l}$$

and

$$\hat{L}_z Y_{l,m_l} = m_l \hbar Y_{l,m_l}$$

with the restriction that  $l = 0, 1, 2, \dots$  and  $m_l = 0, \pm 1, \pm 2, \dots, \pm l$  give a degeneracy of  $2l + 1$  for each energy level. If these states are states corresponding to an electron orbiting around a nucleus, they become nondegenerate in the presence of a magnetic field which couples to the angular momentum of the electron via an effect known as the Zeeman effect. The number of discrete states observed in the Zeeman effect is related to the orbital angular momentum quantum number  $l$ . In a famous experiment by Stern and Gerlach in 1921, where they passed Ag atoms in a magnetic field, they observed that the splitting was into only 2 bands. This seems to indicate that  $2l + 1 = 2$  or  $l = 1/2$ . The resolution was that this angular momentum is a different kind of angular momentum and is referred to as spin angular momentum or simply spin. Spin is an intrinsic property of the electron like its mass and

charge. Thus we have  $s = 1/2$  and  $m_s = \pm 1/2$  corresponding to the spin angular momentum of the electron corresponding to the angular momentum like operators  $\hat{S}^2$  and  $\hat{S}_z$  so that  $\hat{S}^2\psi(= \hbar^2 s(s+1)\psi$  and  $\hat{S}_z\psi = m_s\hbar\psi$ . We will come back to spin at the end of the discussion on the Hydrogen atom.