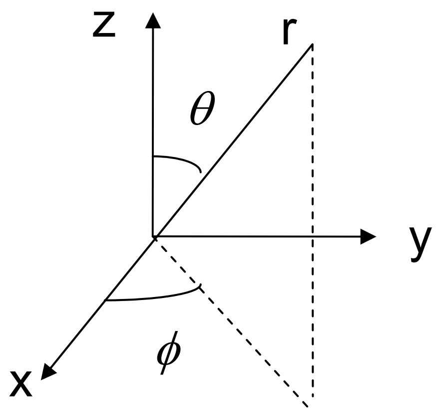
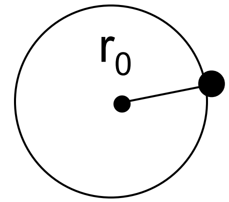
On to 3 dimensions: (x, y, z) $\rightarrow$ (r, θ, ϕ)





motion of particle on the surface of a sphere

$\equiv$ 3D <u>Rigid rotor</u>

$$\left.\begin{array}{l} 0 \le r \le \infty \\ 0 \le \theta \le \pi \\ 0 \le \phi \le 2\pi \end{array}\right\}$$

volume element $r^2 \sin\theta\, dr\, d\theta\, d\phi$

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$\frac{-\hbar^2}{2\mu r_0^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=EY$$

$Y(\theta, \phi)$ = wave function

$$\beta = \frac{\partial\mu r_0^2}{\hbar^2}E$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\beta\sin^2\theta Y=-\frac{\partial^2 Y}{\partial\phi^2}$$

$$\Rightarrow Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

separation of variables

spherical harmonics

$$\frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\beta\sin^2\theta \quad = \quad \frac{-1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

depends only on θ depends only on ϕ

$\Rightarrow$ this must be equal to a constant

Chapter 7, continued 3D Rigid Rotor

$$\begin{cases} \frac{1}{\Theta}\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\beta\sin^2\theta=m_\ell^2 \\ \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m_\ell^2 \end{cases}$$

$$\Phi_{m_\ell}=Ae^{im_\ell\phi},\qquad m_\ell=0,\pm1,\pm2,\ldots$$

(but see below)

$$\left.\begin{aligned} &\beta=\ell(\ell+1),\quad \ell=0,1,2,\ldots \\ &m_\ell=-\ell,-\ell+1,\ldots 0,\ldots,\ell-1,\ell \end{aligned}\right\}$$

quantization conditions

$\ell=0 \quad\rightarrow\quad m_\ell=0$ s

$\ell=1 \quad\rightarrow\quad m_\ell=-1,0,1$ p

$\ell=2 \quad\rightarrow\quad m_\ell=-2,-1,0,1,2$ d

} H atom

$$Y(\theta,\phi)=Y_\ell^{m_\ell}(\theta,\phi)=\Theta_\ell^{m_\ell}(\theta)\Phi_{m_\ell}(\phi)$$

θ,φ equations → two quantum #s

$$\beta = \frac{2\mu r_o^2 E}{\hbar^2} = \frac{2I}{\hbar^2} E$$

$$E = \frac{\hbar^2}{2I}\ell\left(\ell+1\right), \qquad \ell = 0,1,2,\ldots$$

$$\hat{H}Y_\ell^{m_\ell} = \frac{\hbar^2}{2I}\ell\left(\ell+1\right)Y_\ell^{m_\ell}$$

degeneracy = $2\ell+1$

$$\hat{\ell}^2 Y_\ell^{m_\ell} = \hbar^2\ell\left(\ell+1\right)Y_\ell^{m_\ell}$$

$\hat{\ell}^2$ and $\hat{H}$ obviously commute

$\hat{\ell}^2$: "angular momentum" operator

$$\left|\vec{\ell}\right| = \hbar\sqrt{\ell\left(\ell+1\right)}$$

components of the angular momentum operator

$$\hat{\ell}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)$$

$$\hat{\ell}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right) = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi} \right)$$

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

$$\left[\hat{\ell}_x, \hat{\ell}_y \right] = i\hbar\hat{\ell}_z$$

$$\left[\hat{\ell}_y, \hat{\ell}_z \right] = i\hbar\hat{\ell}_x$$

$$\left[\hat{\ell}_z, \hat{\ell}_x \right] = i\hbar\hat{\ell}_y$$

$$\hat{\ell}_z Y_\ell^{m\ell} = m_\ell \hbar Y_\ell^{m\ell}$$

Can simultaneously know the magnitude of the angular momentum and one of its components

Spherical harmonics

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$ spherically symmetric $\longrightarrow$ s

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta \longrightarrow p_z$$

$$Y_1^{\pm 1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

$$\sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi \longrightarrow p_x$$

$$\sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi \longrightarrow p_y$$

$$Y_2^0 \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \longrightarrow d_z^2$$

$$Y_2^{\pm 1} \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$$

$$\sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos\phi \longrightarrow d_{xz}$$

$$\sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi \longrightarrow d_{yz}$$

$$Y_2^{\pm 2} \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

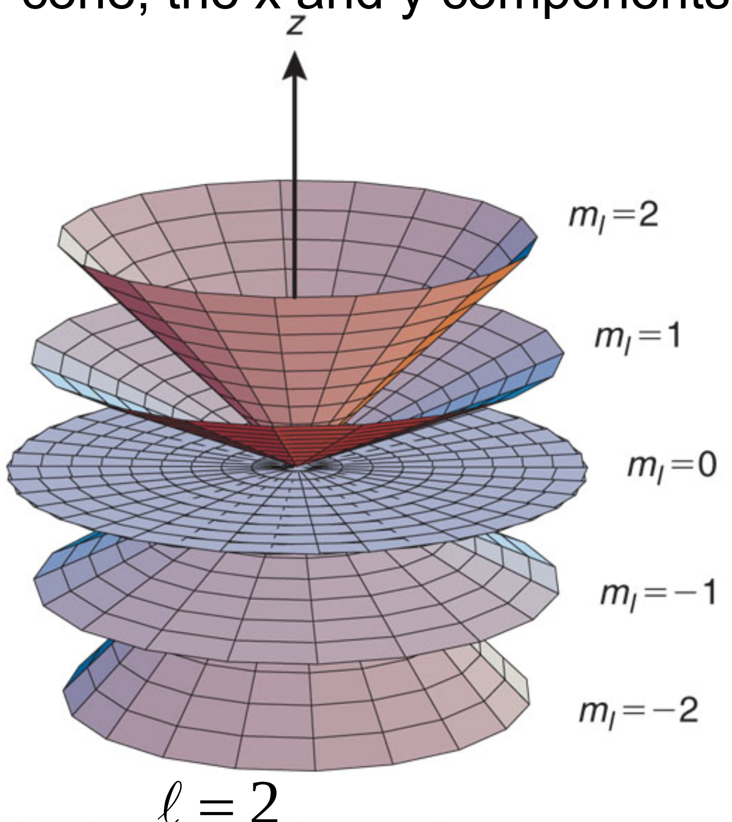
$$\sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi \longrightarrow d_{x^2-y^2}$$

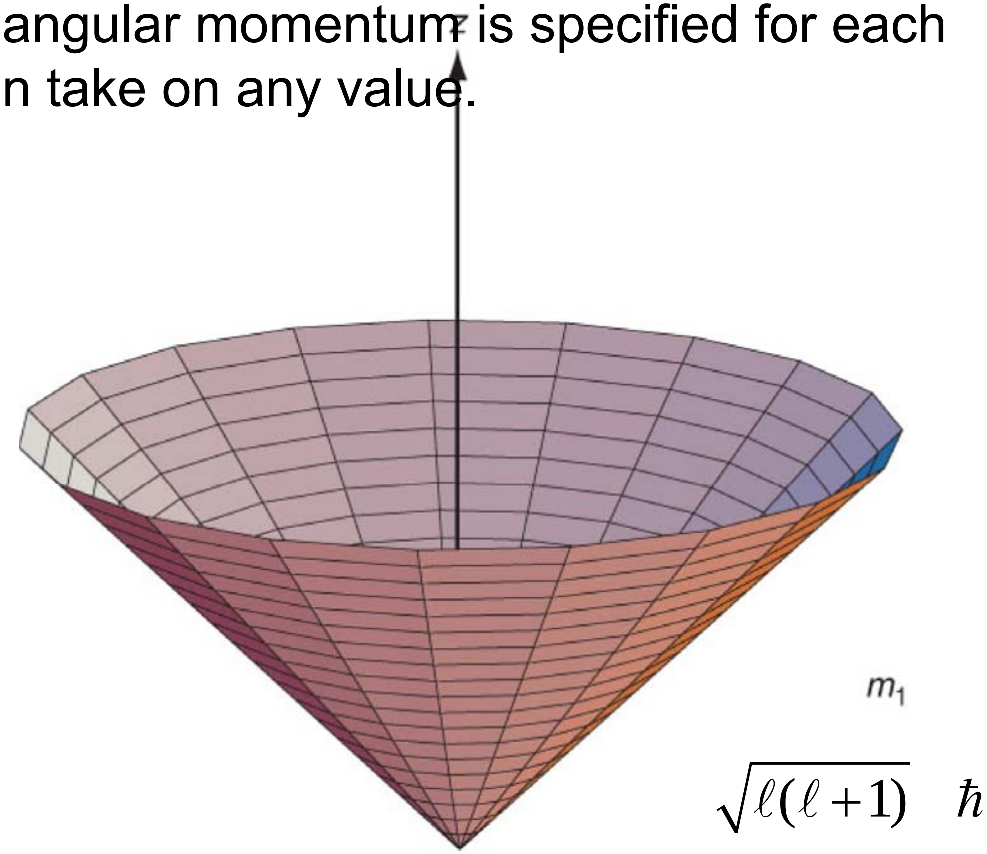
$$\sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi \longrightarrow d_{xy}$$

Consider a sphere of radius $\sqrt{\ell(\ell+1)}\hbar$

For ℓ=2, the allowed solutions can be represented as 4 cones and 1 disk.

Although the z component of the angular momentum is specified for each cone, the x and y components can take on any value.





You might find the graphical representations in the supplementary material to be helpful