Central Potential

- Another important problem in quantum mechanics is the central potential problem
  - This means V = V(r) only
  - This means angular momentum is conserved
- This problem is important because
  - We can find simultaneous eigenfunctions for the operators H, L^2, L_z
  - Many two particle systems in which the potential energy depends only on their relative position can be reduced to a central potential problem
  - Hydrogen and hydrogen-like atoms have V(r) given by the Coulomb potential

Central Potential

- There is a lot of calculation here so we will have to be content to set the problem up and then state the results

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

where in rectangular coordinates $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

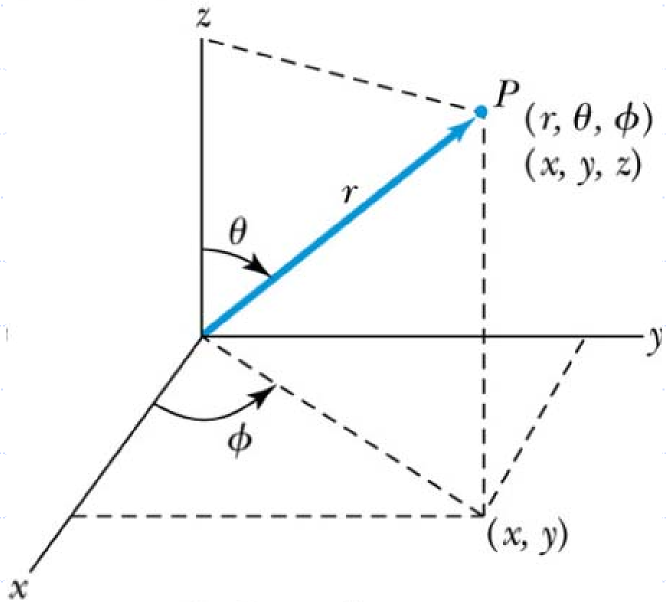
where in spherical coordinates $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)$

We solve this by separation of variables

First let $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$

Hydrogen Atom

- Spherical coordinates



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

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1} \frac{z}{r} \quad \text{(Polar angle)}$$

$$\phi = \tan^{-1} \frac{y}{x} \quad \text{(Azimuthal angle)}$$

Central Potential

- As when we used separation of variables before, we algebraically manipulate the separate variables to be on one side or the other of the = and then set them equal to a constant

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

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\}=-l(l+1) \qquad (2)$$

  - We'll come back to (1) later

Now let $Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$ and repeat the process

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+l(l+1)\sin^2\theta=m^2 \qquad (3)$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m^2 \qquad (4)$$

Central Potential

- Solution to (3)

$$\Phi(\varphi) = e^{im\varphi}$$

And applying the condition $\Phi(\varphi) = \Phi(2\pi + \varphi)$

we must have $m = 0, \pm 1, \pm 2, \ldots$

- Solution to (4)

$$\Theta(\theta) = AP_l^m(\cos\theta)$$

where $P_l^m(\cos\theta)$ are the associated Legendre polynomials

and for the solution to remain finite

$l = 0, 1, 2, \ldots$ with $m = -l, -l+1, \ldots, l-1, l$

Central Potential

- More generally we group these two solutions together
  - The Y_{lm} are called the spherical harmonics

$$Y_{lm}(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$$

$$=(-1)^m\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}e^{im\varphi}P_l^m(\cos\theta)\ \text{for m} \geq 0$$

$$Y_{l-m}(\theta,\varphi)=(-1)^m Y_{lm}^*(\theta,\varphi)$$

Central Potential

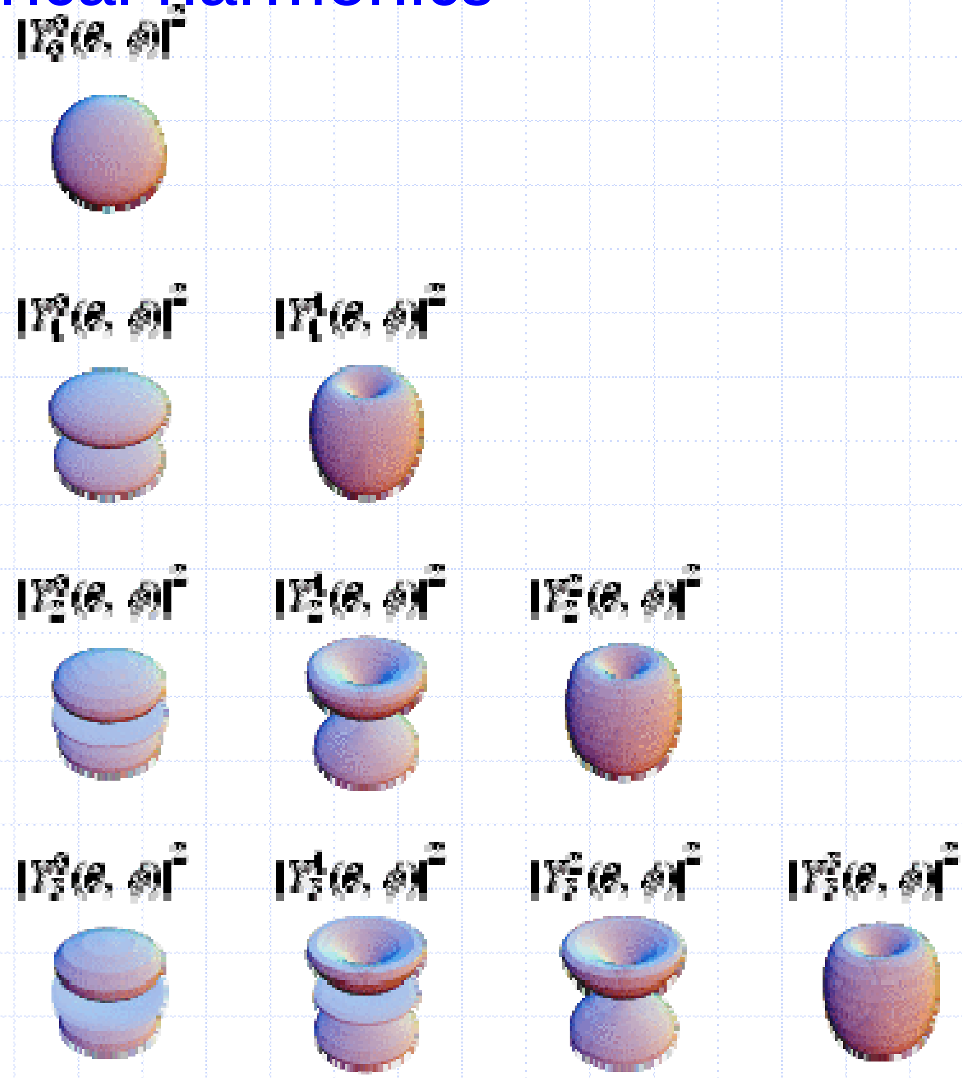
- Spherical harmonics

Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

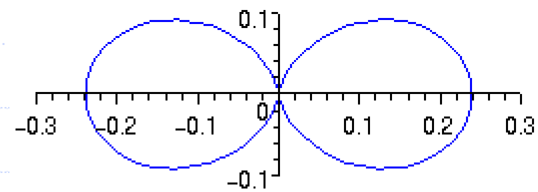
Central Potential

- Spherical harmonics

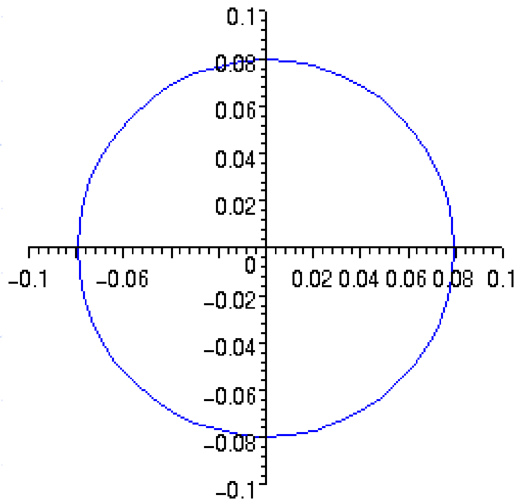


Central Potential

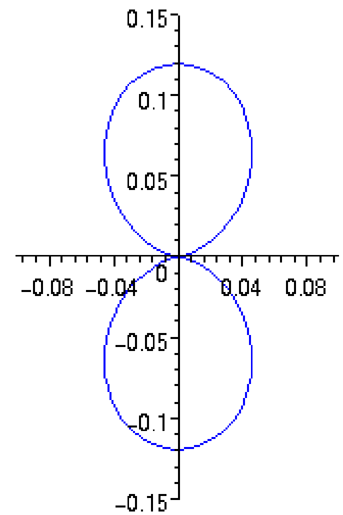
- Polar plots of spherical harmonics (Y*Y)
  - Z axis is horizontal



L,M=1,0



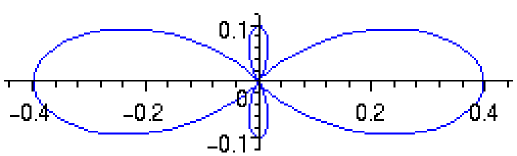
L,M=0,0



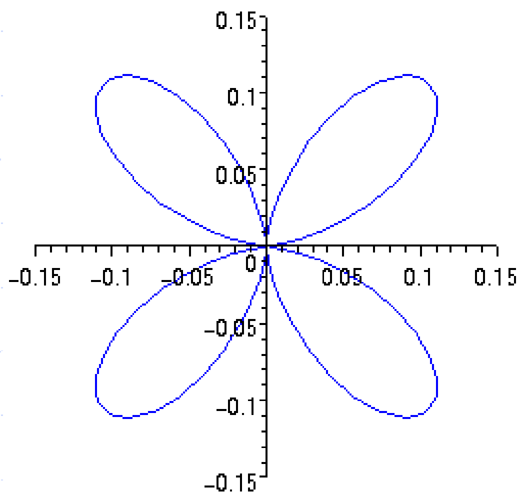
L,M=1,1

Central Potential

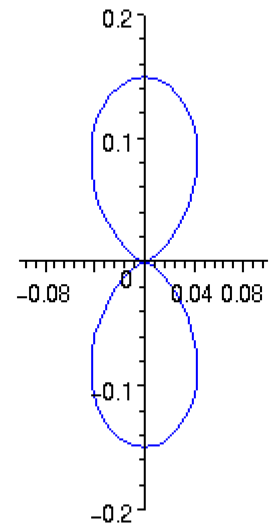
- Polar plots of spherical harmonics (Y*Y)
  - Z axis is horizontal



L,M=2,0



L,M=2,1



L,M=2,2

Central Potential

- Comments
  - The spherical harmonics are the angular solution to ANY central potential problem
  - The shape of the potential V(r) only affects the radial part of the wave function
  - There spherical harmonics are orthonormal

$$\int_0^{2\pi}\int_0^{\pi}\left[Y_l^m(\theta,\varphi)\right]^*\left[Y_{l'}^{m'}(\theta,\varphi)\right]\sin\theta d\theta d\varphi=\delta_{ll'}\delta_{mm'}$$

Angular Momentum

- As we mentioned already, angular momentum is very important in both classical quantum mechanics
  - Angular momentum is conserved for an isolated system and a particle in a central potential
  - Orbital angular momentum (L)
    - We usually call this angular momentum
  - Intrinsic angular momentum (S)
    - We usually call this spin
  - Total angular momentum (J)
    - Sum of orbital plus spin angular momentum

Angular Momentum

- In classical mechanics

$$\vec{L} = \vec{r} \times \vec{p}$$

$$L_x = yp_z - zp_y,\ L_y = zp_x - xp_z,\ L_z = xp_y - yp_x$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

- Using quantum operators

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

Angular Momentum

- In spherical coordinates

$$L_x = \frac{\hbar}{i}\left(-\sin\varphi \frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

$$L_y = \frac{\hbar}{i}\left(\cos\varphi \frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

- And then

$$L^2 = \vec{L}\cdot\vec{L} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

- Which (believe it or not) you have already seen

Angular Momentum

- This is the most important slide today
- Thus we have

$$L^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 Y_{lm}(\theta,\varphi)$$

$$L_z Y_{lm}(\theta,\varphi) = m\hbar Y_{lm}(\theta,\varphi)$$

- Angular momentum is quantized

The allowed values of l are $0,1,2,\ldots$

Sometimes we use letter names for l instead $s, p, d, f, g, \ldots$

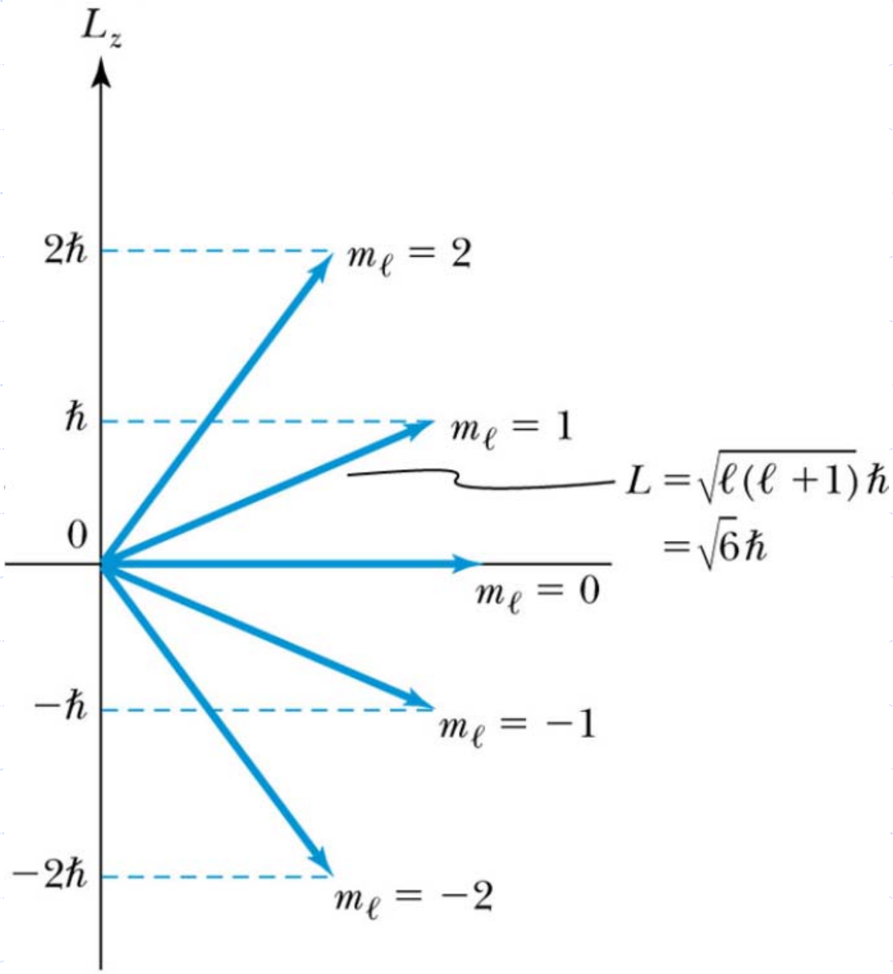
The allowed values of m are $0, \pm 1, \ldots, \pm l$

The eigenvalues of L^2 are $l(l+1)\hbar^2$

The eigenvalues of L_z are $m\hbar$

Hydrogen Atom

- Orbital angular momentum for l=2



Angular Momentum

- The condition that two physical quantities are simultaneously observable is [A,B]=AB-BA=0

Proof

Let $\hat{A}\psi = a\psi$ and $\hat{B}\psi = b\psi$

$$\hat{A}\hat{B}\psi = \hat{A}b\psi = b\hat{A}\psi = ab\psi$$

$$\hat{B}\hat{A}\psi = \hat{B}a\psi = a\hat{B}\psi = ab\psi$$

$$\left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\psi = 0$$

$$\left[\hat{A}, \hat{B}\right] = 0$$

Angular Momentum

- You can work these out yourself

$$[L_x, L_y] = i\hbar L_z$$

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

$$[L^2, L_x] = 0, [L^2, L_y] = 0, [L^2, L_z] = 0$$

$$[L^2, L] = 0$$

$$[x, p_x] = i\hbar$$

$$[x, y] = [x, z] = [y, z] = 0$$

$$[p_x, p_y] = [p_x, p_z] = [p_y, p_z] = 0$$

Angular Momentum

- If the operators don't commute one can't measure the corresponding physical quantities simultaneously
  - Examples
    - x and p_x
    - L_x, L_y, L_z
- We can only find eigenstates of L^2 and one of $L_{x,}$ L_y, and L_z
  - Usually we pick z
  - This is arbitrary unless there is preferred direction in space set by an external magnetic field e.g.
- Note in the previous picture a few slides back that L never points in the z direction
  - This is because L_x and L_y can not be precisely known

Central Potential

- The results we have arrived at hold true for any central potential
- Thus we've learned quite a lot about the hydrogen atom without really solving it explicitly
- Note the difference in the expression for angular momentum between the Bohr model and the QM calculation
  - L_Z=n h-bar versus L_Z=m h-bar
  - Electron moves in orbits versus electron probability distribution over all space
  - Energy determined by angular momentum versus energy determined by principle quantum number n