Quantum Mechanics and Atomic Physics Lecture 14: Angular Momentum Operators http://www.physics.rutgers.edu/ugrad/361 Prof. Sean Oh

Last time

- Solved for S.E. in 3D using "particle in a box" example
- Using *separation of variables* we found that the total wavefunction is:



FIGURE 6.1 Infinite potential box.

$$\begin{aligned} \Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}) &= \mathbf{X} \mathbf{y} \mathbf{z} = \mathbf{A} \sin \frac{n_{\mathbf{x}} \pi \mathbf{x}}{a} \sin \frac{n_{\mathbf{y}} \pi \mathbf{y}}{a} \sin \frac{n_{\mathbf{z}} \pi \mathbf{z}}{a} \\ n_{\mathbf{x}} &= 1, 2, 3, \cdots, n_{\mathbf{z}} = 1, 2, 3, \cdots, n_{\mathbf{z}} = 1, 2, 3, \cdots \end{aligned}$$

$$\mathbf{A} = \sqrt{\frac{\mathbf{g}}{abc}} = \sqrt{\frac{\mathbf{g}}{\mathbf{v}}}$$

Quantization of energy is:

$$E = \frac{\pi^2 h^2}{am} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

 And found that energy degeneracy increases with energy

Spherical Coordinates

- One of our goals is to solve S.E. in 3D for the Coulomb potential (1/r) which describes the hydrogen atom
- To do this we need to use spherical coordinates



Spherical Coordinates II

$$\hat{f} = \bar{s}\ln\Theta\cos\phi\hat{x} + \bar{s}\ln\Theta\sin\phi\hat{y} + \cos\theta\hat{z}$$

$$\hat{\Theta} = \cos\Theta\cos\phi\hat{x} + \cos\Theta\sin\phi\hat{y} - \bar{s}\ln\Theta\hat{z}$$

$$\hat{d} = -\bar{s}\ln\phi\hat{x} + \cos\phi\hat{y}$$

$$=)\frac{\partial\hat{f}}{\partial\theta} = \cos\Theta\cos\phi\hat{x} + \cos\Theta\sin\phi\hat{y} - \bar{s}\ln\hat{\theta}\hat{z} = 0$$

$$Similarly, \quad \hat{\partial\Phi} = -\hat{f}, \quad \hat{\partial\Phi} = 0$$

$$\hat{f} = \bar{s}\ln\Theta\phi, \quad \hat{\partial\Phi} = \cos\phi\hat{\rho}, \quad \hat{\partial\Phi} = -\bar{s}\ln\phi\hat{f} - \cos\phi\hat{\rho}$$

$$\hat{Sut} \quad \hat{\partial}f = \hat{f} = \hat{\partial}\theta = -\hat{f} = 0$$

$$\hat{f} = \bar{s}\ln\Theta\hat{f} - \hat{f} = -\hat{f} = 0$$

Gradient and Laplacian Operator in spherical coordinates

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{\partial \theta} + \hat{\psi} \frac{1}{r^{3} \ln \theta} \frac{\partial}{\partial \psi}$$

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

We need this for defining angular momentum....

Angular Momentum

Recall that angular momentum is:

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

$$\vec{p} \implies \vec{R}_{op} = -it\vec{r} , \quad \vec{r} \implies \vec{r}_{op} = (x_1 y_1 y_2)$$

$$L_{x} = -i\hbar (y \frac{2}{3y} - 3 \frac{2}{3y})$$

$$L_{y} = -i\hbar (3 \frac{2}{3x} - x \frac{2}{3y})$$

$$L_{z} = -i\hbar (x \frac{2}{3y} - 3 \frac{2}{3x})$$

Note:

No "x" appears in L_x, No "y" appears in L_y, And no "z" appears in L_z.

Commutators of x,y,z components of L

For example:

 $\begin{aligned} \left[L_{X}, L_{Y} \right] &= L_{X} L_{Y} - L_{Y} L_{X} \qquad (commutator) \\ L_{X} L_{Y} &= \left\{ -ith \left(y \frac{3}{3} - 3 \frac{3}{3} y \right) \right\} \left\{ -ith \left(3 \frac{3}{3} - x \frac{3}{3} \right) \right\} \\ &= -th \left(y \frac{3}{3} \frac{3}{3} - 3 \frac{3}{3} y \right) \right\} \left\{ -ith \left(\frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \right) \right\} \\ &= -th \left(\frac{3}{3} \frac{3}{3} \frac{3}{3} + y \frac{3}{3} - yx \frac{3}{3} \frac{3}{3} - 3 \frac{3}{3} \frac{3}{3} x + 3x \frac{3}{3} \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \right) \right\} \left\{ -ith \left(\frac{3}{3} \frac{3}{3} - 3 \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - \frac{1}{3} \frac{3}{3} \frac{3}{3} - \frac{1}{3} \frac{3}{3} \frac{3}{3} + x \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - \frac{1}{3} \frac{3}{3} \frac{3}{3} - \frac{1}{3} \frac{3}{3} \frac{3}{3} + \frac{1}{3} \frac{3}{3} \frac{3}{3} \right) \\ &= -th \left(\frac{3}{3} \frac{3}{3} - \frac{1}{3} \frac{3}{3} \frac{3$

So,
$$[L_{x}, L_{y}] = -t^{2}(y_{x}^{2} - x_{y}^{2})$$

But
 $it_{y} = it(-it(x_{y}^{2} - y_{y}^{2}))$
 $= +t^{2}(x_{y}^{2} - y_{y}^{2})$
 $= -t^{2}(y_{y}^{2} - x_{y}^{2})$
So,
 $(L_{x}, L_{y}] = it_{y}^{2}$
 $(L_{y}, L_{y}] = it_{y}^{2}$.

What does this mean?

- The components of L do not commute with each other!
- No simultaneous eigenstates!
- If you measure $L_x \Rightarrow$ get a certain value
- Next, measure $L_v \Rightarrow$ get a certain value
- Measure L_x again ⇒ in general, you won't get the same value as before!
- We will revisit this in Chapter 8

L operator in spherical coordinates

Lo=-it(Fx+) V: F2 + 0 1 30 + 0 I sine 30 Lop - - it [4 2 - 0 1 2]

Now the x,y,z components in spherical coordinates

First the z component:

$$\begin{aligned} (L_3)_{op} &= \hat{3} \cdot \hat{L}_{op} \quad , \quad (L_x)_{op} &= \hat{3} \cdot \hat{L}_{op} \quad , \quad (L_y)_{op} \cdot \hat{9} \cdot \hat{L}_{op} \\ &\text{use} : \quad \hat{x} = \sin \theta \cos \varphi \hat{r} + \cos \theta \cos \varphi \hat{\theta} - \sin \varphi \hat{q} \\ &\hat{g} = -\sin \theta \sin \varphi \hat{r} + \cos \theta \sin \varphi \hat{\theta} + \cos \varphi \hat{\varphi} \\ &\hat{3} \cdot (\cos \theta \hat{r} - \sin \theta \hat{\theta}) \\ (L_3)_{op} &= (\cos \theta \hat{r} - \sin \theta \hat{\theta}) \cdot \hat{5} - it (\hat{q} \hat{\theta} - \hat{\theta} + \frac{2}{\sin \theta} \hat{\theta}_{q}) \\ &= -ik \sin \theta \hat{\theta} \cdot \hat{\theta} = \hat{1} \quad \hat{2}_{gg} \\ (L_3)_{op} &= -ik \hat{2}_{gg} \\ &\hat{\theta} \cdot \hat{\theta} = 1 \quad , \text{ all others} = \frac{7}{7} e^{r\theta} \end{aligned}$$

Similarly,

$$(L_{x})_{ip} = it \left(\sin \varphi_{\partial \varphi}^{2} + \cot \theta \cos \varphi_{\partial \varphi}^{2} \right)$$

$$(L_{y})_{op} = it \left(-\cos \varphi_{\partial \varphi}^{2} + \cot \theta \sin \varphi_{\partial \varphi}^{2} \right)$$

■ I leave it for you as an exercise to derive these

• Later, we will need to use the expression for L_z

What about important quantity L_{op}^{2} ? $\tilde{L}_{op}^{2} = \tilde{L}_{g}^{2} = \left[-it_{g}^{2} - \tilde{\theta}_{1}^{2} - \tilde{\theta}_{1}^{2}\right] \left[-it_{g}^{2} - \tilde{\theta}_{1}^{2} - \tilde{\theta}_{1}^{2}\right]$

compare to: $\vec{\nabla}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(\frac{i^2}{\partial r} \right) + \frac{1}{r^2} \frac{1}{\sin 2} \frac{\partial}{\partial q} \left(\frac{\sin 2}{\partial q} \right) + \frac{1}{r^2 \sin^2 2} \frac{\partial^2}{\partial q^2}$ $+ \frac{1}{r^2 \sin^2 2} \frac{\partial^2}{\partial q^2}$ $\implies \vec{\nabla}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2} \frac{L_{pp}^2}{r^2}$

Let's relate this to the Hamiltonian

$$H_{op} = -\frac{t^2}{\partial m} \nabla^2 + V(r_i \partial_i \varphi)$$

=>
$$H_{op} = -\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r}\right) + \frac{L_{or}^2}{2mr^2} + V(r_i \theta_i \psi)$$

Central Potentials: V(r)

The S.E. for a particle of mass µ moving in a central potential V(r):

$$-\frac{1}{2\mu}\left\{\frac{1}{2}+\frac{1}{2}\left(r^{2}-\frac{1}{2}\right)+\frac{1}{2}+\frac{1}{2}\frac{1}{2}\sin^{2}\left(\sin\phi^{2}-\frac{1}{2}\right)+\frac{1}{2}\frac{1}{2}\frac{1}{2}\sin\phi^{2}-\frac{1}{2}\frac$$

I've replaced m with μ (to not be confused with new variable I will introduce shortly m_ℓ, and in reality it should be expressed as the reduced mass μ)

Again, let's use separation of variables, like we did last time:

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$$-\frac{\hbar^{2}}{2\mu}\left\{\frac{Y}{r^{2}}\frac{2}{\partial r}\left(r^{2}\frac{\partial R}{\partial r}\right)+\frac{R}{r^{2}}\left(\frac{1}{\sin\theta}\frac{2}{\partial\theta}\left(\sin\theta\frac{2Y}{\partial\theta}\right)+\frac{1}{\sin^{2}\theta}\left(\frac{2^{2}\Psi}{\partial\psi^{2}}\right)\right\}\right\}$$
$$+V(F\cdot\Psi) = E\cdot R\cdot\Psi.$$

Hulppy by r2 RY

$$-\frac{1}{2}\left\{\frac{1}{2}\left\{\frac{1}{2}\left[r^{2}\frac{\partial R}{\partial r}\right]\right\} + \left[V-E\right]r^{2}$$

$$= \frac{1}{2}\left[\frac{1}{2}\left[\frac{1}{2}\left[\frac{\partial R}{\partial r}\right]\right] + \frac{1}{2}\left[\frac{\partial^{2}Y}{\partial \phi^{2}}\right] + \frac{1}{2}\left[\frac{\partial^{2}Y}{\partial \phi^{2}}\right]$$

Some things to note about this equation ...

Separation of variables

LHS =>
$$f(r)$$
 $\begin{cases} f(r) = g(\theta, \varphi) = const. \\ RHS => g(\theta, \varphi) \end{cases}$

(we will come back to this equation)

Let's call the constant:

Let's rewrite the RHS:

$$-\left[\frac{1}{s_{in0}}\frac{2}{30}\left(s_{in0}\frac{2Y}{30}\right)+\frac{1}{s_{in}^{2}0}\left(\frac{2^{2}Y}{2y^{2}}\right)\right]=\alpha Y$$

-



- Let's call the constant $(-m_{\ell}^2)$
- We will discover later that this is called the mangetic quantum number

Solutions to $\Phi(\phi)$

$$=) \frac{d^2 \Psi}{d\varphi^2} = -m_i^2 \Psi$$

$$\overline{\mathcal{P}}(\varphi) = A e^{ime\varphi}$$

You will see later that we don't need the e^{-im\$} term

Normalize:

$$I = \int_{0}^{2\pi} \mathcal{P}^{*} \mathcal{F} d\varphi = \int_{0}^{2\pi} A^{2} e^{-ime\varphi} e^{+ime\varphi} d\varphi$$

$$= A^{2} \cdot 2\pi \implies A = \int_{2\pi}^{2\pi}$$

$$\Rightarrow \overline{P}(\varphi) = \int_{\partial \pi}^{+} e^{im \varphi} \varphi \operatorname{ranges} for \partial \to \partial \pi$$

Single-valuedness requires that:
$$\overline{P}(\varphi) = \overline{P}(\varphi) = \overline{$$

ind

Me = 0, ±1, ±2,

We find that the mangnetic quantum number is quantized!

Let's go back to "separated" S.E.

 $\begin{aligned} \chi &= \lim_{R \to r} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{\partial \mu}{\hbar^2} r^2 \left[v - \overline{E} \right] \\ &= -\frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{1}{\frac{1}{\Psi \sin^2 \Theta}} \frac{d^2 \overline{\Psi}}{d\varphi^2} \\ &+ \frac{m_{\theta}^2}{9in^2 \Theta} \end{aligned}$

- **RHS** depends on θ
- LHS depends on r
- Equal to a constant
 - Let's call it *l(l+1)* Which is also equal to what we've been calling α!

$$\Rightarrow \int_{\text{Sino}} \frac{d}{d\theta} \left(\sin \theta \, d\theta \right) + \left[\ell(l+1) - \frac{m_{l}^{2}}{\sin^{2} \theta} \right] \theta = 0$$

$$\Rightarrow \int_{\text{T2}} \frac{d}{d\theta} \left(r^{2} \frac{dR}{dr} \right) - \left(\frac{2\Lambda}{\pi^{2}} \left(v - E \right) - \frac{\ell(\ell+1)}{r^{2}} \right] R = 0$$

- Solutions to $\Theta(\theta)$:
 - They are associated Legendre Polynomials (see Chapter 6 for full expression):

• A few of them are:

$$P_{20} = 1$$
, $P_{10} = \cos \theta$, $P_{11} = \sin \theta$, $P_{1-1} = -\sin \theta$
 $P_{20} = \frac{1}{2}(3\cos^2 \theta - 1)$

 Note: special cases of m_e=0 are called Regular Legendre Polynomials

Spherical Harmonics

- We usually deal with a combined angular dependence
 Y(θ,φ)=Θ(θ)Φ(φ)
- These are called Spherical Harmonics (see Chapter 6 for full expression):

 Verse (0, q)
- And is *l* called the orbital angular momentum quantum number

Table 6.1 Spherical Harmonics	
$Y_{0,0}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$	$Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$
$Y_{1,\pm 1}(\theta,\phi) = \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}$	$Y_{2,0}(\theta,\phi) = \sqrt{\frac{5}{4\pi}} \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$
$Y_{2,\pm 1}(\theta,\phi) = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\phi}$	$Y_{2,\pm 2}(\theta,\phi) = \sqrt{\frac{15}{32\pi}} \sin^2 \theta \ e^{\pm 2i\phi}$
$Y_{3,0}(\theta,\phi) = \sqrt{\frac{7}{16\pi}}(5\cos^3\theta - 3\cos\theta)$	$Y_{3,\pm 1}(\theta,\phi) = \mp \sqrt{\frac{21}{64\pi}} \sin\theta (5\cos^2\theta - 1) e^{\pm i\phi}$
$Y_{3,\pm 2}(\theta,\phi) = \sqrt{\frac{105}{32\pi}} \sin^2\theta \cos\theta \ e^{\pm 2i\phi}$	$Y_{3,\pm 3}(\theta,\phi) = \mp \sqrt{\frac{35}{64\pi}} \sin^3 \theta e^{\pm 3\omega \phi}$

Radial Solutions

- Solutions to R(r), depend on the potential energy
 - We will revisit this next week

Recall:

Let's go back to:

$$-\frac{1}{2}\left\{\frac{1}{2}\left\{r^{2}\right\}_{r}^{2}\left\{$$

$$L_{op}^{2} = -t^{2} \left[\frac{1}{\sin \varphi} \frac{\partial}{\partial \varphi} \left(\sin \varphi \frac{\partial}{\partial \varphi} \right) + \frac{1}{\sin^{2} \varphi} \frac{\partial^{2}}{\partial \varphi^{2}} \right]$$

$$f(r) = g(0, \varphi) = const$$

$$= -\frac{h^2}{2\mu} \left\{ \frac{1}{k} \frac{2}{3r} \left(r^2 \frac{2k}{3r} \right) \right\} + \left[V - E \right] r^2$$

$$= const = -\frac{1}{2\mu} \left[L_{op}^2 Y \right] \qquad const = -\frac{h^2}{2\mu}$$

$$= \sum_{x \neq y} - \frac{1}{2} \left[L_{op}^{2} Y \right]^{2} = -\frac{x h^{2}}{2 \mu}$$

$$= \sum_{x \neq y} L_{op}^{2} Y = h^{2} x Y = \left[h^{2} \left(l(l+1) \right) \right] Y$$

$$= \sum_{x \neq y} L = \left[l(l+1) h \qquad l = 0, 1, 2, \dots \right]$$

So,
$$d = l(l+1)$$
 and $l = 0, 1, 2, ...$

Total angular momentum is quantized!

What about L₂? L3 = -it 30 $\implies L_3 \overline{\mathcal{D}}(\varphi) = -i k \frac{\partial}{\partial \varphi} \left(A e^{i m_x \varphi} \right)$ = -i²met (Aeimer) = m,t I => Lz = met where |me | < P Since ly ≤ |L| => m, ≤ le(l+1) => m,14l

So, solutions exist only if ℓ is an integer and $\ell \ge m_{\ell}$

Summary/Announcements

- For central potentials (V depends only on r and not on any angles), the angular solution is always, the spherical harmonics $(Y_{l,m}(\theta,\phi))$, well defined quantum angular momentum quantum numbers, *l* and *m*.
- Next time: More about angular momentum and radial solutions for central potentials
 Next homework due on Monday Nov 7