

Notes for Quantum Mechanics

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Lecture 25 Orbital Angular Momentum

Now I would like to go to the subject of orbital angular momentum and we will see that it fits in nicely with the angular momentum we defined as \hat{J} which will come in two types, orbital and spin. Specifically we will define $\hat{J} = \hat{L} + \hat{S}$.

OK lets start. The classical definition of angular momentum is $\vec{L} = \vec{r} \times \vec{p}$. Now lets just make it QM by making things operators

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

$$\text{REMEMBER} \quad [\hat{x}_i, \hat{x}_j] = 0 \quad [\hat{p}_i, \hat{p}_j] = 0 \quad [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$$

First lets check and see if it really is an type of angular momentum. If it is, it must satisfy $[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk} \hat{J}_k$, i.e. $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk} \hat{L}_k$ Lets check it

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] = \\ &[\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}, \hat{x}]\hat{p}_z - \hat{z}[\hat{p}_y, \hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] = [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] = \\ &\hat{y}[\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{y}, \hat{z}\hat{p}_x]\hat{p}_z + \hat{z}[\hat{p}_y, \hat{x}\hat{p}_z] + [\hat{z}, \hat{x}\hat{p}_z]\hat{p}_y = \hat{y}[\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}, \hat{x}\hat{p}_z]\hat{p}_y = \\ &\hat{y}\hat{z}[\hat{p}_z, \hat{p}_x] + \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x + \hat{x}[\hat{z}, \hat{p}_z]\hat{p}_y + [\hat{z}, \hat{x}]\hat{p}_z\hat{p}_y = \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x + \hat{x}[\hat{z}, \hat{p}_z]\hat{p}_y = \\ &i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z \end{aligned}$$

And you can do this for all the other combinations so good. It follows the required commutators.

Next lets see if it is a generator of rotations. Lets look at the operator $(1 - i\frac{\delta\phi}{\hbar}\hat{L}_z)$. We will operate on the position ket $|x', y', z'\rangle$. We can use the definition $\hat{T}(\delta\mathbf{x})|\mathbf{x}\rangle = (1 - i\delta\mathbf{x} \cdot \frac{\hat{p}}{\hbar})|\mathbf{x}\rangle = |\mathbf{x} + \delta\mathbf{x}\rangle$

$$\begin{aligned} (1 - i\frac{\delta\phi}{\hbar}\hat{L}_z)|x', y', z'\rangle &= [1 - i\frac{\delta\phi}{\hbar}(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)]|x', y', z'\rangle = [1 - i\frac{\delta\phi}{\hbar}\hat{x}\hat{p}_y + i\frac{\delta\phi}{\hbar}\hat{y}\hat{p}_x]|x', y', z'\rangle = [1 - ix'\delta\phi\frac{\hat{p}_y}{\hbar} + iy'\delta\phi\frac{\hat{p}_x}{\hbar}]|x', y', z'\rangle \\ &= [1 + iy'\delta\phi\frac{\hat{p}_x}{\hbar} - ix'\delta\phi\frac{\hat{p}_y}{\hbar}]|x', y', z'\rangle = |x' - y'\delta\phi, y' + x'\delta\phi, z'\rangle \end{aligned}$$

So this operator L is a type of angular momentum J

Now we can think of a spinless particle $|\alpha\rangle$, or in position representation $\langle x', y', z' | \alpha \rangle$

We can look at the rotated state $(1 - i\frac{\delta\phi}{\hbar}\hat{L}_z)|\alpha\rangle$ and the position representation

$$\langle x', y', z' | (1 - i\frac{\delta\phi}{\hbar}\hat{L}_z)|\alpha\rangle = \langle x' + y'\delta\phi, y' - x'\delta\phi, z' | \alpha \rangle$$

(note: $\langle x', y', z' | (1 - i \frac{\delta\phi}{\hbar} \hat{L}_z) | \alpha \rangle = \langle x', y', z' | (1 - i \frac{\delta\phi}{\hbar} \hat{L}_z) | \alpha \rangle^\dagger = \langle \alpha | 1 + i \frac{\delta\phi}{\hbar} \hat{L}_z | x', y', z' \rangle^\dagger = \langle \alpha | x'+y'\delta\phi, y'-x'\delta\phi, z' \rangle^\dagger = \langle x'+y'\delta\phi, y'-x'\delta\phi, z' | \alpha \rangle$)

Now its easier to put this in spherical coordinates $\langle x', y', z' | \alpha \rangle \rightarrow \langle r, \theta, \phi | \alpha \rangle$

$$x' = r \sin\theta \cos\phi \quad y' = r \sin\theta \sin\phi \quad z' = r \cos\theta \quad r = \sqrt{x'^2 + y'^2 + z'^2} \quad \theta = \arccos\left(\frac{z'}{r}\right) = \arccos\left(\frac{z'}{\sqrt{x'^2 + y'^2 + z'^2}}\right) \quad \phi = \arctan\left(\frac{y'}{x'}\right)$$

$\langle r, \theta, \phi | (1 - i \frac{\delta\phi}{\hbar} \hat{L}_z) | \alpha \rangle = \langle r, \theta, \phi - \delta\phi | \alpha \rangle = \langle r, \theta, \phi | \alpha \rangle - \delta\phi \frac{d}{d\phi} \langle r, \theta, \phi | \alpha \rangle$ so can identify

$$\langle \mathbf{x} | \hat{L}_z | \alpha \rangle = \langle \mathbf{x} | \alpha \rangle = \frac{\hbar}{i} \frac{d}{d\phi} \langle \mathbf{x} | \alpha \rangle$$

Note that \mathbf{x} is a vector so $\mathbf{x} \rightarrow x', y', z'$ or $\mathbf{x} \rightarrow r, \theta, \phi$

similarly we can find (and after some work converting to spherical coordinates)

$$\hat{L}_z = \hat{x} \hat{p}_y - \hat{y} \hat{p}_x \quad \hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y \quad \hat{L}_y = \hat{z} \hat{p}_x - \hat{x} \hat{p}_z$$

$\langle x', y', z' | \hat{L}_z | \alpha \rangle = \langle x'+y'\delta\phi, y'-x'\delta\phi, z' | \alpha \rangle = \frac{\hbar}{i} \frac{d}{d\phi} \langle \mathbf{x} | \alpha \rangle$ you can do this one in the usual way converting from x,y,z to r,θ,φ

$$\langle x', y', z' | \hat{L}_x | \alpha \rangle = \langle x', y'+z'\delta\phi, z'-y'\delta\phi | \alpha \rangle = \frac{\hbar}{i} \left(-\sin\phi \frac{d}{d\theta} - \cot\theta \cos\phi \frac{d}{d\phi} \right) \langle \mathbf{x} | \alpha \rangle$$

$$\langle x', y', z' | \hat{L}_y | \alpha \rangle = \langle x'-z'\delta\phi, y', z'+x'\delta\phi | \alpha \rangle = \frac{\hbar}{i} \left(-\cos\phi \frac{d}{d\theta} - \cot\theta \sin\phi \frac{d}{d\phi} \right) \langle \mathbf{x} | \alpha \rangle$$

Then we can figure out the raising and lowering operators

$$\hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y = \frac{\hbar}{i} e^{\pm i\phi} \left(\pm i \frac{d}{d\theta} - \cot\theta \frac{d}{d\phi} \right) \langle \mathbf{x} | \alpha \rangle \quad \text{and}$$

$$L^2 = L_z^2 + \frac{1}{2} (L_+ L_- + L_- L_+)$$

$$\langle \mathbf{x} | \hat{L}^2 | \alpha \rangle = -\hbar^2 \left[\frac{1}{\sin^2\theta} \frac{d^2}{d\phi^2} + \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) \right] \langle \mathbf{x} | \alpha \rangle$$

Note that this is the angular part of laplacian in spherical coordinates apart from $\frac{1}{r^2}$. You can derive the Laplacian in spherical coordinates: $\nabla^2 = \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) = \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{1}{\sin^2\theta} \frac{d^2}{d\phi^2} + \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta} \right) \right]$

We can connect this to $\frac{\hat{p}^2}{2m}$ in 3-D. I will derive it here but you will get

$$\langle \mathbf{x} | \frac{\hat{p}^2}{2m} | \alpha \rangle = \frac{1}{2m} \langle \mathbf{x} | \hat{p}^2 | \alpha \rangle = - \left(\frac{\hbar^2}{2m} \right) \nabla^2 \langle \mathbf{x} | \alpha \rangle = - \left(\frac{\hbar^2}{2m} \right) \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \langle \mathbf{x} | \alpha \rangle \right] - \frac{1}{\hbar^2} \langle \mathbf{x} | \hat{L}^2 | \alpha \rangle = - \left(\frac{\hbar^2}{2m} \right) \frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \langle \mathbf{x} | \alpha \rangle \right] + \frac{1}{2mr^2} \langle \mathbf{x} | \hat{L}^2 | \alpha \rangle$$

This will use this to put the angular momentum into the 3-D Schrodinger eqn. It is reminiscent of orbital problems.

$$\text{[note: the classical eqn is } E = \frac{1}{2} m \dot{r}^2 + \frac{L^2}{2mr^2} + V(r)\text{]}$$

Now what follows is important. Ultimately what we want to do is to solve the Schrodinger eqn in 3-D

$$\hat{H} | \alpha \rangle = \left[\frac{\hat{p}^2}{2m} + V(\hat{\mathbf{x}}) \right] | \alpha \rangle = E | \alpha \rangle \quad \text{where } \hat{\mathbf{p}} \text{ and } \hat{\mathbf{x}} \text{ are both vector operators (i.e. they have 3 components - an x,y and z)}$$

Now going into position representation we get

$$- \frac{\hbar^2}{2m} \nabla^2 \langle \mathbf{x} | \alpha \rangle + V(\hat{\mathbf{x}}) \langle \mathbf{x} | \alpha \rangle = E \langle \mathbf{x} | \alpha \rangle \quad \text{Now if } V(\hat{\mathbf{x}}) \text{ is spherically symmetric then } [\hat{H}, \hat{L}^2] = 0 \text{ and } [\hat{H}, \hat{L}_z] = 0.$$

Proof: What I need to do is to prove $[\hat{p}^2, \hat{L}^2] = 0$ $[\hat{p}^2, \hat{L}_z] = 0$ $[V(\mathbf{r}), \hat{L}^2] = 0$ $[V(\mathbf{r}), \hat{L}_z] = 0$

Now since $[\hat{A}, \hat{L}^2] = [\hat{A}, \sum \hat{L}_i^2] = \sum [\hat{A}, \hat{L}_i^2] = \sum \hat{L}_i [\hat{A}, \hat{L}_i] + [\hat{A}, \hat{L}_i] \hat{L}_i$

So all I need to prove is that $[\hat{p}^2, \hat{L}_i] = 0$ and $[V(\mathbf{r}), \hat{L}_i] = 0$

Now if $V(r)$ is spherically symmetric then $\frac{d}{d\phi} V(r) = 0$ and $\frac{d}{d\theta} V(r) = 0$ and $\hat{V}(r)$ in position representation is just $V(r)$

$$\langle x | [\mathbf{V}(r), \hat{L}_z] | \alpha \rangle = \langle x | \mathbf{V}(r) \hat{L}_z | \alpha \rangle - \langle x | \hat{L}_z \mathbf{V}(r) | \alpha \rangle = \frac{\hbar}{i} \left[V(r) \frac{d}{d\phi} \langle x | \alpha \rangle - \frac{d}{d\phi} (V(r) \langle x | \alpha \rangle) \right] = \frac{\hbar}{i} \left[V(r) \frac{d}{d\phi} \langle x | \alpha \rangle - V(r) \frac{d}{d\phi} \langle x | \alpha \rangle - \left(\frac{dV(r)}{d\phi} \right) \langle x | \alpha \rangle \right] = 0 \rightarrow [\mathbf{V}(r), \hat{L}_z] = 0$$

Either you can work it out for \hat{L}_x and \hat{L}_y or as I do, argue that by symmetry $[\mathbf{V}(r), \hat{L}_x] = 0$ and $[\mathbf{V}(r), \hat{L}_y] = 0$

$$\text{Hence } [\mathbf{V}(r), \hat{L}^2] = 0 \quad [\mathbf{V}(r), \hat{L}_z] = 0$$

$$\begin{aligned} [\hat{p}^2, \hat{L}_z] &= [\hat{p}^2, \hat{x} \hat{p}_y - \hat{y} \hat{p}_x] = [\hat{p}^2, \hat{x} \hat{p}_y] - [\hat{p}^2, \hat{y} \hat{p}_x] = \hat{x} [\hat{p}^2, \hat{p}_y] + [\hat{p}^2, \hat{x}] \hat{p}_y - \hat{y} [\hat{p}^2, \hat{p}_x] - [\hat{p}^2, \hat{y}] \hat{p}_x = \\ &= [\hat{p}^2, \hat{x}] \hat{p}_y - [\hat{p}^2, \hat{y}] \hat{p}_x = [\hat{p}_x^2, \hat{x}] \hat{p}_y - [\hat{p}_y^2, \hat{y}] \hat{p}_x = \hat{p}_x [\hat{p}_x, \hat{x}] \hat{p}_y + [\hat{p}_x, \hat{x}] \hat{p}_x \hat{p}_y - \hat{p}_y [\hat{p}_y, \hat{y}] \hat{p}_x - [\hat{p}_y, \hat{y}] \hat{p}_y \hat{p}_x = \\ &= -i\hbar \hat{p}_x \hat{p}_y - i\hbar \hat{p}_x \hat{p}_y + i\hbar \hat{p}_y \hat{p}_x + i\hbar \hat{p}_y \hat{p}_x = -2i\hbar \hat{p}_x \hat{p}_y + 2i\hbar \hat{p}_y \hat{p}_x = -2i\hbar \hat{p}_x \hat{p}_y + 2i\hbar \hat{p}_x \hat{p}_y = 0 \end{aligned}$$

$$\text{now if } [\hat{p}^2, \hat{L}_z] = 0 \rightarrow [\hat{p}^2, \hat{L}_z^2] = 0 \rightarrow [\hat{p}^2, \hat{L}_i^2] = 0 \rightarrow [\hat{p}^2, \hat{L}^2] = 0$$

$$\text{hence } [\hat{H}, \hat{L}^2] = 0 \text{ and } [\hat{H}, \hat{L}_z] = 0. \text{ QED}$$

We have proved before that for any angular momentum $[\hat{L}^2, \hat{L}_z] = 0$. This means that H , \hat{L}^2 and \hat{L}_z share eigenstates, and in fact some of the eigenstates of H are degenerate and we will need the L 's to break the degeneracy. So it becomes very important for 3-D problems to find the eigenstates of \hat{L}^2 and \hat{L}_z .

Aside - why is there a degeneracy? We know that H and the rotation operator commute, i.e. $[H, (1 - i \frac{\delta\phi}{\hbar} \hat{L}_z)] = 0$. This means that $H(1 - i \frac{\delta\phi}{\hbar} \hat{L}_z) |n\rangle = (1 - i \frac{\delta\phi}{\hbar} \hat{L}_z) H |n\rangle = E_n (1 - i \frac{\delta\phi}{\hbar} \hat{L}_z) |n\rangle$ so the states $|n\rangle$ and the rotated state $(1 - i \frac{\delta\phi}{\hbar} \hat{L}_z) |n\rangle$ have the same energy eigenvalue E_n , i.e. there is a degeneracy.

We will call these eigenstates $|n, l, m\rangle$. n is the radial quantum number - or if you wish the quantum number corresponding to energies. l and m will be the quantum numbers for L corresponding to j and m we had before.

Now we are going to just solve $-\frac{\hbar^2}{2m} \nabla^2 \langle x | nlm \rangle + V(\hat{r}) \langle x | nlm \rangle = E \langle x | nlm \rangle$. We will use the usual method of separation of variables where we will use the variables r, θ, ϕ instead of x, y, z . Its easier.

$\langle x | nlm \rangle = \langle r, \theta, \phi | nlm \rangle = R_{nl}(r) Y_l^m(\theta, \phi)$ [Typically we use $\langle r, \theta, \phi | nlm \rangle = R(r) \Theta(\theta) \Phi(\phi)$, but then I would just replace these symbols with the R and Y and that gets confusing. You can think of $R_{nl}(r) = R(r)$ and $Y_l^m(\theta, \phi) = \Theta(\theta) \Phi(\phi)$]

The R 's are the radial solutions and will depend on $V(r)$, the Y 's are the spherical harmonics. [Note $Y_l^m(\theta, \phi) = \frac{1}{\sqrt{2\pi}} e^{-im\phi} P_l^m(\theta)$ where the P 's are the associated Legendre polynomials, but I wont refer to these. Too many names to remember]

Now lets define a particular position ket. $|\vec{n}\rangle$ is a position eigenket of unit length in the \vec{n} direction (it has nothing to do with energy or the n in $|nlm\rangle$) Think of it as $|\vec{n}\rangle = |\theta, \phi\rangle$

We are going to isolate the angular part of our ket and think about $|l, m\rangle$ where $\langle \vec{n} | l, m \rangle = Y_l^m(\theta, \phi) = Y_l^m(\vec{n})$

These things should be eigenkets of \hat{L}^2 and \hat{L}_z so

$$\hat{L}_z |l, m\rangle = m\hbar |l, m\rangle \quad (\text{just like we did for } J) \text{ so } \frac{\hbar}{i} \frac{d}{d\phi} \langle \vec{n} | l, m \rangle = m\hbar \langle \vec{n} | l, m \rangle \text{ and this eqn is easy to solve and we get for the } \phi \text{ dependence } \langle \vec{n} | l, m \rangle \sim e^{im\phi}.$$

Now $\langle \vec{n} | l, m \rangle$ is also an eigenket of \hat{L}^2 (again the eigenvalue is $l(l+1)\hbar^2$)

$$\hat{L}^2 \langle \vec{n} | l, m \rangle = -\hbar^2 \left[\frac{1}{\sin^2\theta} \frac{d^2}{d\phi^2} + \frac{1}{\sin\theta} \left(\sin\theta \frac{d}{d\theta} \right) \right] \langle \vec{n} | l, m \rangle = l(l+1)\hbar^2 \langle \vec{n} | l, m \rangle$$

Now these are eigenkets of a observable so they are orthogonal $\langle l' m' | l m \rangle = \delta_{l' l} \delta_{m' m}$ giving us

$$\int_0^{2\pi} d\phi \int_{-1}^1 d\cos\theta Y_l^{m'}(\theta, \phi) Y_l^m(\theta, \phi) = \delta_{l' l} \delta_{m' m}$$

Now we already know the largest m one can have which is m=l (that is m="el" not one) so

$$\hat{L}_+ |l, l\rangle = 0 \quad \text{so} \quad \frac{\hbar}{i} e^{\pm i\phi} \left(\pm i \frac{d}{d\theta} - \cot\theta \frac{d}{d\phi} \right) \langle \vec{n} | l \rangle = 0 \quad \text{but we know } \langle \vec{n} | l \rangle \sim e^{il\phi}$$

$$\frac{\hbar}{i} e^{i\phi} \left(i \frac{d}{d\theta} - l \cot\theta \right) \langle \vec{n} | l \rangle = 0 \quad \rightarrow \quad \frac{d}{d\theta} \langle \vec{n} | l \rangle = l \cot\theta \langle \vec{n} | l \rangle \quad \text{and we can guess } \langle \vec{n} | l \rangle \sim \sin^l \theta$$

lets check it $\frac{d}{d\theta} \sin^l \theta = l \sin^{l-1} \theta \cos\theta = l \frac{\cos\theta}{\sin\theta} \sin^l \theta = l \cot\theta \sin^l \theta$ i.e. it works

so $\langle \vec{n} | l \rangle = c_l e^{il\phi} \sin^l \theta$ We can figure out the normalization from the eqn above and we get

$$c_l = \left[\frac{(-1)^l}{2^l l!} \right] \sqrt{\frac{(2l+1)(2l)!}{4\pi}} \quad \text{and then as we did in the case of the SHO we can use } L_- \text{ and just get the rest of them.}$$

so $\langle \vec{n} | l, m = l-1 \rangle = \langle \vec{n} | L_- |l, m = l\rangle = e^{-i\phi} \left(-i \frac{d}{d\theta} - \cot\theta \frac{d}{d\phi} \right) e^{il\phi} \sin^l \theta$ and then you have to normalize. We will end up with (for m≥0)

$$Y_l^m(\theta, \phi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)(l+m)!}{4\pi(l-m)!}} e^{im\phi} \frac{1}{\sin^m \theta} \frac{d^{l-m}}{d(\cos\theta)^{l-m}} (\sin\theta)^{2l}$$

for m<0 then $Y_l^{-m}(\theta, \phi) = (-1)^m [Y_l^m(\theta, \phi)]^*$

Now you can see pictures of these later in these notes. What you see in the the pictures is that the spherical harmonics already show the pattern for the hydrogen atoms. This is true because the potential which is spherically symmetric will not change the angular shape. The l quantum numbers 0,1,2,... correspond to s,p,d,...

Now since L is a type of J, it must come in either integer or $\frac{1}{2}$ integer. But as I will show, if it is $\frac{1}{2}$ integer, we get solutions that don't make sense.

Lets take $l = m = \frac{1}{2}$ as the simplest case. Then we have $\langle \vec{n} | \frac{1}{2} \frac{1}{2} \rangle = c_{\frac{1}{2}} e^{i\frac{\phi}{2}} \sin^{\frac{1}{2}} \theta$ If we apply L_- to this we get

$$e^{-i\phi} \left(-i \frac{d}{d\theta} - \cot\theta \frac{d}{d\phi} \right) c_{\frac{1}{2}} e^{i\frac{\phi}{2}} \sin^{\frac{1}{2}} \theta = -c_{\frac{1}{2}} e^{-i\frac{\phi}{2}} \cot\theta \sin^{\frac{1}{2}} \theta = -c_{\frac{1}{2}} e^{-i\frac{\phi}{2}} \frac{\cos\theta}{\sqrt{\sin\theta}}$$

This is infinite at $\theta=0$ or π . It means that some probabilities would be infinite which we believe is not true. So we reject these solutions. **Orbital angular momentum has only integer values.**

