

The hydrogen atom

Angular momentum: Eigenfunctions

We will see that $f_\ell^m = Y_\ell^m$, i.e. the eigenfunctions of L^2 and L_z are the spherical harmonics.

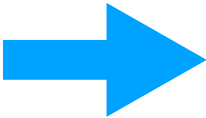
Let's rewrite L_x , L_y , and L_z in spherical coordinates: $\mathbf{L} = -i\hbar(\mathbf{r} \times \nabla)$,

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi};$$

Since: $\mathbf{r} = r\hat{r}$,

$$\mathbf{L} = -i\hbar \left[r(\hat{r} \times \hat{r}) \frac{\partial}{\partial r} + (\hat{r} \times \hat{\theta}) \frac{\partial}{\partial \theta} + (\hat{r} \times \hat{\phi}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right].$$

Here: $(\hat{r} \times \hat{r}) = 0$, $(\hat{r} \times \hat{\theta}) = \hat{\phi}$, and $(\hat{r} \times \hat{\phi}) = -\hat{\theta}$


$$\mathbf{L} = -i\hbar \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right)$$


The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their cartesian components:

$$\hat{\theta} = (\cos \theta \cos \phi) \hat{i} + (\cos \theta \sin \phi) \hat{j} - (\sin \theta) \hat{k};$$

$$\hat{\phi} = -(\sin \phi) \hat{i} + (\cos \phi) \hat{j}.$$

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$$\mathbf{L} = -i\hbar \left[(-\sin\phi \hat{i} + \cos\phi \hat{j}) \frac{\partial}{\partial\theta} - (\cos\theta \cos\phi \hat{i} + \cos\theta \sin\phi \hat{j} - \sin\theta \hat{k}) \frac{1}{\sin\theta} \frac{\partial}{\partial\phi} \right]$$

In components: $L_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cos\phi \cot\theta \frac{\partial}{\partial\phi} \right),$

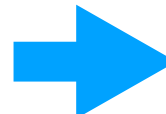
$$L_y = -i\hbar \left(+\cos\phi \frac{\partial}{\partial\theta} - \sin\phi \cot\theta \frac{\partial}{\partial\phi} \right),$$

$$L_z = -i\hbar \frac{\partial}{\partial\phi}.$$

We also need the raising and lowering operators:

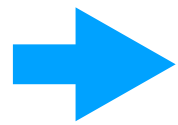
$$L_{\pm} = L_x \pm iL_y = -i\hbar \left[(-\sin\phi \pm i\cos\phi) \frac{\partial}{\partial\theta} - (\cos\phi \pm i\sin\phi) \cot\theta \frac{\partial}{\partial\phi} \right]$$

And: $\cos\phi \pm i\sin\phi = e^{\pm i\phi},$


$$L_{\pm} = \pm\hbar e^{\pm i\phi} \left(\frac{\partial}{\partial\theta} \pm i \cot\theta \frac{\partial}{\partial\phi} \right)$$

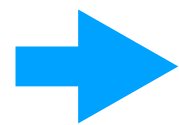
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$$L_{\pm} = \pm \hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right)$$

In particular:

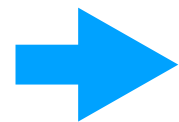
$$L_+ L_- = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} + i \frac{\partial}{\partial \phi} \right),$$



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

We are now in a position to determine $f_{\ell}^m(\theta, \phi)$.

It's an eigenfunction of L^2 , with eigenvalue $\hbar^2 \ell(\ell + 1)$.



$$L^2 f_{\ell}^m = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] f_{\ell}^m = \hbar^2 \ell(\ell + 1) f_{\ell}^m.$$

But this is precisely the “angular equation”:

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -\ell(\ell + 1) \sin^2 \theta Y.$$

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And it's also an eigenfunction of L_z , with the eigenvalue $m\hbar$:

$$L_z f_\ell^m = -i\hbar \frac{\partial}{\partial \phi} f_\ell^m = \hbar m f_\ell^m,$$

which is equivalent to the azimuthal equation: $\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2$.

We have already solved this system of equations!

The result (appropriately normalised) is the spherical harmonic, $Y_\ell^m(\theta, \phi)$.

Conclusion:

Spherical harmonics *are* the eigenfunctions of L^2 and L_z . When we solved the Schrödinger equation by separation of variables, we were inadvertently constructing simultaneous eigenfunctions of the three commuting operators H , L^2 , and L_z :

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 \ell(\ell+1)\psi, \quad L_z\psi = \hbar m\psi.$$

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We can rewrite Schrödinger's equation as follows:

$$\frac{1}{2mr^2} \left[-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + L^2 \right] \psi + V \psi = E \psi.$$

The *algebraic* theory of angular momentum permits ℓ (and hence also m) to take on *half* -integer values:

$$\ell = 0, 1/2, 1, 3/2, \dots; \quad m = -\ell, -\ell + 1, \dots, \ell - 1, \ell.$$

Separation of variables yielded eigenfunctions only for *integer* values.

$$\ell = 0, 1, 2, \dots; \quad m = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell.$$

Are the half-integer solutions spurious?

No, they are of profound importance, as we shall see in the following sections.