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: $\mathbf{L} = -i\hbar(\mathbf{r} \times \boldsymbol{\nabla})$,

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

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

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

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

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

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

$$\hat{\theta} = (\cos\theta\cos\phi)\,\hat{\imath} + (\cos\theta\sin\phi)\,\hat{\jmath} - (\sin\theta)\,\hat{k};$$

$$\hat{\phi} = -(\sin\phi)\,\hat{\imath} + (\cos\phi)\,\hat{\jmath}.$$

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

In components:

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

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

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

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:

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

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

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 $m\boxed{?}$:

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

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:

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

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

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

Are the half-integer solutions spurious?

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