Orbital Angular Momentum of the Hydrogen Atom
Last week, we started with the 3D time-independent Schrödinger equation and moved into **spherical coordinates** (because the Coulomb potential is spherically symmetric).

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{x}) + V(\vec{x}) \Psi(\vec{x}) = E \Psi(\vec{x})
\]

\[
-\frac{\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right] - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \Psi = E \Psi
\]
With some algebraic manipulation, we were able to separate the equation so that we had to solve **two separate** equations:

\[
\left[ \frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{2\mu r^2}{\hbar^2} (V - E) \right] = \ell (\ell + 1)
\]

**radial components only**

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

**angular components only**
The angular differential equation has no dependence on the potential. The solution (known since 1782) is known as the spherical harmonics.

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

Let’s try our last trick of separation of variable again:

\[ Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \]

Plug that in and divide by \( \Theta \Phi \):

\[
\left\{ \frac{1}{\Theta} \left[ \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) \right] + \ell(\ell + 1) \sin^2 \theta \right\} + \left\{ \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} \right\} = 0
\]

polar components only  azimuthal components only
As before, we get \( \ {...} + \ {...} = 0 \), so we assign each to a constant, in this case \( \pm m^2 \)

\[
\left\{ \frac{1}{\Theta} \left[ \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta}{\partial \theta} \right) \right] + \ell (\ell + 1) \sin^2 \theta \right\} = m^2
\]

\[
\left\{ \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} \right\} = -m^2
\]

Let’s solve the second equation. It’s pretty simple:

\[
\Phi(\phi) = e^{im\phi}
\]

Notice that the azimuthal wavefunction is complex. Also notice that there is a constant of integration, \( m \).
Let’s try to restrict the constant of integration by the boundary condition: \( \Phi(\phi + 2\pi) = \Phi(\phi) \)

This means that:

\[
e^{im(\phi + 2\pi)} = e^{im\phi} e^{im2\pi} = e^{im\phi}
\]

And subsequently,

\[
e^{im2\pi} = \cos(m2\pi) + i \sin(m2\pi) = 1
\]

Therefore \( m = 0, \pm 1, \pm 2, \pm 3, \) etc.

As a result of the boundary condition, we have a quantized constant of integration \( m \). This particular constant is the magnetic quantum number.
the spherical harmonics $Y_{\ell}^m(\theta, \phi)$ have the following solutions:

\begin{align*}
Y_0^0(\theta, \varphi) &= \frac{1}{2} \sqrt{\frac{1}{\pi}} \\
Y_{-1}^0(\theta, \varphi) &= \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{-i\varphi} \\
Y_0^1(\theta, \varphi) &= \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta \\
Y_{-1}^1(\theta, \varphi) &= \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{i\varphi} \\
Y_{-2}^0(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{-2i\varphi} \\
Y_{-1}^2(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{-i\varphi} \\
Y_0^2(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{5}{2\pi}} (3\cos^2 \theta - 1) \\
Y_{-1}^3(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{i\varphi} \\
Y_1^2(\theta, \varphi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{2i\varphi}
\end{align*}

where $m$ and $\ell \geq 0$ are integers, and $m$ has the possible values: $-\ell$, $-\ell+1$, ..., -1, 0, 1, ..., $\ell-1$, $\ell$. $\ell$ is the orbital angular momentum quantum number.
The full solution to the Hydrogen atom is:

$$\Psi_{n\ell m}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n - \ell - 1)!}{2n(n + \ell)!}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{\ell} L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{na_0}\right) Y_{\ell}^m(\theta, \phi)$$

here $n$ is the principal quantum number, $a_0$ is the Bohr radius, and $L$ is the associated Laguerre polynomial...

\[
\begin{align*}
L_0^0(x) &= 1 \\
L_1^0(x) &= -x + 1 \\
L_2^0(x) &= x^2 - 4x + 2 \\
L_0^1(x) &= 1 \\
L_1^1(x) &= -2x + 4 \\
L_2^1(x) &= 3x^2 - 18x + 18 \\
L_0^2(x) &= 2 \\
L_1^2(x) &= -6x + 18
\end{align*}
\]
Recap: the general solution to the hydrogen atom is given by:

$$\Psi_{n\ell m}(r, \theta, \phi) = R(r)Y_{\ell}^{m}(\theta, \phi)$$

where three quantum numbers (discrete constants of integration) are required for the solution.

- $n$ (principal quantum number) $= 1, 2, 3$
- $\ell$ (orbital angular momentum quantum number) $= 0, 1, 2, \ldots, n-1$
- $m$ (magnetic quantum number) $= -\ell, -\ell+1, \ldots, \ell-1, \ell$
The energy of a state depends only on \( n \).

\[
E_n = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2n^2}
\]

Same as the Bohr model!

But for each \( n \), there are \( n \) values of \( \ell \).

And for each \( \ell \), there are \( (2\ell+1) \) values of \( m \).
For each $n$, there are $n^2$ states all with the same energy. So if the energy is the same, what’s different about the states?
The quantum number $\ell$ expresses the quantization of the **magnitude** of the orbital angular momentum:

$$L = \hbar \sqrt{\ell (\ell + 1)}$$

The magnetic quantum number $m$ expresses the quantization of the **direction** of orbital angular momentum:

$$L_z = m \hbar$$

Since $L_z = L \cos \theta$, then

$$\cos \theta = \frac{L_z}{L} = \frac{m \hbar}{\sqrt{\ell (\ell + 1) \hbar}} = \frac{m}{\sqrt{\ell (\ell + 1)}}$$

so there are $2\ell + 1$ possible angles of $L$ with respect to the $z$ axis.
Spectroscopic notation:

\[ \ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad ... \]

\[ s \quad p \quad d \quad f \quad g \quad h \quad ... \]

s = sharp
p = principal
d = diffuse
f = fundamental
g = ?

Sober Physicists Don't Find Giraffes Hiding In Kitchens Like Mine...
PRS Question: For the Hydrogen atom in the $n=4, \ell=3$ state, how many possible values are there for the $z$-component of the angular momentum?

A) 4  
B) 5  
C) 6  
D) 7  
E) 8
If $\ell=3$, then $m=-3, -2, -1, 0, 1, 2, 3$.

So the answer is 7.
Since the electron is orbiting the proton, it’s movement constitutes a current. Let’s pretend it’s moving in a circle.

The period of one orbit is \( t = \frac{2\pi r}{v} \)

So the current is \( I = \frac{q}{t} = \frac{-e}{2\pi r / v} = -\frac{ev}{2\pi r} \)

And any current has a **magnetic moment**:

\[
\mu = I \cdot A = -\frac{ev}{2\pi r} \cdot \pi r^2 = -\frac{evr}{2}
\]

Therefore

\[
\frac{\mu}{L} = \frac{-evr/2}{m_e vr} = -\frac{e}{2m_e} \quad \rightarrow \quad \vec{\mu} = -\frac{e}{2m_e} \vec{L}
\]
For convenience, let’s introduce a constant $g$ called the “gyromagnetic-factor” or “g-factor”, where $g=1$.

Then we have:

$$\vec{\mu} = -g \frac{e}{2m_e} \vec{L}$$

When a magnetic moment is placed in an external magnetic field \textbf{in the z direction}, the potential energy of the interaction is:

$$\Delta E = -\vec{\mu} \cdot \vec{B} = - \left(-g \frac{e}{2m_e}\right) \vec{L} \cdot \vec{B} = g \frac{eB}{2m_e} L_z$$

Substituting for $L_z$, we get

$$\Delta E = g \frac{eB}{2m_e} (m\hbar) = mg\mu_B B \quad \text{where} \quad \mu_B \equiv \frac{e\hbar}{2m_e} \approx 5.8 \times 10^{-5} \frac{\text{eV}}{\text{T}}$$
By applying an external magnetic field to the Hydrogen atom, the levels are split according to their \textbf{magnetic quantum number $m$}. This is the “Normal” Zeeman effect.

$$\Delta E = mg\mu_B B$$ where $m = 0, \pm 1, \pm 2, \ldots$

\begin{align*}
-13.6/9 \text{ eV} & \quad 3s \quad 0 & 3p & \quad 3d \\
-13.6/4 \text{ eV} & \quad 2s \quad 0 & 2p \quad 0 \\
-13.6 \text{ eV} & \quad 1s \quad 0
\end{align*}
Selection rules for radiative transitions:

“Allowed” if $\Delta \ell = \pm 1$ and $\Delta m = 0, \pm 1$ ($\Delta n$ can be anything)

“Forbidden” transition can occur, but much less frequently

Notice that the selection rule strongly suggests that the photon has spin 1.
Consider a Balmer transition in a magnetic field. There are many more transitions allowed, but because of the selection rules, only three are possible:

\[ E_\gamma = E_{\text{Bohr}} + g\mu_B B \]
\[ E_\gamma = E_{\text{Bohr}} \]
\[ E_\gamma = E_{\text{Bohr}} - g\mu_B B \]

Balmer lines are now split into three:
In an external B-field, every Bohr-model photon line should split into exactly 3 equally-spaced lines. This is the “normal” Zeeman effect.

- The size of the spacing is $\Delta E = g\mu_B \cdot B$.
- Experimentally, the Zeeman effect does occur, but for many elements (such as in Hydrogen) it is not “normal” in that the spacing is not $g\mu_B \cdot B$. This is known as the “anomalous” Zeeman effect.
- Photon lines can often be split into more than three in an external B-field.
- Even when $B=0$, there can still be observed a splitting.