Quantum Mechanics and Atomic Physics

Lecture 18:
Angular Momentum Raising and Lowering

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Hydrogen Atom Summary

- \( \Psi \) is a product of:
  - \( \Phi \) which is oscillatory
  - \( \Theta \) which is a polynomial in \( \cos \theta \)
  - \( R \) which is a product of a decaying exponential and a polynomial in \( r \)

- \( \Psi \) depends on 3 quantum numbers:
  - **Principal quantum number** \( n = 1, 2, 3, \ldots \)
  - **Orbital angular momentum quantum number** \( \ell = 0, 1, 2, \ldots \) (\( n-1 \))
    - Today we will concentrate on this
  - **Magnetic quantum number** \( m_\ell = 0, \pm 1, \ldots, \pm \ell \) or \( m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell \)
    - Next time we will focus on this

Coulomb Potential:

\[
V(r) = \frac{1}{4\pi \varepsilon_0} \frac{Q_1 Q_2}{r} = -\frac{e^2}{4\pi \varepsilon_0 r}
\]
Last time: Plotting $|\Psi|$ 

- $\Psi_{nlm}$ also have an angular dependence

- Plot $|\Psi|$ in a plane cutting through the nucleus
  - Usually taken to be $\phi=0$ plane or the xz-plane
  - Remember $|\Psi|$ is rotationally symmetric about the z-axis.

- Since we are representing something that is in 3D onto a 2D surface, think of the figures rotating about the z-axis
Wave-functions

No radial nodes
But one angular node

Two radial nodes
(including a central one)
And three angular nodes.

Radial node
(but non-central)

Reed Chapter 7
Probability Densities

Reed Chapter 7

More figures

Figure 7-10: An artist's conception of the three-dimensional appearance of several one-electron atom probability density functions. For each of the drawings a line represents the z axis. If all the probability densities for a given n and l are combined, the result is spherically symmetrical.
A few words on The Effective Potential

- Recall the radial equation with the Coulomb Potential:

\[
\frac{d^2}{dr^2}U(r) + \frac{2\mu}{\hbar^2} \left[ E + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right] U(r) = 0
\]

\[
- \frac{d^2}{dr^2}U(r) + \frac{\ell(\ell+1)}{r^2} U(r) - \frac{2\mu}{\hbar^2} \frac{e^2}{4\pi\varepsilon_0 r} U(r) = \frac{2\mu}{\hbar^2} E U(r)
\]

\[
V_{\text{eff}} = -\frac{2\mu}{\hbar^2} \frac{e^2}{4\pi\varepsilon_0 r} + \frac{\ell(\ell+1)}{r^2}
\]

\[
\Rightarrow -\frac{d^2}{dr^2}U(r) + V_{\text{eff}} U(r) = \frac{2\mu}{\hbar^2} E U(r)
\]

- This looks like the 1D S.E.!
$V_{\text{eff}}$

- $V_{\text{eff}}$ vs. $\rho$, where $\rho = r/a_0$
- Striking difference between $\ell=0$ and $\ell \neq 0$
  - When $\ell \neq 0$ the combination of the two terms in the effective potential leads to potential wells with infinite walls as $r \rightarrow 0$ (see radial nodes in Fig. 7.10 in text book)
- $V_{\text{eff}}=0$ as $r \rightarrow \infty$
- Bohr energy levels get closer together as $n \rightarrow \infty$

Reed Chapter 7
Centrifugal term

- The $\ell(\ell+1)/r^2$ term is known as the “centrifugal” term.
- Contributes a repulsive potential - drives the electron away from the nucleus.
- Stronger repulsion as $\ell$ increases and we expect to find the electron further from the nucleus.
Review of Orbital Angular Momentum

- Recall that the orbital angular momentum in spherical coordinates is:

\[
\begin{align*}
\hat{L} &= \hat{r} \times \hat{p} \\
\hat{p} &= -i \hbar \hat{\nabla} \\
L_x &= i \hbar (\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi}) \\
L_y &= i \hbar (-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi}) \\
L_z &= -i \hbar \frac{\partial}{\partial \phi}
\end{align*}
\]
Is the H atom an eigenstate of $L_x$, $L_y$, $L_z$?

- You should already be able to tell me the answer to this question!
- Let’s start with $L_z$:

Eigenstate means $Q_{xy} \psi = (\text{const}) \psi$

$$L_z \psi_{m_l} = -i \hbar \frac{\partial}{\partial \phi} \psi_{m_l} = -i \hbar \Theta \psi_{m_l}$$

$$\psi = e^{im_\phi} \quad \frac{d \psi}{d \phi} = i m_\phi e^{im_\phi} = i m_\phi \psi$$

$$\Rightarrow L_z \psi = -i \hbar \Theta \psi (im_\phi) = m_\phi \hbar \psi$$

- Yes, it is an eigenstate of $L_z$ with eigenvalue $m_\phi \hbar$!
Now let’s try $L_x$ and $L_y$

$$L_x \psi = i\hbar ( R \Phi \sin \phi \frac{d \Phi}{d \phi} + R \Theta \cot \Theta \cos \phi \frac{d \Theta}{d \phi} )$$

$\neq (\text{const}) \psi$

Similarly

$$L_y \psi \neq (\text{const}) \psi$$

- **So, no, the H atom is not an eigenstate of either $L_x$ or $L_y$.**
- **But we can always evaluate the expectation values…**
What about the expectation values of $L_x$ and $L_y$?

For example, as an exercise you can show that this is true for the (2,1,1) state. See problem 7-21 in your book.
What does this mean?

- So, the vector $\mathbf{L}$ is continuously precessing about the $z$-axis.

- The plane of electron’s orbit is perpendicular to $\mathbf{L}$ and precesses with it.

- There is a fixed value of $L_z$ but $L_x$ and $L_y$ are not fixed and average to zero.
More things to note...

- **Uncertainty principle:**
  - If $L_x$, $L_y$, and $L_z$ were all fixed, the electron would be moving in a definite fixed plane.
  - But then its momentum component perpendicular to the plane would be infinitely uncertain
    - So not bound in the H atom

- Also, H atom Coulomb potential is spherically symmetric but if atom is placed in an external magnetic field $\mathbf{B}$, symmetry is destroyed and the direction of $\mathbf{B}$ is chosen to be the z-axis.
  - We will see this next week!
Is H atom an eigenstate of $L^2$?

- Again you should know the answer to this!

\[ L^2 = L_x^2 + L_y^2 + L_z^2 = \hat{l}_x^2 \hat{l}_x + \hat{l}_y^2 \hat{l}_y + \hat{l}_z^2 \hat{l}_z \]

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

\[ L^2 \psi = -\hbar^2 \left[ \frac{R \Phi}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) + \frac{R \Phi}{\sin^2 \theta} \frac{d^2}{d\phi^2} \right] \]

But $\Phi = e^{i m \phi}$ $\Rightarrow$ $\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi$

\[ L^2 \psi = -\hbar^2 R \Phi \left[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} \right] \]
Recall when we did the separation of variables in an earlier lecture (chapter 6):

\[
\frac{1}{\sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d \Theta}{d \theta} \right) + \left[ l(l+1) - \frac{m_e^2}{\sin^2 \theta} \right] \Theta = \lambda \nabla
\]

\[
\Rightarrow L^2 \Phi = -\hbar^2 \frac{\partial^2 \Phi}{\partial \theta^2} + l(l+1) \hbar^2 R \Theta \Phi
\]

\[
\Rightarrow L^2 \Psi = l(l+1) \hbar^2 \Psi
\]

So, yes, H atom is eigenstate of \( L^2 \) with eigenvalue \( l(l+1) \hbar^2 \).

We derived this already in chapter 6 but we did this by using S.E. directly.
Recall Angular Momentum
Commutation Relations

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 $L_y \Rightarrow$ get a certain value

Measure $L_x$ again $\Rightarrow$ in general, you won’t get the same value as before!

So, once a measurement has been made, knowledge of the other two components is irretrievably lost.
Let’s evaluate commutator $[L^2, L_x]$

\[
[L^2, L_x] = L^2 (L_x \psi) - L_x (L^2 \psi) \\
= (L_x^2 + L_y^2 + L_z^2)(L_x \psi) - L_x (L_x^2 + L_y^2 + L_z^2)\psi \\
= (L_y^2 + L_z^2) L_x \psi - L_x (L_y^2 + L_z^2)\psi \\
= (L_y^2 L_x - L_x L_y) \psi + (L_z^2 L_x - L_x L_z) \psi \\
= [L_y^2, L_x] \psi + [L_z^2, L_x] \psi \\
= [L^2, L_x] = [L_y^2, L_x] + [L_z^2, L_x]
\]
\[
\begin{align*}
[Ly^2, L_x] &= Ly [L_y, L_x] + [Ly, L_x] L_y \\
[L_y^2, L_x] &= L_y [L_y, L_x] + [L_y, L_x] L_y \\
(L_y^2, L_x) &= L_y [L_y, L_x] + [L_y, L_x] L_y \\
\end{align*}
\]

Above comes from Chapter 4:

\[
\]

\[
\begin{align*}
[L_y^2, L_x] &= Ly [-i \hbar L_y] + (-i \hbar) L_y L_y \\
&= -i \hbar L_y L_y + -i \hbar L_y L_y \\
\end{align*}
\]

\[
\begin{align*}
[L_y^2, L_x] &= L_y (i \hbar L_y) + (i \hbar L_y) L_y \\
&= i \hbar L_y L_y + i \hbar L_y L_y \\
\end{align*}
\]

- **Put it all together ....**
We can show similarly that:

\[ [L^2, L_x] = -i h L_y L_z - i h L_z L_y + i h L_y L_z \]
\[ = \emptyset \]

So, \( L^2 \) commutes with each of \( L_x, L_y \) and \( L_z \)

But none of these commute with each other!

We can measure \( L^2 \) and any one of \( L_y, L_y \) and \( L_z \) and get sharp eigenvalues and simultaneous eigenstates.
Raising and lowering angular momentum operators

Let’s introduce:

\[ L_+ = L_x + iL_y \]
\[ L_- = L_x - iL_y \]
\[ L_z = L_x \pm iL_y \]

Like raising and lowering operators of Harmonic Oscillator (H.O.) from chapter 4:

\[ A^+ = \frac{i}{\alpha \sqrt{2}} \left( -\frac{d}{dx} + \alpha^2 x \right) \]
\[ A^- = \frac{i}{\alpha \sqrt{2}} \left( -\frac{d}{dx} - \alpha^2 x \right) \]

Raised/lowered energy eigenvalue by \((\hbar \omega)\)
What do these operators raise and lower?

Let’s find out …

\[
\begin{aligned}
\{L_3, L_\pm\} &= L_3 L_\pm - L_\pm L_3 \\
&= L_3 (L_x \pm iL_y) - (L_x \pm iL_y) L_3 \\
&= L_3 L_x \pm iL_3 L_y - L_x L_3 \mp iL_y L_3 \\
&= [L_3, L_x] \pm i[L_3, L_y]
\end{aligned}
\]
\[ [L_3, L_t] = [L_3, L_x] + i \frac{[L_3, L_y]}{\hbar L_x} \]

\[ = i \hbar L_y + i(\hbar) L_x \]

\[ = i \hbar L_y + \hbar L_x \]

\[
\Rightarrow [L_3, L_t] = \pm \hbar L_t
\]

\[
\Rightarrow (L_3 L_t - L_t L_3) = \pm \hbar L_t
\]

\[
\Rightarrow L_3 L_t = L_t (L_3 \pm \hbar)
\]

Let’s operate on wavefunction ...
Operate this on wavefunction

\[ L_3(L_\pm \Psi) = L_\pm (L_3 \pm \hbar) \Psi \]

\[ \Psi = Y_{l,m} \]

\[ L_3(L_\pm Y_{l,m}) = L_\pm (L_3 \pm \hbar) Y_{l,m} \]

Recall \[ L_3 Y_{l,m} = m_e \hbar Y_{l,m} \]

\[ = L_3(L_\pm Y_{l,m}) = L_\pm (m_e \hbar Y_{l,m} \pm \hbar Y_{l,m}) \]

\[ = \hbar (m_e \pm 1)(L_\pm Y_{l,m}) \]
What does this mean?

- $L_\pm$ operates on wavefunction and yields new function $(L_\pm Y_{\ell m})$, whose z component of angular momentum is exactly $\hbar$ more/less than that possessed by $Y_{\ell m}$.

- $L_+$ and $L_-$ raise or lower the state of the z component of angular momentum of $Y_{\ell m}$ by one unit in terms of $\hbar$.

- Similar to case of H.O.
Summary/Announcements

Next time:

The Stern-Gerlach Experiment
- evidence for quantized angular momentum

Next homework due on Monday Nov 11.

Reminder: Quiz on next Mon Nov 11 on Chapters 5/6.