Quantum Mechanics and Atomic Physics

Lecture 18:

Angular Momentum Raising and Lowering

http://www.physics.rutgers.edu/ugrad/361

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Hydrogen Atom Summary

$\psi_{n\ell m_\ell}(r,\theta,\varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$

Coulomb Potential:

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{Q_1 Q_2}{r} = \frac{-e^2}{4\pi\varepsilon_0 r}$$

- Ψ is a product of
  - Φ which is $e^{im\varphi}$
  - Θ which is a polynomial in $\cos\theta$
  - R which is a product of a decaying exponential and a polynomial in r
- Ψ depends on 3 quantum numbers
  - **Principal quantum number** n=1, 2, 3, …
  - **Orbital angular momentum quantum number** ℓ = 0, 1, 2, … (n-1)
    - Today we will concentrate on this
  - **Magnetic quantum number** m_ℓ = 0, $\pm$1, …. $\pm$ ℓ or $m_\ell = -\ell, -\ell+1, \ldots \ell-1, \ell$
    - Next time we will focus on this

Review of Orbital Angular Momentum

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

$$\vec{L} = \vec{r} \times \vec{p} \qquad \vec{p} = -i\hbar\vec{\nabla}$$

$$L_x = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)$$

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

$$L_z = -i\hbar\frac{\partial}{\partial\varphi}$$

← From HW 8 or Reed Prob. 6-7

Is the Hydrogen wavefunction (ψ_{nlm}) 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 $Q_{op}\Psi = (\text{const})\Psi$

$$L_z \Psi_{n\ell m_\ell} = -i\hbar \frac{\partial}{\partial\varphi} R\Theta\Phi = -i\hbar R\Theta \frac{d}{d\varphi}\Phi$$

$$\Phi = e^{im_\ell\varphi} \qquad \frac{d}{d\varphi}\Phi = im_\ell e^{im_\ell\varphi} = im_\ell \Phi$$

$$\Rightarrow L_z\Psi = -i\hbar R\Theta\Phi(im_\ell) = m_\ell\hbar\Psi$$

- Yes, it is an eigenstate of L_z with eigenvalue $m_\ell$hbar!

Now let's try L_x and L_y

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

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

Similarly

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

- So, no, ψ_{nlm} is <u>not</u> 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?

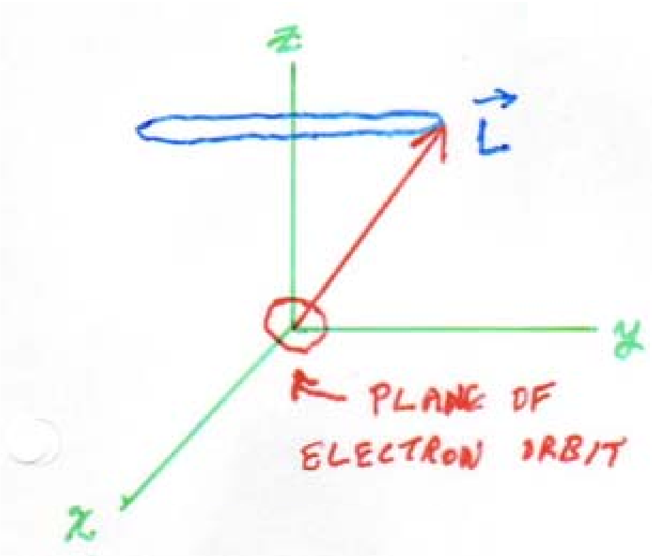
$$\langle L_x \rangle = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \psi^* L_x \psi \, r^2 \sin\theta \, d\varphi \, d\theta \, dr$$

$$\Rightarrow \quad \langle L_x \rangle = 0$$

$$\langle L_y \rangle = 0$$

- 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 **L** is continuously precessing about the z-axis.
- The plane of electron's orbit is perpendicular to **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…

- <u>Uncertainty principle:</u>
  - 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

How about the following questions?

- Does this mean hydrogen atom has a well-defined L_z but not L_x or L_y?
- Considering that Coulomb potential is spherically symmetric, how can there be a special axis called z-axis at all?
- But if Hydrogen atom is placed in an external magnetic field **B**, symmetry is destroyed and the direction of **B** is chosen to be the z-axis.
  - We will see this next week!

Is ψ_{nlm} an eigenstate of L^2?

- Again you should know the answer to this!

$$L_\varphi^2 = L_x^2 + L_y^2 + L_z^2 = L_x L_x + L_y L_y + L_z L_z$$

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

$$L_\varphi^2 \psi = -\hbar^2 \left[\frac{R\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{R\Theta}{\sin^2\theta}\frac{d^2\Phi}{d\varphi^2} \right]$$

But $\Phi = e^{im_\ell\varphi} \longrightarrow \dfrac{d^2\Phi}{d\varphi^2} = -m_\ell^2\Phi$

$$L^2\psi = -\hbar^2 R\Phi \left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m_\ell^2}{\sin^2\theta}\Theta \right]$$

- Recall when we did the separation of variables in Lecture 14 (chapter 6):

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell^2}{\sin^2\theta}\right]\Theta=0$$

$$\Rightarrow L^2\psi = -\hbar^2 R\Phi\left[-\ell(\ell+1)\Theta\right] = +\ell(\ell+1)\hbar^2 R\Theta\Phi$$

$$\Rightarrow L^2\psi = \ell(\ell+1)\hbar^2\psi$$

- So, yes, ψ_{nlm} is eigenstate of L^2 with eigenvalue $\ell(\ell+1)$ hbar^2

$$L^2 \psi_{n\ell m} = \ell(\ell+1)\hbar^2 \psi_{n\ell m} \Rightarrow L^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m}$$

Example

$$Y_{2,2}(\theta,\varphi) = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{+2i\varphi}$$

$$L^2 Y_{2,2}(\theta,\varphi) = -\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \right] \left(\sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{2i\varphi} \right)$$

$$= -\sqrt{\frac{15}{32\pi}}\hbar^2 \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,(2\sin\theta\cos\theta)\right) e^{2i\varphi} + (2i)^2 e^{2i\varphi} \right]$$

$$= -\sqrt{\frac{15}{32\pi}}\hbar^2 \left[2\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left((1-\cos^2\theta)\cos\theta \right) e^{2i\varphi} - 4 e^{2i\varphi} \right]$$

$$= -\sqrt{\frac{15}{32\pi}}\hbar^2 \left[\frac{2}{\sin\theta}\left(-\sin\theta + 3\cos^2\theta\sin\theta \right] e^{2i\varphi} - 4 e^{2i\varphi} \right]$$

$$= -\sqrt{\frac{15}{32\pi}}\hbar^2 \left[-2 + 6\cos^2\theta - 4 \right] e^{2i\varphi}$$

$$= \sqrt{\frac{15}{32\pi}} \cdot 6\hbar^2 \left[\underbrace{1 - \cos^2\theta}_{\sin^2\theta} \right] e^{2i\varphi} = \underbrace{6\hbar^2}_{\substack{= \ell(\ell+1)\hbar^2 \\ = 2\cdot(2+1)\hbar^2}} Y_{2,2}(\theta,\varphi)$$

Example

$$L_z \psi_{nlm}(r,\theta,\varphi) = m\hbar\, \psi_{nlm}(r,\theta,\varphi)$$

$$\Leftrightarrow L_z Y_{lm}(\theta,\varphi) = m\hbar\, Y_{lm}(\theta,\varphi)$$

$$L_z = -i\hbar \frac{\partial}{\partial\varphi}$$

$$L_z Y_{2,2}(\theta,\varphi) = -i\hbar \frac{\partial}{\partial\varphi}\left[\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\varphi}\right]$$

$$= -i\hbar(2i)\left[\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\varphi}\right]$$

$$= \underline{2\hbar}\, Y_{2,2}(\theta,\varphi)$$

Example

$$\psi(r,\theta,\varphi) = \frac{1}{\sqrt{2}}\left(\psi_{3,2,1} + \psi_{3,1,1}\right)$$

$$L^2\psi = \frac{1}{\sqrt{2}}\left(L^2\psi_{3,2,1} + L^2\psi_{3,1,1}\right)$$

$$= \frac{1}{\sqrt{2}}\left(2(2+1)\hbar^2\psi_{3,2,1} + 1\cdot(1+1)\hbar^2\psi_{3,1,1}\right)$$

$$= \frac{\hbar^2}{\sqrt{2}}\left(3\psi_{3,2,1} + 2\psi_{3,1,1}\right)$$

$$L_z\psi = \frac{1}{\sqrt{2}}\left(\hbar\psi_{3,2,1} + \hbar\psi_{3,1,1}\right)$$

$$= \hbar\psi$$

So ψ is not an eigenfunction of L^2 but is an eigenfunction of L_z.

Example

- What are the expectation values of H, L^2 and L_z of the following Hydrogen wavefunctions?

a) $\psi(r,\theta,\varphi) = \frac{1}{\sqrt{2}}\left[\psi_{321} + \psi_{322}\right]$

b) $\psi(r,\theta,\varphi) = \frac{1}{5}\left[3\psi_{311} + 4\psi_{420}\right]$

Recall Angular Momentum Commutation Relations

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$[L_x, L_y] \equiv i\hbar L_z$$

$$[L_y, L_z] \equiv i\hbar L_x$$

$$[L_z, L_x] \equiv i\hbar L_y$$

- 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 $[L^2, L_x]$

$$[L^2, L_x] = L^2(L_x\psi) - L_x(L^2\psi)$$
$$= (L_x^2 + L_y^2 + L_z^2)(L_x\psi) - L_x(L_x^2 + L_y^2 + L_z^2)\psi$$
$$= (L_y^2 + L_z^2)L_x\psi - L_x(L_y^2 + L_z^2)\psi$$

$$= (L_y^2 L_x - L_x L_y^2)\psi + (L_z^2 L_x - L_x L_z^2)\psi$$

$$= [L_y^2, L_x]\psi + [L_z^2, L_x]\psi$$

$$[L^2, L_x] \equiv [L_y^2, L_x] + [L_z^2, L_x]$$

$$[L_y^2, L_x] = L_y[L_y, L_x] + [L_y, L_x]L_y$$

$$[L_z^2, L_x] = L_z[L_z, L_x] + [L_z, L_x]L_z$$

From Chapter 4:

$$[AB, C] \equiv A[B, C] + [A, C]B$$

$$[L_y^2, L_x] = L_y(-i\hbar L_z) + (-i\hbar)L_z L_y$$

$$= -i\hbar L_y L_z - i\hbar L_z L_y$$

$$[L_z^2, L_x] = L_z(i\hbar L_y) + (i\hbar L_y)L_z$$

$$= i\hbar L_z L_y + i\hbar L_y L_z$$

- Put it all together ….

$$\Rightarrow [L^2, L_x] = -i\hbar L_y L_z - i\hbar L_z L_y + i\hbar L_z L_y + i\hbar L_y L_z$$
$$= \emptyset$$

- We can show similarly that:

$$\Rightarrow [L^2, L_x] = 0$$
$$[L^2, L_z] = 0$$
$$[L_z, L^2] = 0$$

$$\Rightarrow [L^2, \vec{L}] = \emptyset$$

- So, L^2 commutes with <u>each</u> of L_x, L_y and L_z
- But none of these commute with each other!
- We can measure L^2 and any <u>one</u> of L_y, L_y and L_z and get sharp eigenvalues and simultaneous eigenstates

Raising and lowering angular momentum operators

- Let's introduce:

$$L_+ \equiv L_x + i L_y$$

$$L_- \equiv L_x - i L_y$$

$$L_\pm \equiv L_x \pm i L_y$$

- Like raising and lowering operators of Harmonic Oscillator (H.O.) from chapter 5:

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

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

$$\alpha = \sqrt{\frac{m\omega}{\hbar}}$$

Raised/lowered energy eigenvalue by (hbar ω)

Functional form of $\mathbf{L}_{\pm}$

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

How ?

$$L_{+} = L_x + i L_y = i\hbar \left(\sin\varphi \frac{\partial}{\partial\theta} + \cot\theta \cos\varphi \frac{\partial}{\partial\varphi} \right)$$

$$+ i \cdot i\hbar \left(-\cos\varphi \frac{\partial}{\partial\theta} + \cot\theta \sin\varphi \frac{\partial}{\partial\varphi} \right)$$

$$= \hbar \left[(i \sin\varphi + \cos\varphi) \frac{\partial}{\partial\theta} + \cot\theta (i\cos\varphi - \sin\varphi) \frac{\partial}{\partial\varphi} \right]$$

$$= \hbar \left[e^{i\varphi} \frac{\partial}{\partial\theta} + i \cot\theta (\cos\varphi + i \sin\varphi) \frac{\partial}{\partial\varphi} \right]$$

$$= \hbar \left[e^{i\varphi} \frac{\partial}{\partial\theta} + i \cot\theta\, e^{i\varphi} \frac{\partial}{\partial\varphi} \right] = \hbar e^{i\varphi} \left[\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\theta} \right]$$

What do these operators raise and lower?

- Let's find out …

$$[L_z, L_\pm] \equiv L_z L_\pm - L_\pm L_z$$

$$= L_z(L_x \pm i L_y) - (L_x \pm i L_y) L_z$$

$$= L_z L_x \pm i L_z L_y - L_x L_z \mp i L_y L_z$$

$$[L_z, L_x] \qquad \pm i [L_z, L_y]$$

$$[L_z, L_\pm] = \underbrace{[L_z, L_x]}_{i\hbar L_y} \pm i \underbrace{[L_z, L_y]}_{-i\hbar L_x}$$

$$= i\hbar L_y \mp i(i\hbar) L_x$$

$$= i\hbar L_y \pm \hbar L_x$$

$$\Rightarrow [L_z, L_\pm] = \pm\hbar L_\pm$$

$$\Rightarrow (L_z L_\pm - L_\pm L_z) = \pm\hbar L_\pm$$

$$\Rightarrow L_z L_\pm = L_\pm (L_z \pm \hbar)$$

- Let's operate on wavefunction …

Operate this on wavefunction

$$L_z(L_\pm \psi) = L_\pm (L_z \pm \hbar)\psi$$

$$\psi = Y_{l,m_l}$$

$$L_z(L_\pm Y_{l,m_l}) = L_\pm (L_z \pm \hbar) Y_{l,m_l}$$

Recall $\quad L_z Y_{l,m_l} = m_l \hbar Y_{l,m_l}$

$$\Rightarrow L_z(L_\pm Y_{l,m_l}) = L_\pm (m_l \hbar Y_{l,m_l} \pm \hbar Y_{l,m_l})$$

$$= \hbar (m_l \pm 1)(L_\pm Y_{l,m_l})$$

What does this mean?

- $L_{\pm}$ operates on wavefunction and yields new function ($L_{\pm} Y_{\ell m_\ell}$), whose z component of angular momentum is exactly hbar more/less than that possessed by $Y_{\ell m_\ell}$
- L_+ and L_- raise or lower the state of the z component of angular momentum of $Y_{\ell m_\ell}$ by one unit in terms of hbar.

- Similar to case of H.O.

What effect does $L_{\pm}$ operators have on the ℓ eigenvalue?

$$[L^2, L_\pm] = L^2 L_\pm - L_\pm L^2$$

$$= L^2 (L_x \pm i L_y) - (L_x \pm i L_y) L^2$$

$$= L^2 L_x \pm i L^2 L_y - L_x L^2 \mp i L_y L^2$$

$$[L^2, L_x] = 0 \qquad i[L^2, L_y] = 0$$

$$\Rightarrow [L^2, L_\pm] = 0$$

$$L^2 (L_\pm Y_{\ell, m_\ell}) = L_\pm (L^2 Y_{\ell, m_\ell})$$

$$L^2 \psi = \ell(\ell+1) \hbar^2 \psi$$

$$\Rightarrow L^2 (L_\pm Y_{\ell, m_\ell}) = \ell(\ell+1)\hbar^2 (L_\pm Y_{\ell, m_\ell})$$

- When L^2 operates on wavefunction ($L_\pm Y_{\ell m_\ell}$) the result is the same (same eigenvalue) as when it operates on wavefunction ($Y_{\ell m_\ell}$) alone!
- It has no effect on ℓ eigenvalue of $Y_{\ell m_\ell}$

What wavefunction does $L_\pm$ return?

- Recall H.O.: $A^+ \psi_n = i\sqrt{n+1}\,\psi_{n+1}$

  $A^- \psi_n = -i\sqrt{n}\,\psi_{n-1}$

  $A^\pm \psi_n \neq \psi_{n\pm1}$

- Similarly, $L_\pm Y_{\ell,m_\ell} \neq Y_{\ell,m_\ell\pm1}$

  $L_\pm Y_{\ell,m_\ell} = K^\pm_{\ell,m_\ell} Y_{\ell,m_\ell\pm1}$

$$K^\pm_{\ell,m_\ell} = \hbar\sqrt{\ell(\ell+1) - m_\ell(m_\ell\pm1)} = \hbar\sqrt{(\ell\mp m_\ell)(\ell\pm m+1)}$$

The proof in Reed (page 281) is wrong! Correct proof requires concepts beyond the scope of this course. You can find the correct proof in Griffiths page 166.

Correction in Reed

- In particular,

$$\langle Y_{lm} | L_+^2 Y_{lm} \rangle = 0$$

$$\langle Y_{lm} | L_+ Y_{lm} \rangle = 0$$

$$L_+^2 Y_{lm} = \text{Const} \cdot Y_{l\, m+2}$$

More about $L_\pm$

- Just like harmonic raising and lowering operators, $L_+ Y_{\ell\ell} = 0$, $L_- Y_{\ell,-\ell} = 0$

- Check:

$$L_+ Y_{22} = \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\frac{\partial}{\partial\varphi}\right)\left(\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\varphi}\right)$$

$$Y_{22} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\varphi}$$

$$\cot\theta = \frac{\cos\theta}{\sin\theta}$$

$$= \hbar e^{i\varphi}\sqrt{\frac{15}{32\pi}}\left(2\sin\theta\cos\theta\, e^{2i\varphi} + i\cot\theta\sin^2\theta\,(2i)\,e^{2i\varphi}\right)$$

$$= \hbar e^{i\varphi}\sqrt{\frac{15}{32\pi}}\left(2\sin\theta\cos\theta - 2\sin\theta\cos\theta\right)e^{2i\varphi}$$

$$= 0$$

Questions

- What is the expectation value of H(Hamiltonian), L^2, and L_z of $\psi = AL_+\psi_{321}$, where A is just a normalization constant?

Summary/Announcements

- Next time:
  - The Stern-Gerlach Experiment
    - evidence for quantized angular momentum

- Next homework due on Monday Nov 21.