Lectures 20 -21

Transitions between hydrogen stationary states

The energy of the emitted light (photons) is given by the difference in energy between the initial and final states of hydrogen atom

$$E_\gamma = E_i - E_f = -E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right] = -13.6\,\text{eV}$$

$$E_\gamma = h\underset{\substack{\uparrow \\ \text{frequency}}}{\nu} \longleftarrow \text{(Planck formula)}$$

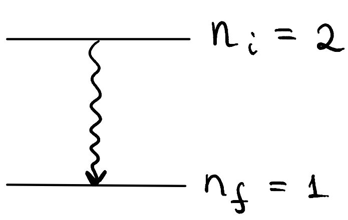
The wavelength is given by $\lambda = c/\nu \Rightarrow$

$$\frac{1}{\lambda} = \frac{1}{hc}E_\gamma = \underbrace{\frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2}_{\text{Rydberg constant}}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

Rydberg constant $R = 1.097 \times 10^7\,\text{m}^{-1}$

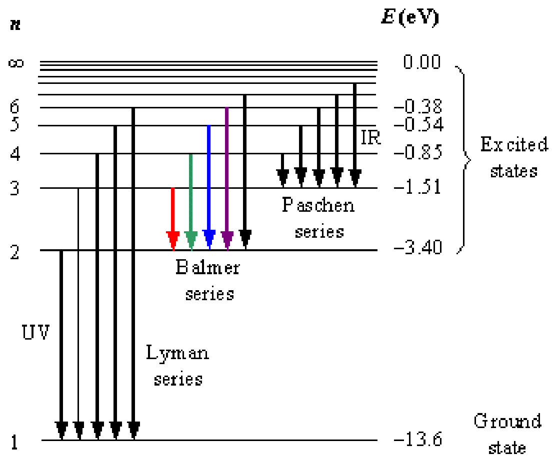
$$\boxed{\frac{1}{\lambda} = R\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]}$$

Example:



$$\lambda = 10^{-7}\,\frac{1}{1.097}\,\frac{1}{1 - 1/4}\,\text{m}$$

$$= 121.5 \times 10^{-9}\,\text{m} = 121.5\,\text{nm}$$



Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated.

Paschen series: transitions to the n_f = 3 state (infrared).

Balmer series: transitions to the n_f = 2 state (visible).

Lyman series: transitions to the ground n_f = 1 state (ultraviolet).

The wavelengths (nm) in the **Lyman series** are all ultraviolet: $n_f = 1$

n_i	2	3	4	5	6	7	8	9	10	11	∞
Wavelength (nm)	**121.6**	102.5	97.2	94.9	93.7	93.0	92.6	92.3	92.1	91.9	91.15

Balmer series $n_f = 2$

Transition of *n*	3→2	4→2	5→2	6→2	7→2	8→2	9→2	∞→2
Name	H-α	H-β	H-γ	H-δ	H-ε	H-ζ	H-η	
Wavelength (nm) [2]	656.3	486.1	434.1	410.2	397.0	388.9	383.5	364.6
Color	Red	Blue-green	Violet	Violet	Violet	Violet	(Ultraviolet)	(Ultraviolet)

Note: The **visible spectrum** is the portion of the electromagnetic spectrum that is visible to (can be detected by) the human eye. Electromagnetic radiation in this range of wavelengths is called visible light or simply light. A typical human eye will respond to wavelengths in air from about 380 to 750 nm.

Another note: at room temperature most of hydrogen atoms are in the ground state; so one needs to populate excited states to see the emission spectra.

Angular momentum

Classically, angular momentum of a particle with respect to the origin is defined as

$$\boxed{L = r \times p} \quad \begin{cases} L_x = y p_z - z p_y \\ L_y = z p_x - x p_z \\ L_z = x p_y - y p_x \end{cases}$$

Quantum angular momentum operator is obtained by taking

$$p_x \to -i\hbar \frac{\partial}{\partial x}$$

$$p_y \to -i\hbar \frac{\partial}{\partial y}$$

$$p_z \to -i\hbar \frac{\partial}{\partial z}.$$

Review: $[r_i, p_j] = i\hbar \delta_{ij}$
$[r_i, r_j] = 0$
$[p_i, p_j] = 0$
$i, j = x, y, z$

Let's check if operators L_x and L_y commute:

$$[L_x, L_y] = [y p_z - z p_y, z p_x - x p_z]$$

$$= [y p_z, z p_x] - \underbrace{\cancel{[z p_y, z p_x]}}_{z,\, p_x,\, p_y \text{ all commute}}^{0} - \underbrace{\cancel{[y p_z, x p_z]}}_{p_z,\, x,\, y \text{ all commute}} + [z p_y, x p_z]$$

$$= \underbrace{y p_x}_{\text{commute with } z, p_z} \overbrace{[p_z, z]}^{-i\hbar} + \underbrace{p_y x}_{\text{commute with } z, p_z} \overbrace{[z, p_z]}^{i\hbar} = i\hbar \underbrace{(x p_y - y p_x)}_{L_z}$$

$$= i\hbar L_z$$

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

Note that we do not need to do all this work to get two other commutators since we can use cyclic permutation of indices (from definition of cross product):

$$x \to y, \quad y \to z, \quad z \to x.$$

$$\boxed{\begin{array}{ccc} L_x & = & y p_z - z p_y \\ \downarrow & & \downarrow\downarrow \quad \downarrow\downarrow \\ L_y & = & z p_x - x p_z \\ \downarrow & & \downarrow\downarrow \quad \downarrow\downarrow \\ L_z & = & x p_y - y p_x \end{array}}$$

$$\vec{a} \times \vec{b} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \end{vmatrix}$$

$$\boxed{\begin{array}{l} [L_x, L_y] = i\hbar L_z \\ [L_y, L_z] = i\hbar L_x \\ [L_z, L_x] = i\hbar L_y \end{array}}$$

What is the significance of this?
Since L_x L_y, and L_z do not commute, they are incompatible observables. Incompatible observables can not have a complete set of common eigenfunctions.

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle L_z \rangle|$$

What about the square of the total angular momentum L^2?

$$[\vec{L}^2, L_x] = \overset{0}{\cancel{[L_x^2, L_x]}} + [L_y^2, L_x] + [L_z^2, L_x]$$

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

$$= -i\hbar \cancel{L_y L_z} - i\hbar \cancel{L_z L_y} + i\hbar \cancel{L_z L_y} + i\hbar \cancel{L_y L_z} = 0$$

We used:

$$\boxed{[AB, C] = A[B, C] + [A, C]B}.$$

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

Class exercise:

(1) Find $[L_z, L_+]$ and $[L_z, L_-]$, where

$L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$.

(2) Find $[L^2, L_\pm]$.

Solution:

$$[L_z, L_\pm] = [L_z, L_x \pm iL_y] = \overbrace{[L_z, L_x]}^{i\hbar L_y}$$

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

$$= \pm\hbar L_\pm \qquad \boxed{[L_z, L_\pm] = \pm\hbar L_\pm}$$

$$[L^2, L_\pm] = [L^2, L_x \pm iL_y] = \boxed{0}$$

What are eigenvalues and eigenfunctions of the angular momentum operators?

Since L_x, L_y and L_z do not commute and there are no complete set of common eigenfunctions, we will look for simultaneous eigenfunctions of L^2 and one of the components. We will pick L_z .

First, we will use **algebraic technique** to the find the eigenvalues. This technique is very similar to the one we used to find allowed energies of the harmonic oscillator.

Eigenvalue problem:

We are looking for eigenvalues λ and μ :

$$L^2 f = \lambda f \qquad L_z f = \mu f$$

f is the corresponding eigenfunction.

Step 1

It f is eigenfunction of L^2 , then $L_\pm f$ is also eigenfunction, with the same eigenvalue λ;

$$L^2(L_\pm f) = L_\pm(\underbrace{L^2 f}_{\lambda f}) = L_\pm \lambda f = \lambda(L_\pm f)$$

Step 2 **Class exercise #2:**

What is $L_z(L_\pm f)$? Hint: add and subtract $L_\pm L_z f$

$$L_z(L_\pm f) = L_z L_\pm f - L_\pm L_z f + L_\pm L_z f$$

$$= \underbrace{(L_z L_\pm - L_\pm L_z)}_{\pm\hbar L_\pm} f + L_\pm \underbrace{L_z f}_{\mu f} =$$

$$= \pm\hbar L_\pm f + L_\pm \mu f = (\mu \pm \hbar)(L_\pm f)$$

$$\boxed{L_z(\underbrace{L_\pm f}) = (\mu \pm h)(L_\pm f)}$$

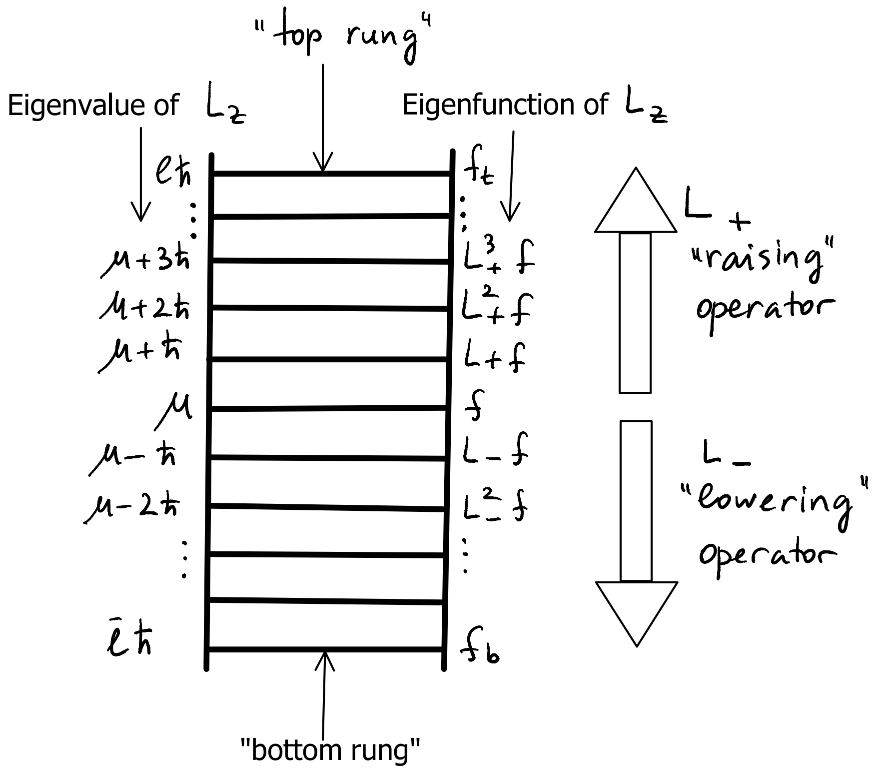
new eigenvalue

Therefore, $(L_\pm f)$ is an eigenfunction of L_z with new eigenvalue $\mu \pm \hbar$.
We name L_+ "raising" operator since it increases the eigenvalue of L_z by $\hbar$ and, L_- "lowering operator" since it lowers the eigenvalue of L_z by $\hbar$.

(Remember $a_\pm$ for harmonic oscillator!)

Step 3 Ladder of angular momentum states.

For each λ ,we now have the "ladder" of states:



If we keep applying L_+ , we have to eventually reach the "top rung" since the z-component can not exceed the total. We call the corresponding eigenfunction f_t and the corresponding eigenvalue $\ell\hbar$.

$$\boxed{L_+ f_t = 0}$$

At the "top rung" $L_z f_t = \hbar \ell f_t$

$$L^2 f_t = \lambda f_t .$$

Step 4

We now find this λ .
To accomplish that, we need to know how to express $L_\pm L_\mp$ via L^2 and L_z . We will find out why in a moment.

Class exercise #3:

Prove that $$\boxed{L_\pm L_\mp = L^2 - L_z^2 \pm \hbar L_z}$$

$$L_\pm L_\mp = (L_x \pm i L_y)(L_x \mp i L_y)$$

$$= L_x^2 + L_y^2 \pm i L_y L_x \mp i L_x L_y = L_x^2 + L_y^2$$

$$\mp i \underbrace{(L_x L_y - L_y L_x)}_{[L_x, L_y] = i\hbar L_z} = L^2 - L_z^2 \mp i i \hbar L_z$$

$$= L^2 - L_z^2 \pm \hbar L_z$$

Therefore, $L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z.$

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t$$

$$= \underbrace{L_- L_+ f_t}_{\text{since } L_+ f_t = 0} + \underbrace{L_z^2 f_t}_{\hbar^2 \ell^2} + \hbar \underbrace{L_z f_t}_{\hbar \ell} = \underbrace{\hbar^2 \ell(\ell+1)}_{=\lambda} f_t$$

$$\boxed{\lambda = \hbar^2 \ell(\ell+1)}$$

ℓ is maximum eigenvalue of L_z

$$\boxed{L_z f_t = \hbar \ell f_t}$$

Step 5

Now, we note that there must be "bottom rung" for the same reason and

$$L_- f_b = 0$$ corresponding eigenfunction

$$L_z f_b = \hbar \bar{\ell} f_b$$

Lowest eigenvalue of L_z

$$L^2 f_b = \lambda f_b$$ remember that eigenvalue of L^2 is the same for the entire ladder

Again, we use: $L^2 f_b = (\cancel{L_+ L_-} + L_z^2 - \hbar L_z) f_b$ since $L_- f_b = 0$

$$= \underbrace{L_z^2 f_b}_{\hbar^2 \bar{\ell}^2} - \hbar \underbrace{L_z f_b}_{\hbar \bar{\ell}} = \hbar^2 \bar{\ell}^2 f_b - \hbar^2 \bar{\ell} f_b = \hbar^2 \bar{\ell}(\bar{\ell}-1) f_b$$

$$L^2 f_b = \underbrace{\hbar^2 \bar{\ell}(\bar{\ell}-1)}_{=\lambda} f_b$$

$$\boxed{\lambda = \hbar^2 \bar{\ell}(\bar{\ell}-1)}$$

Step 6

We now compare results of the previous two steps, where we got λ from conditions for bottom and top rungs:

$$\lambda = \underbrace{\hbar^2 \ell(\ell+1)}_{\text{top}} = \underbrace{\hbar^2 \bar{\ell}(\bar{\ell}-1)}_{\text{bottom}}$$

$$\ell(\ell+1) = \bar{\ell}(\bar{\ell}-1) \Rightarrow$$

(1) $\bar{\ell} = \ell + 1 \rightarrow$ can't be since bottom step of the ladder can not be higher then the top step!

or

$\boxed{(2) \quad \bar{\ell} = -\ell}$ ← **our result**

Our results:

We were looking for information about eigenvalues λ and μ:

$$L^2 f = \lambda f \qquad L_z f = \mu f$$

(1) We found that $\mu = m\hbar$ $\qquad \boxed{L_z f = \hbar m f}$.

let's just call this quantity *m*

(2) The values of m range from -*l* to *l*. There are *N* integer steps between *m* = -*l* and *m* = *l*.

$$\ell = -\ell + N \Rightarrow \ell = N/2 \Rightarrow$$

l and m can be integer or half-integer.

Summary:

Eigenfunctions f_ℓ^m of L^2 and L_z are labeled by *m* and *l*:

$$L^2 f_\ell^m = \hbar^2 \ell(\ell+1) f_\ell^m, \qquad L_z f_\ell^m = \hbar m f_\ell^m.$$

$$\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$$

For a given value of *l*, there are *2l+1* values of *m*: $m = -\ell, -\ell+1, \ldots, \ell-1, \ell.$