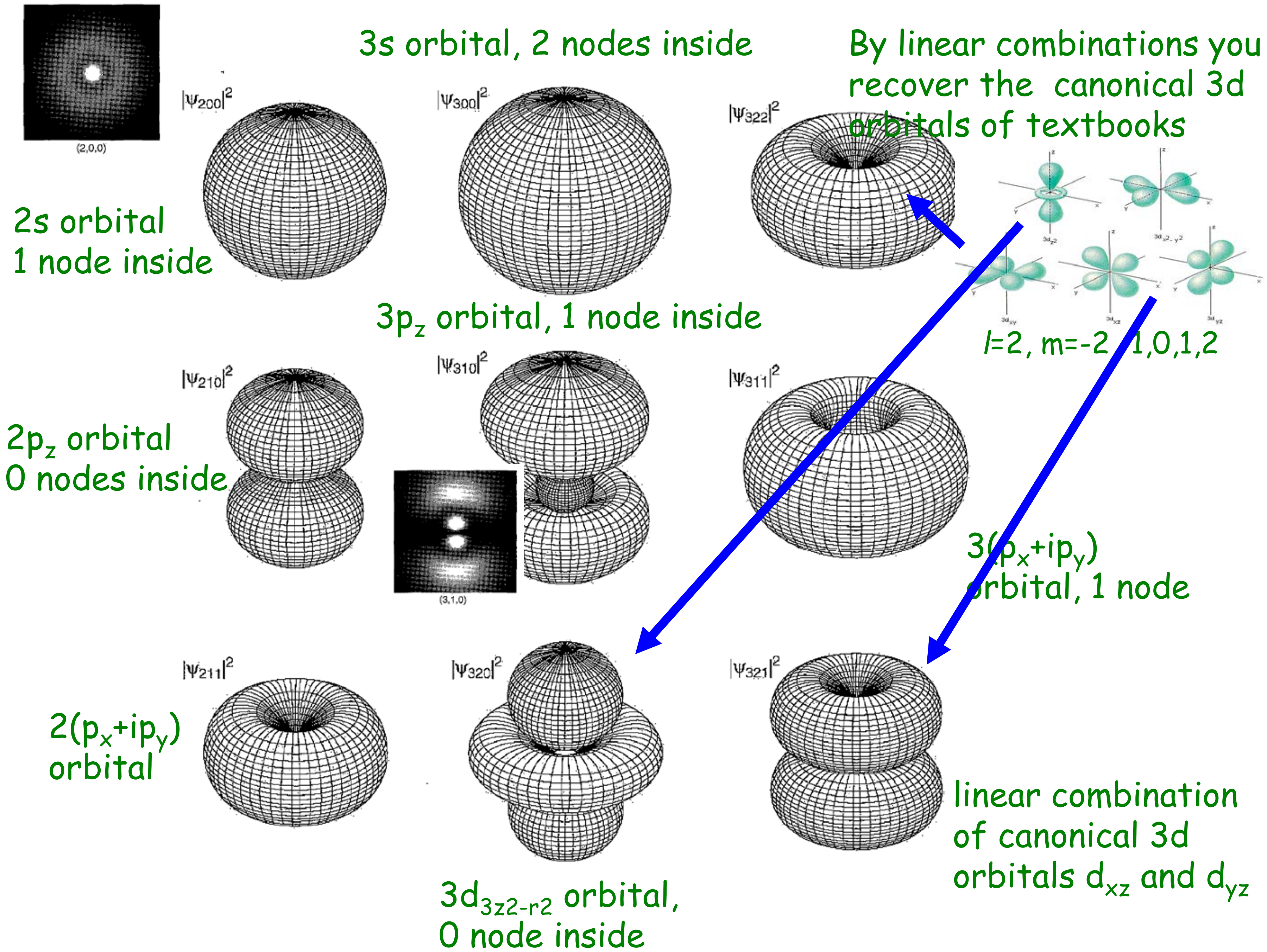

3s orbital, 2 nodes inside
By linear combinations you recover the canonical 3d orbitals of textbooks
(2,0,0)
|ψ200|²
|ψ300|²
|ψ322|²
2s orbital
1 node inside
3pz orbital, 1 node inside
l=2, m=-2,-1,0,1,2
|ψ210|²
|ψ310|²
|ψ311|²
2pz orbital
0 nodes inside
(3,1,0)
3(px+ipy)
orbital, 1 node
|ψ211|²
|ψ320|²
|ψ321|²
2(px+ipy)
orbital
linear combination
of canonical 3d
orbitals dxz and dyz
3d3z2-r2 orbital,
0 node inside

And as usual, the wave functions are orthonormal:

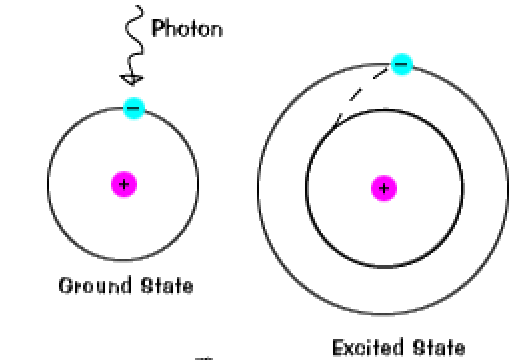
$$\int \psi_{nlm}^{*} \psi_{n'l'm'} r^2 \sin\theta \, dr \, d\theta \, d\phi = \delta_{nn'} \delta_{ll'} \delta_{mm'}$$

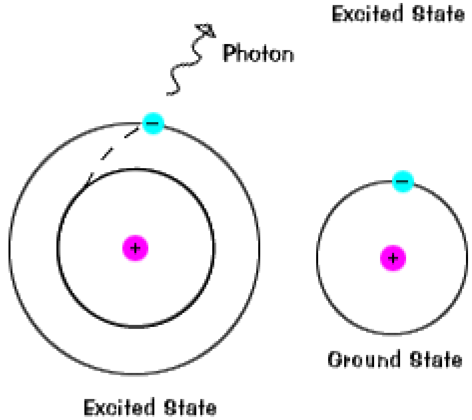
Because of radial equation. ($\delta_{nn'}$)

Because of spherical harmonics. ($\delta_{ll'} \delta_{mm'}$)

4.2.2: The Spectrum of Hydrogen

$n_i=1$, $n_f=2$, absorption





$n_i=2$, $n_f=1$
emission

Emission of photons:

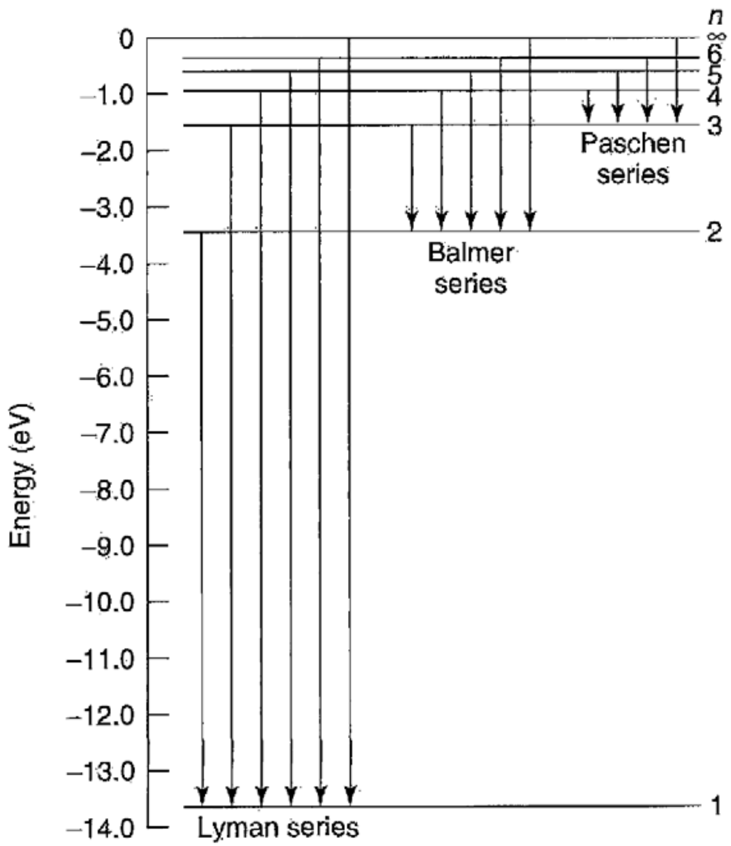
$$E_\gamma = E_i - E_f = -13.6 \text{ eV} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$E_\gamma = h\nu \qquad \lambda = c/\nu.$$

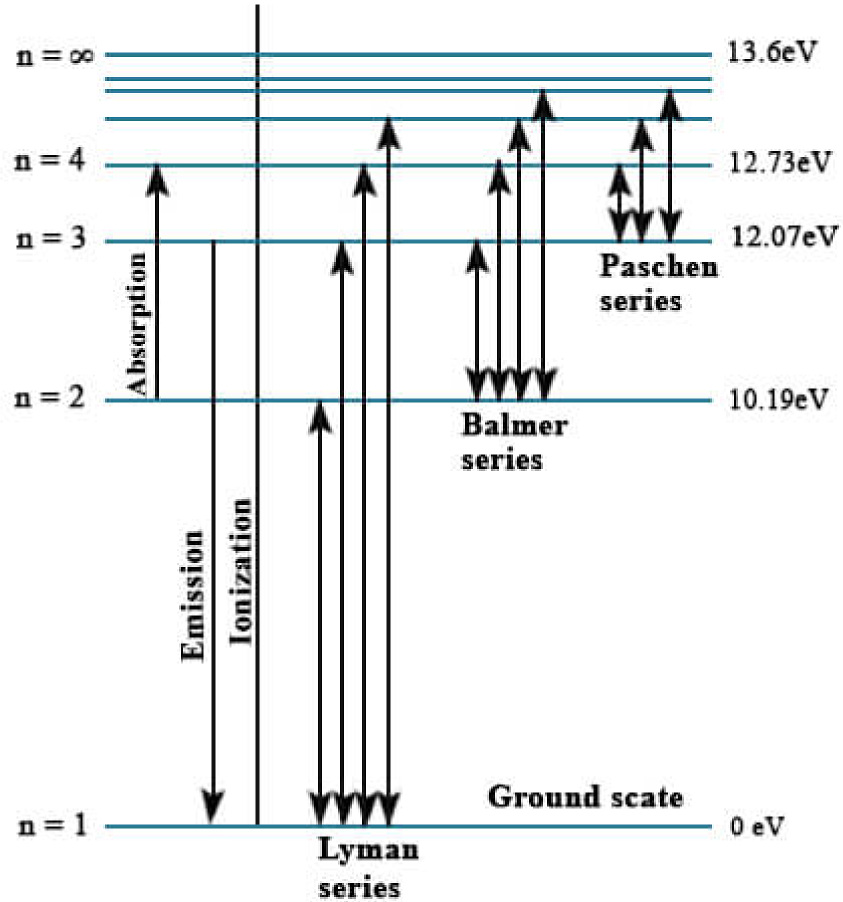
$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$R \equiv \frac{m}{4\pi c \hbar^3} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}$$

R= Rydberg constant; formula found before Sch Eq, just empirically.

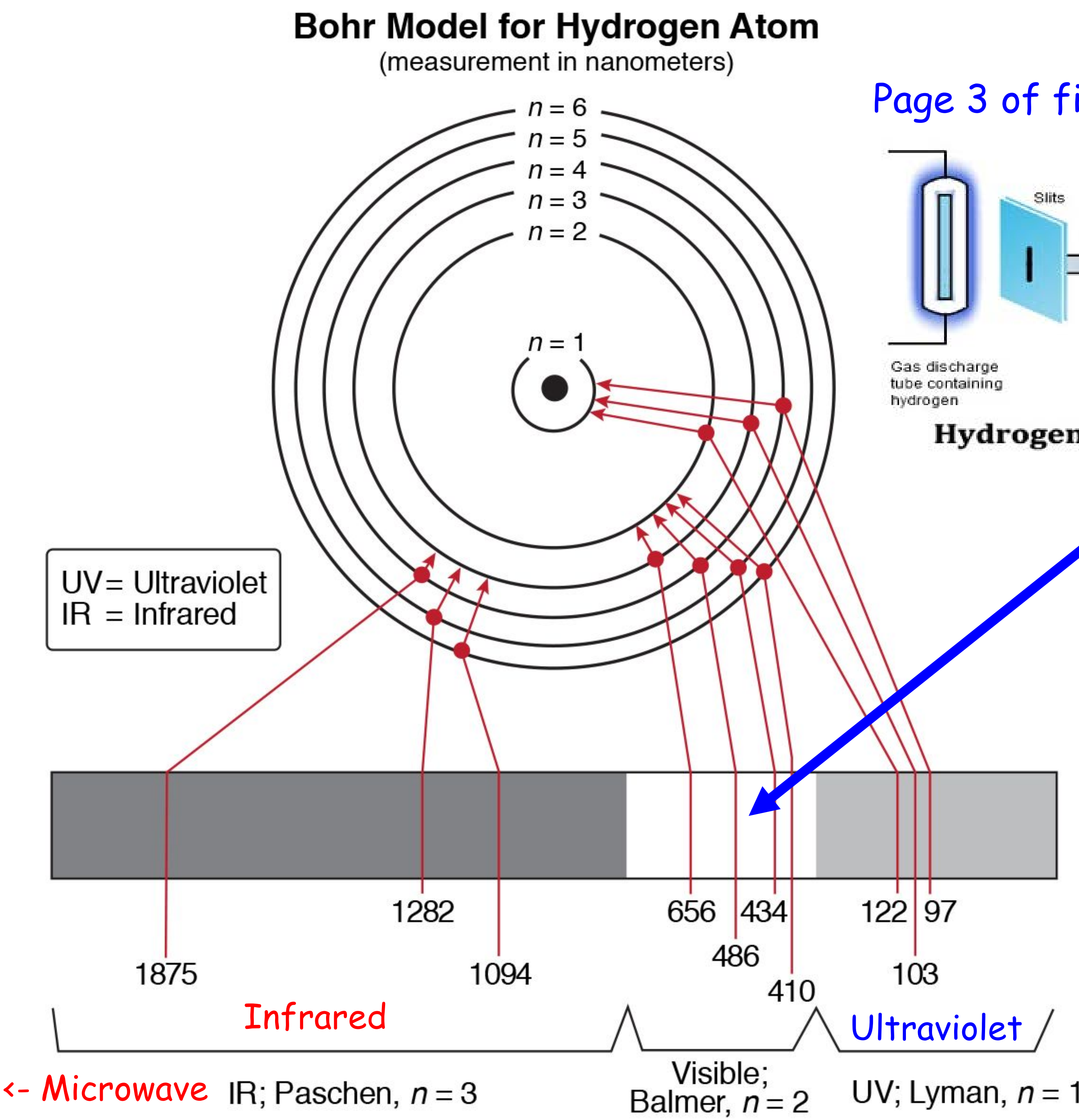


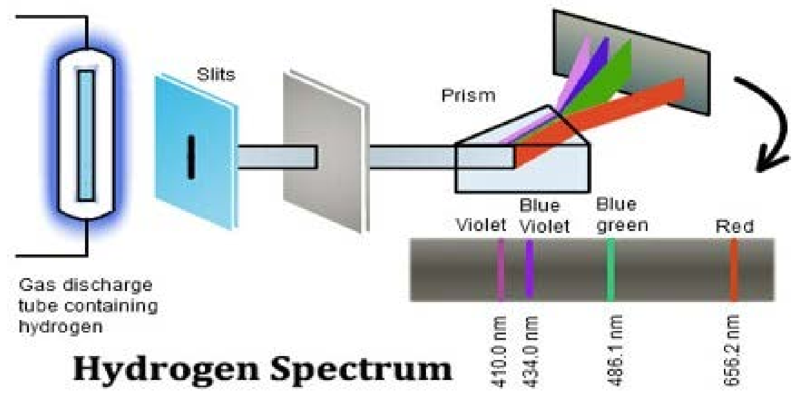
n
∞
6
5
4
3
2
1
0
−1.0
−2.0
−3.0
−4.0
−5.0
−6.0
−7.0
−8.0
−9.0
−10.0
−11.0
−12.0
−13.0
−14.0
Energy (eV)
Paschen series
Balmer series
Lyman series



n = ∞
n = 4
n = 3
n = 2
n = 1
13.6eV
12.73eV
12.07eV
10.19eV
0 eV
Absorption
Emission
Ionization
Paschen series
Balmer series
Lyman series
Ground scate

Page 3 of first lecture Aug 2020





Example:
$(1/\lambda)=R(1/1^2 - 1/2^2)$
$\sim 1/(122 \text{ nm})$

X rays γ rays ...

4.3: Angular Momentum

We wish to find out what is the meaning of "*l*" and "*m*" in the quantum numbers *(n,l,m)*.

Let us start with the classical formula for angular momentum: $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ ←

$$\begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

Component by component in Cartesian coordinates this is:

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x.$$

To move into quantum mechanics we follow the usual recipe:

$$p_x \to -i\hbar\partial/\partial x, \; p_y \to -i\hbar\partial/\partial y, \; p_z \to -i\hbar\partial/\partial z$$

Do these operators commute? (HW)

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

$$= \underbrace{[y p_z, z p_x]}_{y p_x [p_z, z]} - \underbrace{[y p_z, x p_z]}_{y x \underbrace{[p_z, p_z]}_{0}} - \underbrace{[z p_y, z p_x]}_{p_y p_x \underbrace{[z, z]}_{0}} + \underbrace{[z p_y, x p_z]}_{x p_y [z, p_z]}$$

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

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

If operators do not commute, then we cannot know them simultaneously, as shown in the general theorem of Ch. 3. For example:

$$\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i}\langle i\hbar L_z \rangle\right)^2 = \frac{\hbar^2}{4}\langle L_z \rangle^2$$

However, something special happens with the square of the angular momentum:

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

It commutes with L_x (and with L_y and with L_z):

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

… we need a "mini theorem" now …

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

$L_y [L_y, L_x] = L_y (L_y L_x - L_x L_y)$

$[L_y, L_x] L_y = (L_y L_x - L_x L_y) L_y$

$[L_y^2, L_x] = L_y [L_y, L_x] + [L_y, L_x] L_y$ used in HW

In general $[A^2, B] = A [A,B] + [A,B] A$. You will use this theorem in HW. Applying this theorem multiple times:

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

$$= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z$$

$$= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z(i\hbar L_y) + (i\hbar L_y)L_z$$

$$= 0.$$

The same holds for all components:

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

Because L^2 commutes with at least one component (usually chosen to be L_z) then we should find **eigenstates of both operators simultaneously**.

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

Then our mission is to find λ and μ and *f*.

To solve this problem we will use a procedure very similar to that of the Harmonic Oscillator with the *lowering and raising operators.*