ORBITAL ANGULAR MOMENTUM IN THE ONE-e⁻ ATOM

- Classically, a radial force (i.e. a spherically symmetric potential) such as Coulomb's cannot exert a torque ($\vec{r} \times \vec{F} = 0$), so the associated angular momentum remains constant ($\vec{L} = \vec{r} \times \vec{p} = \text{const.}$).
- In atoms $\hat{L}$ (L^2 and L_z specifically) also remains constant (in a given state) so most experiments involve measurements of E and L.
- We will now find expressions for L and L_z within Schrodinger's theory of the one-e⁻ atom, and we will find that they also OBEY QUANTIZATION RELATIONS:

$$L_z = m_\ell \hbar$$

$$L = \sqrt{\ell(\ell+1)}\,\hbar \qquad (\text{or } L^2 = \ell(\ell+1)\hbar^2)$$

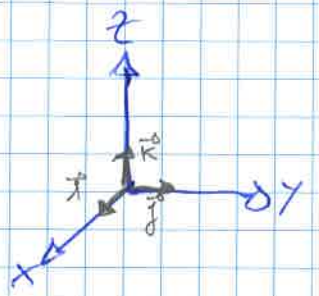
Eq. V.1

- These are analogous to the energy quantization E_n ($n = 1, 2, 3 \ldots$) but they involve the quantum numbers $\ell = 0, 1, 2 \ldots$ and $m_\ell = -\ell, -\ell+1, \ldots, +\ell$
- Bohr's atomic model had some primitive form of L quantization, but we will see that was wrong!
- This is the 1st time in this course that we study L with Schr. Q-MEC, since in Section III you saw only 1D systems (where L does not exist).

The angular momentum vector $\vec{L}$ of a particle, relative to the origin, is defined as

$$\vec{L} = \vec{r} \times \vec{p}$$

($\vec{r}$: position wrt origin ; $\vec{p}$: linear momentum)



Evaluating the cross product (e.g. components + 'right hand'):

$$\vec{L} = (L_x, L_y, L_z) \quad ; \quad \vec{p} = (p_x, p_y, p_z) \; ; \; \vec{r} = (x, y, z)$$

$$\left.\begin{aligned} L_x &= y p_z - z p_y \\ L_y &= z p_x - x p_z \\ L_z &= x p_y - y p_x \end{aligned}\right\}$$

AND since each component of the linear momentum has an associated operator $p_{x_i} = -i\hbar \frac{\partial}{\partial x_i}$

$$\Rightarrow \left\{\begin{aligned} L_{x,op} &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ L_{y,op} &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ L_{z,op} &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \end{aligned}\right.$$

Transforming to spherical coordinates (V(r) symmetry) $\left\{\begin{aligned} x &= r \sin\theta \cos\varphi \\ y &= r \sin\theta \sin\varphi \\ z &= r \cos\theta \end{aligned}\right.$,

the L_{x_i} operators become (e.g. Appendix M, E&R): (chain rule, $\operatorname{ctg}\theta = \frac{\cos\theta}{\sin\theta}$)

$$\boxed{\begin{aligned} L_{x,op} &= i\hbar \left(\sin\varphi \frac{\partial}{\partial\theta} + \operatorname{ctg}\theta \cos\varphi \frac{\partial}{\partial\varphi} \right) \\ L_{y,op} &= i\hbar \left(-\cos\varphi \frac{\partial}{\partial\theta} + \operatorname{ctg}\theta \sin\varphi \frac{\partial}{\partial\varphi} \right) \\ L_{z,op} &= -i\hbar \frac{\partial}{\partial\varphi} \end{aligned}}$$

EQ V.2

We will also need the square of the magnitude of the $\vec{L}$ vector:

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

Squaring Eq. 2, adding and manipulating one can get to (App. M):

$$L^2_{op} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \qquad \text{Eq. V.3}$$

• We first will find the expectation values of L_z and L^2.

$$\overline{L_z} = \int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} \psi^* L_{z,op}\,\psi \; \underbrace{r^2\sin\theta\, dr\, d\theta\, d\varphi}_{\text{volume element in spherical coords, } d\tau}$$

call it: $\int$ for short

$$\overline{L_z} = \int \psi^* L_{z,op}\,\psi\, d\tau = \int e^{\frac{iE_n t}{\hbar}} \psi^*_{n\ell m_\ell} L_{z,op}\, e^{-\frac{iE_n t}{\hbar}}\, d\tau = \int \psi^*_{n\ell m_\ell} L_{z,op}\,\psi_{n\ell m_\ell}\, d\tau$$

($f(t)$ only)

Likewise for the expectation value of L^2:

$$\overline{L^2} = \int \psi^*_{n\ell m_\ell} L^2_{op}\,\psi_{n\ell m_\ell}\, d\tau$$

Let's find this part of the first integrand first: (or HOW L_z OPERATOR ACTS ON ψ)

$$L_{z,op}\,\psi_{n\ell m_\ell} = -i\hbar\frac{\partial \psi_{n\ell m_\ell}}{\partial \varphi} = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\left[-i\hbar\frac{d\Phi_{m_\ell}(\varphi)}{d\varphi}\right]$$

(EQ 2) ↑ ; ↑ $\psi_{n\ell m_\ell} = R(r)\,\Theta(\theta)\,\Phi(\varphi)$

Since we found the azimuthal solution $\Phi = e^{i m_\ell \varphi}$:

$$\frac{d\Phi_{m_\ell}(\varphi)}{d\varphi} = i m_\ell e^{i m_\ell \varphi} = i m_\ell \Phi_{m_\ell}(\varphi)$$

$$\Rightarrow -i\hbar\frac{\partial \psi_{n\ell m_\ell}}{\partial \varphi} = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\left[-i\hbar\, i m_\ell\,\Phi_{m_\ell}(\varphi)\right] = m_\ell \hbar\, R\Theta\Phi$$

$$\Rightarrow \boxed{L_{z,op}\,\psi_{n\ell m_\ell} = m_\ell \hbar\,\psi_{n\ell m_\ell}}$$

(EQ 4) "L_z operator acting on an eigenfunction ψ returns the same ψ multiplied by $m_\ell \hbar$."

Let's do the same for L^2_{op}:

$$L^2_{op}\,\psi_{n\ell m_\ell} = R_{n\ell}\,L^2_{op}\left[\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\varphi)\right]$$

↑ L^2_{op} does not operate on r (EQ 3) and $R_{n\ell}$ only depends on r.

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

($\Phi \neq f(\theta)$) ; $\frac{d^2\Phi}{d\varphi^2} = -m_\ell^2\Phi$

So "Φ COMES OUT OF THE OPERATOR":

$$= \Phi\left(+\hbar^2\right)\underbrace{\left[-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_\ell^2\Theta}{\sin^2\theta}\right]}_{\ell(\ell+1)\cdot\Theta}$$

since Θ are solutions to polar eq. (II(θ))

BUT WE KNOW $H_{\ell m_\ell}$ ARE SOLUTIONS TO POLAR DIFFERENTIAL EQUATION (assoc. legendre diff. eq.): (EQ II(θ))

so the term in [ ] $= \ell(\ell+1) H_{\ell m_\ell}$

$$\Rightarrow L^2_{OP}\, \psi_{n\ell m_\ell} = R_{n\ell}\cdot \Phi_{m_\ell}\, \hbar^2 \cdot \ell(\ell+1) H_{\ell m_\ell}$$

$$\Rightarrow \boxed{L^2_{OP}\, \psi_{n\ell m_\ell} = \ell(\ell+1)\hbar^2\, \psi_{n\ell m_\ell}} \quad \text{(EQ V.5)}$$

"The L^2 operator acting on an eigenf. $\psi_{n\ell m_\ell}$ returns the same $\psi_{n\ell m_\ell}$ multiplied by $\ell(\ell+1)\hbar^2$"

Now we're ready to find the expectation values at last:

(EQ V.6) $$\boxed{\overline{L_z} = \int \psi^*_{n\ell m_\ell} L_{zOP}\, \psi_{n\ell m_\ell}\, d\tau = m_\ell \hbar \int \psi^*_{n\ell m_\ell} \psi_{n\ell m_\ell}\, d\tau = m_\ell \hbar}$$

(EQ V.7) $$\boxed{\overline{L^2} = \int \psi^*_{n\ell m_\ell} L^2_{OP}\, \psi_{n\ell m_\ell}\, d\tau = \ell(\ell+1)\hbar^2 \int \psi^*_{n\ell m_\ell} \psi_{n\ell m_\ell}\, d\tau = \ell(\ell+1)\hbar^2}$$

$\int \psi^*_{n\ell m_\ell} \psi_{n\ell m_\ell}\, d\tau = 1$ (PROBABILITY DENSITY NORMALIZED!)

Now note the difference between:

QUANTIZATION RELATIONS (EQ's 1)
$$\begin{cases} L_z = m_\ell \hbar \\ L^2 = \ell(\ell+1)\hbar^2 \end{cases}$$
These say that ANY measurement of the angular momentum will ALWAYS YIELD EXACTLY: $L_z = m_\ell \hbar$, $L^2 = \ell(\ell+1)\hbar^2$

EXPECTATION VALUES (EQ's 6 & 7)
$$\begin{cases} \overline{L_z} = m_\ell \hbar \\ \overline{L^2} = \ell(\ell+1)\hbar^2 \end{cases}$$
These say that ON AVERAGE, we will obtain these values, but fluctuations might be possible a priori.

- To get to the quantization relations we have to prove that there are NO FLUCTUATIONS in L^2, L_z.
- Note that if there are no fluctuations: $\overline{A}^2 = \overline{A^2}$, i.e. "the average of the square equals the square of the average" IF AND ONLY IF ALL INDIVIDUAL MEASUREMENTS ARE THE SAME.
- EXAMPLE (Tables 7.3 & 7.4)

FLUCTUATING: $A = 1, 2, 3$; $\bar{A} = \frac{1+2+3}{3} = 2$; $\boxed{\bar{A}^2 = 4}$

$A^2 = 1, 4, 9$; $\boxed{\overline{A^2} = \frac{1+4+9}{3} = \frac{14}{3} = 4.67}$

"STANDARD DEVIATION" $\Delta A = \sqrt{\overline{A^2} - \bar{A}^2}$

$\Delta A = 0.82$

NON-FLUCTUATING: $A = 2, 2, 2$; $\bar{A} = \frac{2+2+2}{3} = 2$; $\bar{A}^2 = 4$

$A^2 = 4, 4, 4$; $\overline{A^2} = \frac{12}{3} = 4$

$\Delta A = 0$

Thus we need to find the expectation value of L_z^2 and L^4:

$$\overline{L_z^2} = \int \psi^* \underbrace{L_{z,op} \cdot L_{z,op}}_{L^2_{z,op}} \psi \, d\tau = \int \psi^* (m_\ell \hbar)^2 \psi \, d\tau = (m_\ell \hbar)^2 = \overline{L_z}^2 \quad \checkmark$$

$L^2_{z,op}$ OPERATES TWICE ON ψ: MULTIPLIES BY $m_\ell \hbar$ EACH TIME; CONSTANT COMES OUT AND ψ IS NORMALIZED

$$\overline{L^4} = \int \psi^* L_z^2 L^2 \psi \, d\tau = \ell^2(\ell+1)^2 \hbar^4 \int \psi^* \psi \, d\tau = \overline{L^2}^2 \quad \checkmark$$

$\Rightarrow$ so we have proven the QUANTIZATION RELATIONS! (EQ's 1)

This simplicity of the operators L_z and L^2 is non trivial. They contain a mix of the coordinates θ, φ and their 1st and 2nd derivatives, YET WHEN APPLIED TO THE EIGENFUNCTIONS THEY SIMPLY MULTIPLY THEM BY A CONSTANT!

$$L_{z\,op}\,\psi_{n\ell m_\ell} = m_\ell \hbar\, \psi_{n\ell m_\ell} \quad ; \quad L^2_{op}\,\psi_{n\ell m_\ell} = \ell(\ell+1)\hbar^2\,\psi_{n\ell m_\ell}$$

- The operators linked to the x and y components of $\vec{L}$ do NOT have this property:

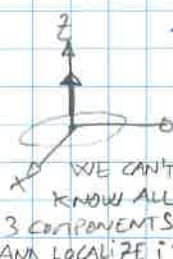
$$\left| \begin{array}{l} L_{x,op}\,\psi_{n\ell m_\ell} \neq \text{CONSTANT}\cdot\psi_{n\ell m_\ell} \\ L_{y,op}\,\psi_{n\ell m_\ell} \neq \text{CONSTANT}\cdot\psi_{n\ell m_\ell} \end{array} \right|$$

but they instead produce new functions of r, θ, φ (different than ψ).

- That's why we say that L^2 and L_z ARE QUANTIZED but L_x and L_y ARE NOT.
- In other words the $\psi_{n\ell m_\ell}$ states of the one-e⁻ atom do not have a definite (clearly defined) x or y component of the orbital angular momentum.
- It can be shown, however, that their average values are 0:

$$\overline{L_x} = \overline{L_y} = 0$$

- The uncertainty in the EXACT values of L_x and L_y derives from Heisenberg's uncertainty principle:
  - SAY $\vec{L}$ IS POINTING EXACTLY ALONG THE Z-AXIS (we know exactly all 3 components and we choose the z-axis accordingly)
  - THEN THE PARTICLE MUST MOVE ON THE XY PLANE $\Rightarrow p_z = 0 \Rightarrow \Delta p_z = 0$.
  - THEN IN ORDER TO KEEP $\Delta z \cdot \Delta p_z \geq \hbar$ WE GET $\Delta z \to \infty$ (NOT A BOUND STATE OF AN ATOM)



WE CAN'T KNOW ALL 3 COMPONENTS OF $\vec{L}$ AND LOCALIZE IT!

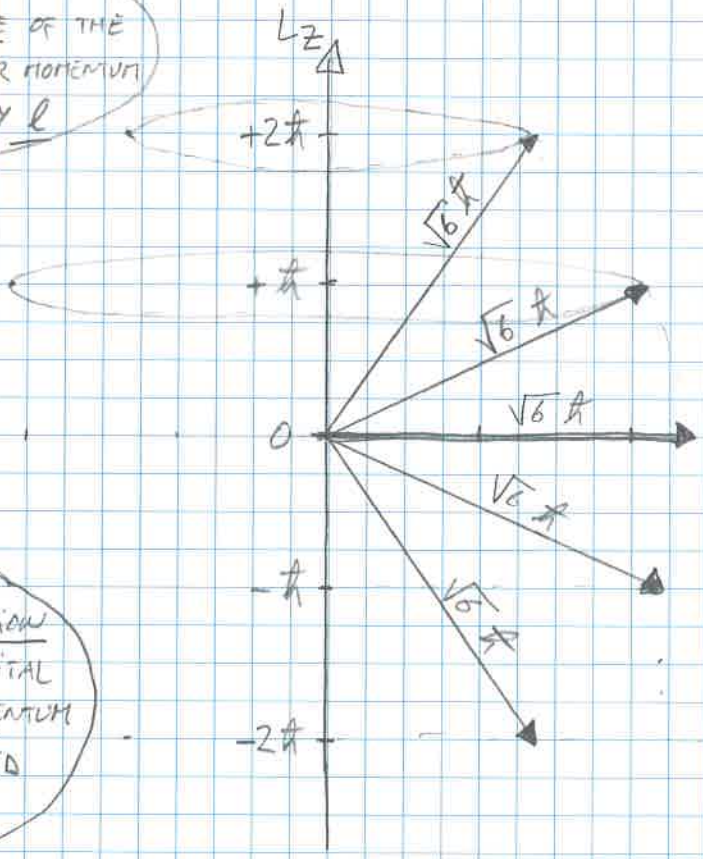
These properties of the orbital angular momentum:

$$L^2 = l(l+1)\hbar^2 \quad ; \quad L_z = m_l \hbar \quad ; \quad \bar{L}_x = \bar{L}_y = 0$$

are often represented in the VECTOR MODEL FOR $\vec{L}$:

$\vec{L}$ has definite length $\sqrt{l(l+1)}\,\hbar$ and definite z projection $m_l \hbar$.

THE MAGNITUDE OF THE ORBITAL ANGULAR MOMENTUM IS QUANTIZED BY l

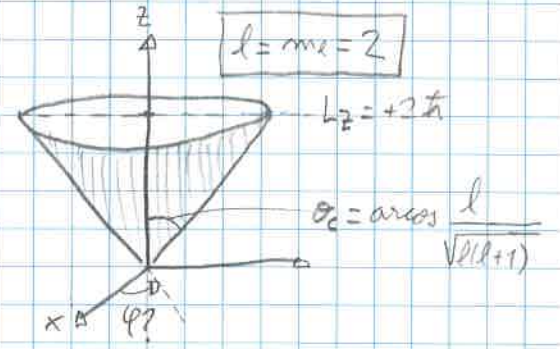


$l = 2$

$\vec{L}$ modulus: $L = \sqrt{2(2+1)}\,\hbar = \sqrt{6}\,\hbar = 2{,}45\,\hbar$

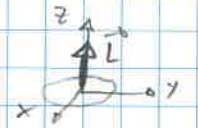
$\vec{L}$ z component: $L_z = m_l \hbar$ $(m_l = -2, -1, 0, 1, 2)$

THE ORIENTATION OF THE ORBITAL ANGULAR MOMENTUM IS QUANTIZED BY m_l



⇒ SPACE QUANTIZATION OF $\vec{L}$: IT CAN'T TAKE ANY DIRECTION!

- In any of these states (5 for $l=2$), $\vec{L}$ can be anywhere on a cone around the z axis: thus it has definite L and L_z.
- Because L_z can be known precisely, L_x and L_y become undefined, as a consequence of Heisenberg's uncertainty principle (i.e. φ unknown)
- For $l = m_l$ we recover classical behavior when $l \to \infty \Rightarrow \theta_L = 0°$, like a classical orbit in x-y plane with $\vec{L}$ having only L_z component.



(see VECTOR MODEL slides)

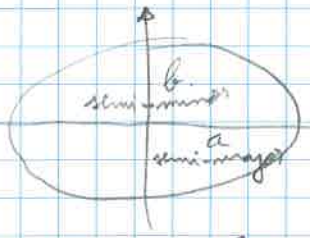
NOTE THAT:

- Bohr model had $L = n\hbar = \hbar$ for the ground state, $n=1$.
  Quantum mechanics says $L = \sqrt{\ell(\ell+1)}\,\hbar = 0$ when $n=1$, since $\ell=0$.
  EXPERIMENTAL EVIDENCE SUPPORTS CLEARLY $L=0$ when $n=1$.
  (e.g. atomic spectra).

  IF we want an analogy with a classical picture (with the corresponding caveats and limits), the motion in the $\ell=0$ states can be seen as ENTIRELY RADIAL, where the e^- would pass through the nucleus in the oscillation, which could take place in any direction. This view also agrees with the spherically symmetric charge distribution and the increased radial probab. densities near $r=0$ for the $\ell=0$ states.
  (Keep in mind limits of classical picture, though).

- Energies E_n do not depend on ℓ, orbital angular momentum magnitude
  CLASSICAL ANALOG: 2-BODY PROBLEM, SAME ENERGY BUT DIFFERENT L, eccentr.

$$\ell = \sqrt{1 + \frac{2EL^2}{K^2\mu}} \quad \begin{cases} E<0,\ L=L_0 \Rightarrow e=0 \Rightarrow \text{CIRCULAR ORBIT} \\ E<0,\ L<L_0 \Rightarrow e>0 \Rightarrow \text{ELLIPTIC ORBIT} \end{cases}$$



$$\ell = \sqrt{1 - \frac{b^2}{a^2}} \qquad \left(L_0 = \sqrt{\frac{-K^2\mu}{2E}}\right)$$

"ENERGY DEPENDS ON a"
"ANG. MOM. DEPENDS ON b". (max. for $b=a$)

(μ: reduced mass; $K^2 = (Gm_1m_2)^2$)

- m_ℓ determines the space orientation of $\vec{L}$, and of the atom itself.

  ⇒ not surprising that E_n energies do not depend on m_ℓ;
  in a spherically symmetrical (Coulomb) potential there is no preferred direction, thus the energy of the atom (without external perturbations) does not depend on its orientation.

NOTE ON 'EIGENVALUE EQUATIONS'

Common type of equations in more formal quantum mechanics, which have the form:

DYNAMICAL QUANTITY: f

$$\hat{f}_{OP}\,\psi = f\,\psi$$

EIGENVALUE EQUATION

- $\hat{f}_{OP}$: OPERATOR CORRESPONDING TO f.
- ψ: EIGENFUNCTION OF THE OPERATOR $\hat{f}_{OP}$ (ψ DESCRIBES A QUANTUM STATE)
- f: EIGENVALUE of the OPERATOR $\hat{f}_{OP}$

We've seen at least these 3 examples so far:

$$\hat{\ell}_{OP}\,\psi = E\,\psi \quad \text{with } E = -\frac{E_1}{n^2} \quad (n = 1, 2, 3\ldots)$$

(TISE-3D Coulomb: $\hat{\ell}_{OP} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r)$)

$$\hat{L}_{z\,OP}\,\psi = L_z\,\psi \quad \text{with } L_z = m_\ell \hbar \quad (m_\ell = -\ell, -\ell+1, \ldots, 0, \ldots \ell-1, \ell)$$

$$\hat{L}^2_{OP}\,\psi = L^2\,\psi \quad \text{with } L^2 = \ell(\ell+1)\hbar^2 \quad (\ell = 0, 1 \ldots n)$$

Thus ψ are eigenfunctions of $\hat{\ell}_{OP}$, $\hat{L}_{z\,OP}$, $\hat{L}^2_{OP}$, BUT NOT OF $\hat{L}_{x\,OP}$, $\hat{L}_{y\,OP}$.