Back to θ-Equation : Key Messages Extracted from Derivation

Why $\lambda = \ell(\ell+1)$ with $\ell = 0, 1, 2, \ldots$? [Worked out in Appendix A]

- There is one θ-Eq. for a value of m_ℓ
- $m_\ell = 0$ is simplest. θ-Eq. becomes $\frac{d}{dv}\left[(1-v^2)\frac{dP}{dv}\right] + \lambda P = 0$
- Series solution : $P(v) = \sum_{p=0}^{\infty} a_p v^p$ [p counts from zero]

  Recursive relation : $\boxed{\frac{a_{p+2}}{a_p} = \frac{p(p+1)-\lambda}{(p+1)(p+2)}}$ $\quad \frac{a_{p+2}}{a_p} \to 1$ (large p)

  $\Rightarrow P(v)$ bad behavior!
- Terminate Series $\to$ Polynomial
- Termination needs $\lambda = \ell(\ell+1)$, $\ell = 0, 1, 2, 3, \ldots$ [a physics-imposed requirement]
- Resultant Polynomials $P_\ell(v) = P_\ell(\cos\theta)$ = Legendre Polynomials

  Even ℓ : even terms of v ; Odd ℓ : odd terms of v [up to v^ℓ]

Putting Information Together : Any $U(\vec{r}) = U(r)$

$\hat{H}\psi = E\psi$ (TISE) $\qquad \psi(r,\theta,\phi) = R(r)\cdot Y_{\ell m_\ell}(\theta,\phi)$

$Y_{\ell m_\ell}(\theta,\phi)$ are solutions to the θ-ϕ Equation: (See Eq. (12))

$$\boxed{\frac{1}{\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y_{\ell m_\ell}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y_{\ell m_\ell}}{\partial\phi^2} = -\ell(\ell+1)Y_{\ell m_\ell}} \quad (12)$$

- $Y_{\ell m_\ell}(\theta,\phi)$ works for all $U(r)$
- "One Size Fits All"

$R(r)$ and E can be obtained by solving the radial equation:

$$\boxed{\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(E-U(r)\right)R = \ell(\ell+1)R} \quad (13)$$

- $U(r)$ enters
- One value of ℓ gives an Eq. (13) to solve

This page summarizes results after solving θ-ϕ part of the problem.

Names

ℓ = "orbital quantum number"

[related to magnitude of orbital angular momentum $|\vec{L}|$]

m_ℓ = "magnetic quantum number"

[related to one component (z-component) of orbital angular momentum L_z]

Recall: Orbital Angular Momentum $\vec{L} = \vec{r} \times \vec{p}$

$\therefore$ We need to discuss Angular Momentum in QM (see later)

F. Radial Equation and Energy Eigenvalues: General $U(r)$

- Inspect Radial Equation (13)

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(E - U(r)\right)R = l(l+1)R$$

l enters ($\underbrace{l=0,1,2,\ldots}_{\text{from } \theta\text{-}\phi \text{ eq.}}$)

To solve for energy eigenvalue E and radial part $R(r)$

- $\underbrace{l=0 \Rightarrow \text{one problem}}_{\text{many solutions}}$, $\underbrace{l=1 \Rightarrow \text{another problem}}_{\text{many solutions}}$, $\underbrace{l=2 \Rightarrow \text{yet another problem}}_{\text{many solutions}}$

$E_{n0} \leftrightarrow R_{n0}(r)$ — counts solutions for $l=0$

$E_{n1} \leftrightarrow R_{n1}(r)$ — counts solutions for $l=1$

$E_{n2} \leftrightarrow R_{n2}(r)$ — counts solutions for $l=2$

$\therefore$ In general (any $U(r)$), $R_{nl}(r) \leftrightarrow \underbrace{E_{nl} = \text{energy eigenvalues}}_{\text{depends on } n \text{ and } l \text{ (but not } m_l\text{)}}$

Name: n = principal quantum number

<u>Meaning</u>: <u>Without</u> knowing explicit form of $U(r)$

An Allowed energy $E_{n\ell}$ has <u>wavefunctions</u>:

$$\left.\begin{cases} R_{n\ell}(r)\, Y_{\ell\ell}(\theta,\phi) & [m_\ell = +\ell] \\ R_{n\ell}(r)\, Y_{\ell\,\ell-1}(\theta,\phi) & [m_\ell = \ell-1] \\ \vdots & \vdots \\ R_{n\ell}(r)\, Y_{\ell 0}(\theta,\phi) & [m_\ell = 0] \\ \vdots & \vdots \\ R_{n\ell}(r)\, Y_{\ell\,-\ell}(\theta,\phi) & [m_\ell = -\ell] \end{cases}\right\} (2\ell+1) \text{ values of } m_\ell$$

<u>different</u> eigenstates but <u>same</u> $E_{n\ell}$

<u>Key Point</u>: $\boxed{\text{Each eigenvalue } E_{n\ell} \text{ has at least}^{\dagger} \text{ a degeneracy of } (2\ell+1)}$ (14)

† "At least" means this statement is true for <u>any</u> $U(r)$. For specific form of $U(r)$ [e.g. $-\frac{1}{r}$], degeneracy may be higher. The additional degeneracy is "accidental", i.e. due to special $U(r)$.

$\therefore$ energy eigenstates: $\psi_{n\ell m_\ell}(r,\theta,\phi) \sim R_{n\ell}(r)\cdot Y_{\ell m_\ell}(\theta,\phi)$

all have energy eigenvalue $E_{n\ell}$

Why 3 indices? 3D problem + well behaved ψ in r, θ, ϕ coordinates

Thus, Specifying energy alone does <u>not uniquely</u> specify an energy eigenstate

- To pin point a particular $\psi_{n\ell m_\ell}$, need to examine
  - What does quantum number ℓ specify?
  - What does quantum number m_ℓ specify?

G. Orbital Angular Momentum

- "Orbital": To prepare for other angular momenta in QM, e.g. spin
- "Think Classical" $\vec{L} = \vec{r} \times \vec{p}$ [1D problems: Don't need it]

"Go Quantum"

$$\begin{aligned}
\hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\
\hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\
\hat{L}_z &= \underbrace{\hat{x}\hat{p}_y - \hat{y}\hat{p}_x}_{\text{general}} = \underbrace{\frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)}_{\text{using Schrödinger's way of imposing } [\hat{x},\hat{p}_x]=i\hbar \text{, etc.}}
\end{aligned} \tag{15}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

magnitude squared of orbital angular momentum

Commutators:

$$\boxed{\begin{gathered}[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0 \\ [\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \;;\; [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \;;\; [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y\end{gathered}} \tag{16}$$

H. Physical Meaning of ℓ in $Y_{\ell m_\ell}(\theta,\phi)$

Ans: For a state with quantum number ℓ, the magnitude of orbital angular momentum is $L = \sqrt{\ell(\ell+1)}\,\hbar$

Since $\ell = 0, 1, 2, \cdots \Rightarrow L$ takes on discrete/quantized values

Let's see Why.

- Need $\hat{L}^2$ in spherical coordinates
- From Eq.(15), go from (x, y, z) to (r, θ, ϕ)

(Ex.)

$$\hat{L}_x = i\hbar\left(\sin\phi \frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \quad (17)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \quad (18)$$

[$\hat{L}_z$ is simplest]

Example: $\hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = ?$ in spherical coordinates

Consider an arbitrary function $\mathcal{F}$: $\frac{\partial \mathcal{F}}{\partial \phi} = \frac{\partial \mathcal{F}}{\partial x}\underbrace{\frac{\partial x}{\partial \phi}} + \frac{\partial \mathcal{F}}{\partial y}\underbrace{\frac{\partial y}{\partial \phi}} + \frac{\partial \mathcal{F}}{\partial z}\underbrace{\frac{\partial z}{\partial \phi}}$

$$\frac{\partial x}{\partial \phi} = \frac{\partial}{\partial \phi}(r\sin\theta\cos\phi) = -r\sin\theta\sin\phi = -y$$

$$\frac{\partial y}{\partial \phi} = \frac{\partial}{\partial \phi}(r\sin\theta\sin\phi) = r\sin\theta\cos\phi = x$$

$$\frac{\partial z}{\partial \phi} = \frac{\partial}{\partial \phi}(r\cos\theta) = 0$$

$$\frac{\partial \mathcal{F}}{\partial \phi} = \left[-y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}\right]\mathcal{F} \quad \text{for arbitrary } \mathcal{F}$$

$$\Rightarrow \frac{\partial}{\partial \phi} = x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \quad \text{or} \quad \boxed{\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi} = -i\hbar\frac{\partial}{\partial \phi}} \qquad (18)$$

[c.f. $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$] ϕ : coordinate

L_z : conjugate momentum

Ex: How about $\hat{L}_x$, $\hat{L}_y$, $\hat{L}^2$?

- Construct $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ in spherical coordinates

Key Point }

$$\boxed{\hat{L}^2 = -\hbar^2 \underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]}_{\text{looks familiar [See }\theta\text{-}\phi\text{ eq. in Eq.(12)]}}} \quad (19)$$

[See also θ & ϕ parts in ∇^2]

<u>Eigenvalues/Eigenstates of $\hat{L}^2$?</u>

$$\hat{L}^2 Y_{\ell m_\ell}(\theta,\phi) = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y_{\ell m_\ell}}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y_{\ell m_\ell}\right]$$

$$= -\hbar^2\cdot\left[-\ell(\ell+1)\right]Y_{\ell m_\ell} \quad (\text{using Eq.}(12))$$

$$= \ell(\ell+1)\hbar^2\, Y_{\ell m_\ell}(\theta,\phi) \quad (20)$$

Solved eigenvalue problem of $\hat{L}^2$ <u>without effort</u>!

$$\boxed{Y_{\ell m_\ell}(\theta,\phi) \text{ is an eigenstate of } \hat{L}^2 \text{ with eigenvalue } \ell(\ell+1)\hbar^2}$$

$\therefore$ For state $\psi_{n\ell m_\ell} \sim R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi)$ [energy $E_{n\ell}$]

$$\hat{L}^2 \psi_{n\ell m_\ell} = R_{n\ell}(r)\, \hat{L}^2\, Y_{\ell m_\ell}(\theta,\phi) = [\ell(\ell+1)\hbar^2]\, \psi_{n\ell m_\ell}$$

$\Rightarrow$ $\boxed{L = |\vec{L}| = \text{magnitude of orbital angular momentum} = \sqrt{\ell(\ell+1)}\,\hbar}$

Meaning:

ℓ	0	1	2	3	4	$\cdots$	
$L = \lvert\vec{L}\rvert$	0	$\sqrt{2}\hbar$	$\sqrt{6}\hbar$	$\sqrt{12}\hbar$	$\sqrt{20}\hbar$	$\cdots$	[Can't take on other values]
Symbol: (stands for ℓ)	s	p	d	f	g	$\cdots$	[convention]

Observation: ψ_{nlm_l} is an eigenstate of $\hat{H}$ with energy eigenvalue E_{nl} AND an eigenstate of $\hat{L}^2$ with eigenvalue $l(l+1)\hbar^2$ [more later...]

- ψ_{nlm_l} is a simultaneous eigenstate [共同本徵態] of $\hat{H}$ and $\hat{L}^2$

Inspect:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(r)$$

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

$$= -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + U(r)\right] + \frac{\hat{L}^2}{2mr^2} \qquad (21)$$

$$\therefore [\hat{H}, \hat{L}^2] = 0 \quad \text{(commute)}$$

$[\hat{A}, \hat{B}] = 0$ then $\hat{A}$ and $\hat{B}$ share simultaneous eigenstates

- Apply previous knowledge: $\psi_{n\ell m_\ell}(r,\theta,\phi)$
  - Measure energy? Outcome: 100% certain to be $E_{n\ell} \Rightarrow \Delta E = 0$
    [even do it for 1M copies]
  - Measure L^2? Outcome: 100% certain to be $\ell(\ell+1)\hbar^2 \Rightarrow \Delta L^2 = 0$

$\therefore\ (\Delta E)\cdot(\Delta L^2) = 0$ [can possibly be zero as the case here]

[No uncertainty relation between commute quantities]

- Contrast: $[\hat{x}, \hat{p}] = i\hbar \neq 0$ <u>CANNOT</u> find simultaneous eigenstates

e.g. $\psi_p \sim e^{ikx}$ has definite momentum ($\hbar k$)

but ψ_p does not have definite position

and $\Delta x \cdot \Delta p \geq \hbar/2$ [never zero]

I. Physical Meaning of m_ℓ : What does it specify?

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} = -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{L}_z Y_{\ell m_\ell}(\theta,\phi) = -i\hbar P_\ell^{m_\ell}(\cos\theta)\frac{\partial}{\partial\phi}e^{im_\ell\phi} = m_\ell\hbar\, Y_{\ell m_\ell}(\theta,\phi) \qquad (22)^{+}$$

$\therefore$ $\boxed{Y_{\ell m_\ell}(\theta,\phi) \text{ is an eigenstate of } \hat{L}_z \text{ with eigenvalue } m_\ell\hbar}$

$Y_{\ell m_\ell}$ is a simultaneous eigenstate of $\hat{L}^2$ and $\hat{L}_z$

[Note: $[\hat{L}^2, \hat{L}_z] = 0$, they share simultaneous eigenstates]

It follows that $\hat{L}_z \psi_{n\ell m_\ell} = m\hbar\, \psi_{n\ell m_\ell}$

$\therefore$ $\psi_{n\ell m_\ell}$ (OR $Y_{\ell m_\ell}$) is a state of definite L_z giving $(m_\ell\hbar)$

+ Solved eigenvalue problem of $\hat{L}_z$ without effort!

Putting together: Any $U(r)$

TISE Solutions: $\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\cdot Y_{\ell m_\ell}(\theta,\phi)$

$$\left.\begin{array}{l} \text{Energy Eigenvalue} = E_{n\ell} \\ L^2 \text{ eigenvalue} = \ell(\ell+1)\hbar^2 \\ L_z \text{ eigenvalue} = m_\ell\hbar \end{array}\right\} \text{all } 100\% \text{ certain}$$

i.e.
$$\boxed{\psi_{n\ell m_\ell}(r,\theta,\phi) \text{ is a simultaneous eigenstate of } \underset{\underset{E_{n\ell}}{\uparrow}}{\hat{H}},\ \underset{\underset{\ell(\ell+1)\hbar^2}{\uparrow}}{\hat{L}^2},\ \underset{\underset{m_\ell\hbar}{\uparrow}}{\hat{L}_z}} \quad (23)$$

Note: $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$ are mutually commuting operators

Up to now, we don't need to invoke explicit form of $U(r)$, but we already know much about TISE solutions. [Only used symmetry of $U(r)$]

J. Unusual Features of QM Orbital Angular Momentum

$[\hat{L}^2, \hat{L}_z] = 0 \quad \Rightarrow$ Can find simultaneous eigenstates of $\hat{L}^2$ and $\hat{L}_z$ (which are $Y_{\ell m_\ell}$)

But $[\hat{L}_x, \hat{L}_y] \neq 0$, $[\hat{L}_y, \hat{L}_z] \neq 0$, $[\hat{L}_z, \hat{L}_x] \neq 0$ [c.f. $[\hat{x}, \hat{p}_x] \neq 0$]

$\Rightarrow$ If we know one component definitely (say L_z), we cannot know L_x and L_y

$\therefore$ $\boxed{\text{At best, we can find simultaneous eigenstates of } \underline{\hat{L}^2 \text{ and one component}}}$ [†]

- Which component? Any one will do!
- Why z-component L_z? $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$ (simple!) and it is completely general!

  $U(r)$ has no sense of direction. You pick a direction, then call it $\hat{z}$-direction.

[†] In classical mechanics, $\vec{L} = \vec{r} \times \vec{p}$. In central force problems, $\vec{L}$ is conserved. We know its direction and its magnitude (and thus all components).

$Y_{\ell m_\ell}(\theta, \phi)$

- $\ell = 0\,(s),\ 1\,(p),\ 2\,(d),\ 3\,(f),\ 4\,(g), \cdots$
- Given ℓ: $m_\ell = \underbrace{-\ell, -\ell+1, \cdots, 0, \cdots, \ell-1, \ell}_{(2\ell+1)\text{ values}}$

<u>Example</u>: $\ell = 2$ (d)

$L = \sqrt{2(2+1)}\,\hbar = \sqrt{6}\,\hbar$ [length of $\vec{L}$]

$L_z = \underbrace{-2\hbar, -\hbar, 0, +\hbar, +2\hbar}$ [z-component of $\vec{L}$]

[$m_\ell = -2, -1, 0, 1, 2$]

<u>Inspect</u>: Biggest $L_z = 2\hbar$ ["Biggest" $\Rightarrow$ Largest projection of $\vec{L}$ onto z-direction]

Length of $\vec{L}$ is $L = \sqrt{6}\,\hbar \approx 2.45\hbar > 2\hbar$ [Generally, $\sqrt{\ell(\ell+1)} > \ell$]

- Once a direction (called $\hat{z}$-direction) is chosen, $\vec{L}$ <u>cannot</u> point in that direction ($\because L_z^{max} < L$)

$\therefore$ $\boxed{\vec{L} \text{ can never point in any specific direction}}$ (24)

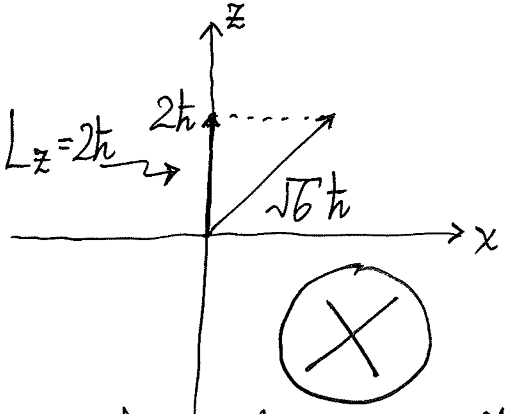
Here, we try to visualize QM quantity ($\vec{L}$ here, operators) classically.

- We could take results $\hat{L}^2 Y_{\ell m_\ell} = (\ell(\ell+1)\hbar^2) Y_{\ell m_\ell}$; $\hat{L}_z Y_{\ell m_\ell} = (m_\ell \hbar) Y_{\ell m_\ell}$ and move on. No problem. Don't interpret results classically.
- Or find a way to picture the QM results

K. The "Vector Model": A Picture representing QM results

- $L_z = m_\ell \hbar$ $\quad (m_\ell = -\ell, \dots, 0, \dots +\ell)$ finite number of values
- $\vec{L}$ cannot point in any specific direction
- $\vec{L}$ is somewhere on a cone such that $L_z = m_\ell \hbar$

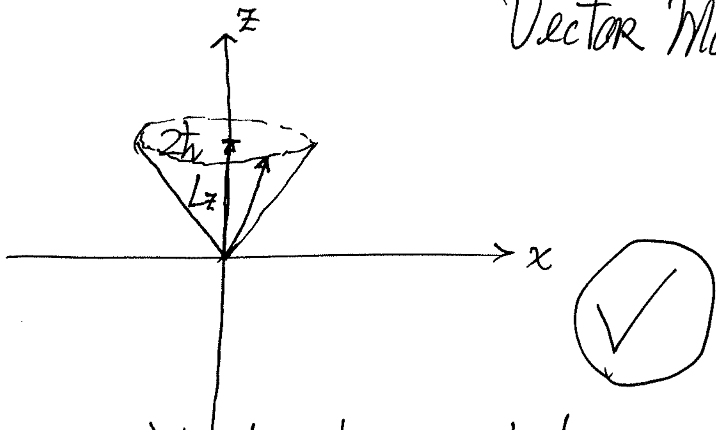
$m_\ell = 2 \quad (\ell = 2)$



- $\vec{L}$ points in specific direction
- $\underbrace{\text{Can know } L_x, L_y \text{ as well!}}_{\text{QM says No!}}$

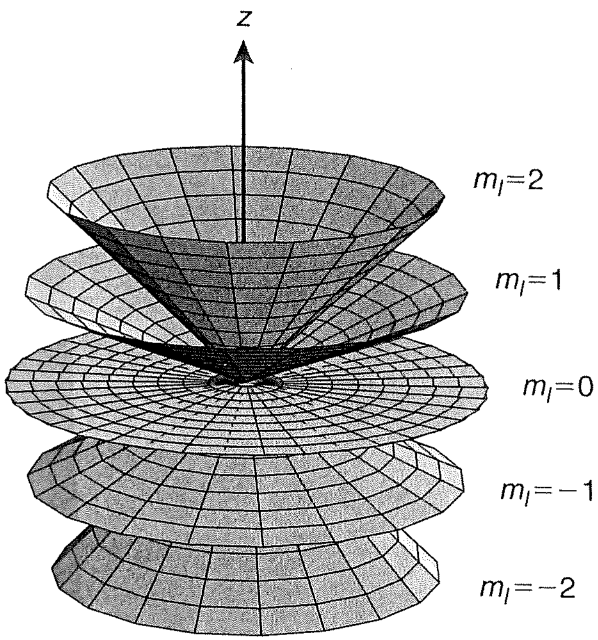
$m_\ell = 2 \quad (\ell = 2)$

Vector Model/Picture



- $\vec{L}$'s direction not known (somewhere on cone)
- $L_z = 2\hbar$ [doesn't matter where on cone is $\vec{L}$]
- $L = \sqrt{6}\,\hbar$ [on cone]

- To display the five $m_\ell (= 2, 1, 0, -1, -2)$ values, there are 5 cones



All possible orientations of an angular momentum vector with $l = 2$. The z component of the angular momentum is shown in units of $\hbar$.

There are $(2\ell+1)$ conical surfaces for a given ℓ.

- Projections $L_z = 2\hbar, \ \hbar, \ 0, \ -\hbar, \ -2\hbar$
- length $L = \sqrt{6}\,\hbar$ (all 5 cones)
- In books with jargons...
  - $\underbrace{\text{there are conical surfaces at specific angles on which } \vec{L} \text{ could lie}}$

"spatial quantization"

"space quantization"

- Vector Model:
  - Just a picture
  - Useful for visualizing how angular momenta add