

3D-Central Force Problems II. Levi-Civita: ϵ_{ijk} .

Last time: * $[\mathbf{x}, \mathbf{p}] = i\hbar \rightarrow$ use to obtain vector commutation rules: generalize from 1-D to 3-D
 * we have conjugate position and momentum components in Cartesian coordinates

Correspondence Principle Recipe
 Cartesian coordinates and vector analysis
 Symmetrize (make it Hermitian)
 classical mechanics in $\hbar \rightarrow 0$ limit

Derived key results:

$$[f(\mathbf{x}), \mathbf{p}_x] = i\hbar \frac{\partial f}{\partial \mathbf{x}} \Rightarrow [f(\mathbf{r}), \mathbf{p}_x] = i\hbar \frac{\partial f}{\partial \mathbf{r}} \frac{d\mathbf{r}}{d\mathbf{x}} = i\hbar \frac{\partial f}{\partial \mathbf{r}} \frac{\mathbf{x}}{r}$$

$$[f(\mathbf{r}), \mathbf{q} \cdot \mathbf{p}] = i\hbar \frac{\partial f}{\partial \mathbf{r}} \mathbf{r} \text{ based on } \frac{\partial f}{\partial \mathbf{r}} \left(\frac{\partial \mathbf{r}}{\partial \mathbf{x}} + \frac{\partial \mathbf{r}}{\partial \mathbf{y}} + \frac{\partial \mathbf{r}}{\partial \mathbf{z}} \right) \text{ and } \mathbf{r} = [\mathbf{x}^2 + \mathbf{y}^2 + \mathbf{z}^2]^{1/2}$$

$$*\mathbf{p}_r = \mathbf{r}^{-1} (\mathbf{q} \cdot \mathbf{p} - i\hbar) \leftarrow \boxed{\text{(came from symmetrization in Cartesian coordinates)}}$$

$$*\mathbf{p}^2 = \mathbf{p}_r^2 + \mathbf{r}^{-2} \mathbf{L}^2 \leftarrow \boxed{\text{separated } \mathbf{p}_\parallel \text{ from } \mathbf{p}_\perp}$$

operator algebra gave simple separation of variables
 not necessary (or possible) to symmetrize

$$*\mathbf{H} = \frac{\mathbf{p}_r^2}{2\mu} + \left[\frac{\mathbf{L}^2}{2\mu r^2} + V(\mathbf{r}) \right]$$

$V_\ell(r)$ radial effective potential
 We do not yet know anything about the eigenstates and the eigenvalues and eigenstates of \mathbf{L}^2 and \mathbf{L}_i .

need to show we can ignore the order of \mathbf{L}^2 and r^2

TODAY [purpose is mostly to practice commutation rule [,], and angular momentum algebras]

* Obtain angular Momentum Commutation Rules \rightarrow Block diagonalize \mathbf{H}

* ϵ_{ijk} Levi-Civita Antisymmetric Tensor
 useful in derivations, vector commutators, and remembering stuff.

Next Lecture: Begin derivation of all angular momentum matrix elements starting from the Commutation Rule definitions of angular momentum components.

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GOALS

1. $[\mathbf{L}_i, f(r)] = 0$ any scalar function of scalar r .

2. $[\mathbf{L}_i, \mathbf{p}_r] = 0$ difficult - need to use ϵ_{ijk} !

3. $[\mathbf{L}_i, \mathbf{p}_r^2] = 0$

4. $[\mathbf{L}_i, \mathbf{L}^2] = 0$ (but $[\mathbf{L}_i, \mathbf{L}_j^2] \neq 0!$)

5. *C.S.C.O.* $\mathbf{H}, \mathbf{L}^2, \mathbf{L}_i \rightarrow$ enable block diagonalization of \mathbf{H}

\mathbf{L}^2 and \mathbf{L}_i block-diagonalize \mathbf{H} according to different eigenvalues of \mathbf{L}^2 and \mathbf{L}_i .

Items 1-4 are chosen to show that all terms in \mathbf{H} commute with \mathbf{L}^2 and \mathbf{L}_i

\mathbf{L}_i : choose \mathbf{L}_z for example

1. $[\mathbf{L}_z, f(\mathbf{r})] = [\mathbf{x}\mathbf{p}_y - \mathbf{y}\mathbf{p}_x, f(\mathbf{r})] = \mathbf{x}[\mathbf{p}_y, f] + [\mathbf{x}, f]\mathbf{p}_y - \mathbf{y}[\mathbf{p}_x, f] - [\mathbf{y}, f]\mathbf{p}_x$

$[\mathbf{x}, f] = 0, \quad [\mathbf{y}, f] = 0$ because $[\vec{\mathbf{q}}, f(\mathbf{r})] = 0\hat{i} + 0\hat{j} + 0\hat{k}$

recall $[f(\mathbf{r}), \mathbf{p}_x] = i\hbar \frac{\partial f}{\partial r} \frac{\partial r}{\partial x} = i\hbar \frac{\partial f}{\partial r} \frac{x}{r}$

$[\mathbf{L}_z, f(\mathbf{r})] = -i\hbar \frac{\partial f}{\partial r} \left[x \frac{y}{r} - y \frac{x}{r} \right] = 0$

2. $[\mathbf{L}_z, \mathbf{p}_r] = [\mathbf{L}_z, \mathbf{r}^{-1}(\mathbf{q} \cdot \mathbf{p} - i\hbar)] = [\mathbf{L}_z, \mathbf{r}^{-1} \mathbf{q} \cdot \mathbf{p}]$ (already know that $[\mathbf{L}_z, \mathbf{r}^{-1} i\hbar] = 0$)

$= \mathbf{L}_z \mathbf{r}^{-1} \mathbf{q} \cdot \mathbf{p} + \mathbf{r}^{-1} [\mathbf{L}_z, \mathbf{q} \cdot \mathbf{p}]$ $\frac{1}{r}$ is $f(\mathbf{r})$ and we just showed this commutation rule = 0

$[\mathbf{L}_z, \mathbf{q} \cdot \mathbf{p}] = \mathbf{q} \cdot [\mathbf{L}_z, \vec{\mathbf{p}}] + [\mathbf{L}_z, \vec{\mathbf{q}}] \cdot \mathbf{p}$ two vector commutators on RHS

Note that vector $\vec{\mathbf{q}}$ is a not scalar $f(\mathbf{r})!$

need to define special notational trick to evaluate these DIFFICULT COMMUTATORS

Either $A' = A$ or $\mathbf{H}_{AA'} = 0$. If $A = A'$, it is still possible to find linear combination of different eigenstates of \mathbf{A} (with same- A eigenvalues of \mathbf{A}) that diagonalizes the associated block of \mathbf{H} .

$$[\mathbf{H}, \mathbf{A}] = 0$$

$$0 = \langle A | [\mathbf{H}, \mathbf{A}] | A' \rangle = \langle A | [-\mathbf{A}\mathbf{H} + \mathbf{H}\mathbf{A}] | A' \rangle = (-A + A') \mathbf{H}_{AA'}$$

so either $A = A'$ or $\mathbf{H}_{AA'} = 0$

Now for something very special and useful

Levi-Civita Symbol	ϵ_{ijk}
cyclic order	$\epsilon_{xyz} = \epsilon_{yzx} = \epsilon_{zxy} = +1$
adjacent interchange	$\epsilon_{yxz} = \epsilon_{zyx} = \epsilon_{xzy} = -1$ (anti-cyclic order)
2 repeated indices	$\epsilon_{xxy} = \text{etc.} = 0$

I claim $[\mathbf{L}_i, \mathbf{p}_j] = i\hbar \sum_k \epsilon_{ijk} \mathbf{p}_k$. This will become the *definition* of a “vector operator” \square with respect to \mathbf{L} ! [[vector = 1st rank tensor]

Nonlecture: Verify claim for 1 of $3 \times 3 = 9$ possible cases

let $i = x, j = y$

Do This!

$$[\mathbf{L}_x, \mathbf{p}_y] = [\mathbf{y}\mathbf{p}_z - \mathbf{z}\mathbf{p}_y, \mathbf{p}_y] = y[\mathbf{p}_z, \mathbf{p}_y] + [\mathbf{y}, \mathbf{p}_y]\mathbf{p}_z - z[\mathbf{p}_y, \mathbf{p}_y] - [\mathbf{z}, \mathbf{p}_y]\mathbf{p}_y$$

$$= 0 + i\hbar\mathbf{p}_z - 0 - 0$$

Now check this using ϵ_{ijk}

$$[\mathbf{L}_x, \mathbf{p}_y] = i\hbar \sum_k \epsilon_{xyk} \mathbf{p}_k = i\hbar [\cancel{\epsilon_{xyx}\mathbf{p}_x} + \cancel{\epsilon_{xyy}\mathbf{p}_y} + \epsilon_{xyz}\mathbf{p}_z]$$

$$= i\hbar\mathbf{p}_z. \quad \text{OK}$$

All other 8 cases go similarly. Feel the power of ϵ_{ijk} !

Other important Commutation Rules

$[\mathbf{L}_i, \mathbf{p}_j] = i\hbar \sum_k \epsilon_{ijk} \mathbf{p}_k$	general definition of a “vector” operator	$\vec{\mathbf{q}}$ and $\vec{\mathbf{p}}$ are examples of vector operators. Classify as vectors with respect to \mathbf{L} !
$[\mathbf{L}_i, \mathbf{q}_j] = i\hbar \sum_k \epsilon_{ijk} \mathbf{q}_k$		
$[\mathbf{L}_i, \mathbf{L}_j] = i\hbar \sum_k \epsilon_{ijk} \mathbf{L}_k$	general definition of an “angular momentum.” Works even for spin where a $\mathbf{q} \times \mathbf{p}$ definition cannot exist. This is the MOST IMPORTANT STEP	

All angular momentum matrix elements will be derived next lecture from these commutation rules.

FOR THE READER: VERIFY ONE COMPONENT OF EACH OF THE THREE ABOVE COMMUTATORS

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$[\mathbf{L}_i, \mathbf{L}_j] = i\hbar \sum_k \epsilon_{ijk} \mathbf{L}_k$ is identical to

$$\mathbf{L} \times \mathbf{L} = i\hbar \mathbf{L}$$

(expect 0! because vector cross product $|\vec{A} \times \vec{B}| = |A| |B| \sin \theta_{AB}$)

$$\begin{aligned} \mathbf{L} \times \mathbf{L} &= \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ \mathbf{L}_x & \mathbf{L}_y & \mathbf{L}_z \\ \mathbf{L}_x & \mathbf{L}_y & \mathbf{L}_z \end{pmatrix} = \hat{i} \begin{pmatrix} \mathbf{L}_y \mathbf{L}_z - \mathbf{L}_z \mathbf{L}_y \end{pmatrix} + \hat{j} \begin{pmatrix} \mathbf{L}_z \mathbf{L}_x - \mathbf{L}_x \mathbf{L}_z \end{pmatrix} + \hat{k} \begin{pmatrix} \mathbf{L}_x \mathbf{L}_y - \mathbf{L}_y \mathbf{L}_x \end{pmatrix} \\ &= i\hbar [\hat{i} \mathbf{L}_x + \hat{j} \mathbf{L}_y + \hat{k} \mathbf{L}_z] = i\hbar \mathbf{L} \end{aligned}$$

note reversal of x and z terms

This vector cross product definition of \mathbf{L} is more general than $\mathbf{q} \times \mathbf{p}$ because there is no way to define spin in $\mathbf{q} \times \mathbf{p}$ form but $\mathbf{S} \times \mathbf{S} = i\hbar \mathbf{S}$ is quite meaningful.

Ask:

Can one generalize that, if $\mathbf{L} \times \mathbf{L} = i\hbar \mathbf{L}$ (instead of 0), and the $[\mathbf{L}_i, \mathbf{L}_j]$ and $[\mathbf{L}_i, \mathbf{p}_j]$ commutation rules have similar forms, that $\mathbf{L} \times \mathbf{p} = i\hbar \mathbf{p}$? NO! Check for yourself!

2. Continued. use $\mathbf{p}_r = \mathbf{r}^{-1}(\mathbf{q} \cdot \mathbf{p} - i\hbar)$

$$\begin{aligned} [\mathbf{L}_z, \mathbf{p}_r] &= \mathbf{r}^{-1} \mathbf{q} \cdot [\mathbf{L}_z, \vec{\mathbf{p}}] + \mathbf{r}^{-1} [\mathbf{L}_z, \vec{\mathbf{q}}] \cdot \vec{\mathbf{p}} && \text{already know that this commutes with } \mathbf{L}_z \\ &\text{evaluate the first term} && \text{vector commutators} \\ [\mathbf{L}_i, \vec{\mathbf{p}}] &= i\hbar \sum_k (\hat{i} \epsilon_{ixk} + \hat{j} \epsilon_{iyk} + \hat{k} \epsilon_{izk}) \mathbf{p}_k \\ &\text{sum of 3 terms} \\ \mathbf{q} \cdot [\mathbf{L}_i, \vec{\mathbf{p}}] &= i\hbar \sum_k (\underbrace{\mathbf{x} \epsilon_{ixk}} + \underbrace{\mathbf{y} \epsilon_{iyk}} + \underbrace{\mathbf{z} \epsilon_{izk}}) \mathbf{p}_k && \text{only one of these terms is nonzero (but use simpler form)} \\ &= i\hbar \sum_{j,k} \epsilon_{ijk} \mathbf{q}_j \mathbf{p}_k && \text{call this an index-j sum} \quad (1) \end{aligned}$$

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and evaluate the second term $[\mathbf{L}_i, \vec{q}] \cdot \vec{p}$

$$[\mathbf{L}_i, \vec{q}] = i\hbar \sum_k \left[\hat{i}\epsilon_{ixk} + \hat{j}\epsilon_{iyk} + \hat{k}\epsilon_{izk} \right] \mathbf{q}_k$$

$$[\mathbf{L}_i, \vec{q}] \cdot \mathbf{p} = i\hbar \sum_k \left[\epsilon_{ixk} \mathbf{q}_k \mathbf{p}_x + \epsilon_{iyk} \mathbf{q}_k \mathbf{p}_y + \epsilon_{izk} \mathbf{q}_k \mathbf{p}_z \right] \text{ (a 2nd-index sum)}$$

$$= i\hbar \sum_{j,k} \epsilon_{ijk} \mathbf{q}_k \mathbf{p}_j = i\hbar \sum_{k,j} \epsilon_{ikj} \mathbf{q}_j \mathbf{p}_k$$

sum is over j and k, so
can permute the k ↔ j
labels

$$= -i\hbar \sum_{k,j} \epsilon_{ijk} \mathbf{q}_j \mathbf{p}_k \quad (2)$$

| — switch order of j and k

putting Eqs. (1) and (2) together

$$\vec{q} \cdot [\mathbf{L}_i, \vec{p}] + [\mathbf{L}_i, \vec{q}] \cdot \vec{p} = i\hbar \sum_{j,k} \left[\epsilon_{ijk} \mathbf{q}_j \mathbf{p}_k - \epsilon_{ijk} \mathbf{q}_j \mathbf{p}_k \right] = 0!$$

The 2 terms from the $[\mathbf{L}, \mathbf{p} \cdot \mathbf{q}]$ are combined here.

- Elegance and power of ϵ_{ijk} notation!
- We have shown, for $\mathbf{p}_r = \mathbf{r}^{-1}(\mathbf{q} \cdot \mathbf{p} - i\hbar)$, that:
 - * $[\mathbf{L}_i, \mathbf{p}_r] = 0$ for all i
 - * easy now to show $[\mathbf{L}_i, \mathbf{p}_r^2] = 0$

Finally $[\mathbf{L}_i, \mathbf{L}^2] = \sum_j [\mathbf{L}_i, \mathbf{L}_j^2] = \sum_j \left(\mathbf{L}_j [\mathbf{L}_i, \mathbf{L}_j] + [\mathbf{L}_i, \mathbf{L}_j] \mathbf{L}_j \right)$

$$= \sum_j \left[\mathbf{L}_j \left(i\hbar \sum_k \epsilon_{ijk} \mathbf{L}_k \right) + \left(i\hbar \sum_k \epsilon_{ijk} \mathbf{L}_k \right) \mathbf{L}_j \right]$$

sum is over j
and k, so can
permute the
j & k indices

same trick: permute j ↔ k indices in second term

Thus $\epsilon_{ijk} = -\epsilon_{ikj}$

$$-\left(i\hbar \sum_k \epsilon_{ijk} \mathbf{L}_j \right) \mathbf{L}_k$$

$$[\mathbf{L}_i, \mathbf{L}^2] = 0$$

But be careful: \mathbf{L}_i and \mathbf{L}_j^2 do not commute even though \mathbf{L}_i and \mathbf{L}^2 do commute

$$[\mathbf{L}_i, \mathbf{L}_j^2] = \mathbf{L}_j [\mathbf{L}_i, \mathbf{L}_j] + [\mathbf{L}_i, \mathbf{L}_j] \mathbf{L}_j = i\hbar \left(\mathbf{L}_j \sum_k \epsilon_{ijk} \mathbf{L}_k + \left(\sum_k \epsilon_{ijk} \mathbf{L}_k \right) \mathbf{L}_j \right) \neq 0$$

because this is a sum only over k, can't combine and cancel terms. See detail on next page.

for $i=x, j=y$

$$[\mathbf{L}_x, \mathbf{L}_y^2] = \mathbf{L}_y [\mathbf{L}_x, \mathbf{L}_y] + [\mathbf{L}_x, \mathbf{L}_y] \mathbf{L}_y = i\hbar [\mathbf{L}_y \mathbf{L}_z + \mathbf{L}_z \mathbf{L}_y] \neq 0!$$

so we have shown

$$[\mathbf{L}^2, \mathbf{L}_i] = 0$$

$$[\mathbf{L}^2, f(\mathbf{r})] = 0$$

$$[\mathbf{L}_i, f(\mathbf{r})] = 0$$

$$[\mathbf{L}^2, \mathbf{p}_r] = 0$$

$$[\mathbf{L}_i, \mathbf{p}_r] = 0$$

$\therefore \mathbf{L}^2, \mathbf{L}_i, \mathbf{H}$ all commute — Complete Set of Mutually Commuting Operators

eigenfunction of \mathbf{L}^2 with
eigenvalue $\hbar^2 L(L+1)$

So what does this tell us about $\langle \mathbf{L} | \mathbf{H} | \mathbf{L}' \rangle = ?$ also $\langle M_L | \mathbf{H} | M'_L \rangle$

$$L_z |LM_L\rangle = \hbar M_L |LM_L\rangle$$

$$\text{Both } H_{LL'} = 0 \text{ and } H_{M_L, M'_L} = 0$$

BLOCK DIAGONALIZATION OF \mathbf{H} !

Basis functions

$$\psi = \underbrace{\chi(\mathbf{r})}_{\text{radial special}} \underbrace{|L^2, L_z\rangle}_{\text{angular universal}} = |nLM_L\rangle$$

└─ eigenfunctions of \mathbf{L}_z
└─ eigenfunctions of \mathbf{L}^2
└─ which radial eigenfunction?

Next time I will show, starting from

$$[\mathbf{L}_i, \mathbf{L}_j] = i\hbar \sum_k \epsilon_{ijk} \mathbf{L}_k, \text{ that}$$

$$* \quad \mathbf{L}^2 |nLM_L\rangle = \hbar^2 L(L+1) |nLM_L\rangle \quad L = 0, 1, \dots$$

$$* \quad \mathbf{L}_z |nLM_L\rangle = \hbar M_L |nLM_L\rangle \quad M_L = -L, -L+1, \dots, L$$

also derive all \mathbf{L}_x and \mathbf{L}_y matrix elements in $|nLM_L\rangle$ basis set.

Translation and Rotation Operators

We are interested in QM operators that cause translation or rotation of an initially localized state: $|x_0, y_0, z_0\rangle$ or $|\alpha_0, \beta_0, \gamma_0\rangle$ (where α, β, γ are Euler angles that relate the body-fixed axis system to the laboratory-fixed axis system).

Translations are related to $\hat{p}_x, \hat{p}_y, \hat{p}_z$ operators and rotations are related to $\hat{L}_x, \hat{L}_y, \hat{L}_z$ operators. How do we demonstrate these relationships?

Begin by asking what does $e^{-i\hat{p}_x\delta/\hbar}$ do to an initially localized state $|x_0, y_0, z_0\rangle$.

An initially localized state is an eigenfunction of $\hat{x}, \hat{y}, \hat{z}$ operators

$$\hat{x}|x_0, y_0, z_0\rangle = x_0|x_0, y_0, z_0\rangle$$

similarly for \hat{y} and \hat{z}

What does $e^{-i\hat{p}_x\delta/\hbar}$ do to $|x_0, y_0, z_0\rangle$? We want to know to what eigenvalue(s) of \hat{x} does $e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle$ belong? We ask for $\hat{x}[e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle]$ and we use the

commutation rule $[\hat{x}, f(\hat{p}_x)] = i\hbar \frac{df}{dp_x}$

$$\hat{x}\left[e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle\right] = \left(e^{-i\hat{p}_x\delta/\hbar}\hat{x} + [\hat{x}, e^{-i\hat{p}_x\delta/\hbar}]\right)|x_0, y_0, z_0\rangle$$

$$f(\hat{p}_x) = e^{-i\hat{p}_x\delta/\hbar}$$

$$\frac{df}{dp_x} = (-i\delta/\hbar)e^{-i\hat{p}_x\delta/\hbar}$$

$$[\hat{x}, f(\hat{p}_x)] = (i\hbar)(-i\delta/\hbar)e^{-i\hat{p}_x\delta/\hbar} = \delta e^{-i\hat{p}_x\delta/\hbar}$$

Put it all together:

$$\hat{x}\left[e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle\right] = e^{-i\hat{p}_x\delta/\hbar}[x_0 + \delta]|x_0, y_0, z_0\rangle$$

$$\hat{x}\left[e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle\right] = (x_0 + \delta)\left[e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle\right]$$

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This means that $e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle$ belongs to the $(x_0 + \delta)$ eigenvalue of \hat{x} !

$$e^{-i\hat{p}_x\delta/\hbar}|x_0, y_0, z_0\rangle = |x_0 + \delta, y_0, z_0\rangle$$

So we know how to build an operator that causes translations of a localized state in the x , y , or z directions: $\hat{T}_x, \hat{T}_y, \hat{T}_z$.

But we know that $[\hat{p}_i, \hat{p}_j] = 0$ for all components of linear momentum. This means that for all linear translations, $[\hat{T}_i, \hat{T}_j] = 0$. *The sequence of the linear translations does not matter!* What about rotations of the initially localized state $|\alpha_0, \beta_0, \gamma_0\rangle$?

What does $e^{-i\phi\hat{L}_z/\hbar}$ do to $|\alpha_0, \beta_0, \gamma_0\rangle$?

Consider

$$\hat{\alpha} \left[e^{-i\phi\hat{L}_z/\hbar} |\alpha_0, \beta_0, \gamma_0\rangle \right].$$

Following an argument similar to that for the translational operators

$$\hat{\alpha} e^{-i\phi\hat{L}_z/\hbar} |\alpha_0, \beta_0, \gamma_0\rangle = (\alpha_0 + \phi) e^{-i\phi\hat{L}_z/\hbar} |\alpha_0, \beta_0, \gamma_0\rangle$$

$\hat{\alpha} e^{-i\phi\hat{L}_z/\hbar} |\alpha_0, \beta_0, \gamma_0\rangle$ belongs to the $\alpha_0 + \phi$ eigenvalue of $\hat{\alpha}$.

Now show something beautiful: that infinitesimal rotations about different axes do not commute!

$$e^{-i\phi\hat{L}_z/\hbar} e^{-i\theta\hat{L}_y/\hbar} |\alpha_0, \beta_0, \gamma_0\rangle = \left(e^{-i\theta\hat{L}_y/\hbar} e^{-i\phi\hat{L}_z/\hbar} + \left[e^{-i\phi\hat{L}_z/\hbar}, e^{-i\theta\hat{L}_y/\hbar} \right] \right) |\alpha_0, \beta_0, \gamma_0\rangle$$

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Expand the exponentials for infinitesimal θ, ϕ : 1st two terms in the power series expansion of $e^{-i\alpha}$: $1 - i\alpha$.

$$\begin{aligned} \left[e^{-i\theta\hat{L}_y/\hbar}, e^{-i\phi\hat{L}_z/\hbar} \right] &= [1, 1] - [1, -i\phi\hat{L}_z/\hbar] + [-i\theta\hat{L}_y/\hbar, 1] - \left(-\frac{i}{\hbar} \right) [\phi\hat{L}_z, \theta\hat{L}_y] \\ &= 0 + 0 + 0 + \left(-\frac{i}{\hbar} \right) (\phi\theta) i\hbar\hat{L}_x \end{aligned}$$

Reversing the order of the rotations about the y and z axes results in a *non-zero* rotation by $\theta\phi$ about the x -axis!

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