Radial momentum operator and angular momentum operator

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton

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Here we discuss the expressions of radial momentum in the quantum mechanics in the spherical coordinate and cylindrical coordinate. The obvious candidate for the radial momentum is $\hat{p}_r = \dfrac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}\cdot\hat{\boldsymbol{p}}$, where $\dfrac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}$ is the unit vector in the radial direction. Unfortunately, this operator is nor Hermitian. So it is not observable. We newly define the symmetric operator given by

$$\hat{p}_r = \frac{1}{2}\left(\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}\cdot\hat{\boldsymbol{p}} + \hat{\boldsymbol{p}}\cdot\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}\right),$$

as the radial momentum. This operator is Hermitian.

1. Definition Angular momentum

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}},$$

$$\hat{\boldsymbol{L}}^2 = \hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{L}} = (\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})\cdot(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}) = \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + i\hbar(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}). \qquad (1)$$

The proof of this is straightforward:

$$\begin{aligned}
\hat{L}_x{}^2 &= (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y)(\hat{y}\hat{p}_z - \hat{z}\hat{p}_y) \\
&= \hat{y}\hat{p}_z\hat{y}\hat{p}_z - \hat{y}\hat{p}_z\hat{z}\hat{p}_y - \hat{z}\hat{p}_y\hat{y}\hat{p}_z + \hat{z}\hat{p}_y\hat{z}\hat{p}_y \\
&= \hat{y}^2\hat{p}_z{}^2 + \hat{z}^2\hat{p}_y{}^2 - (\hat{y}\hat{p}_y\hat{p}_z\hat{z} + \hat{z}\hat{p}_z\hat{p}_y\hat{y}) \\
&= \hat{y}^2\hat{p}_z{}^2 + \hat{z}^2\hat{p}_y{}^2 - [\hat{y}\hat{p}_y(\hat{z}\hat{p}_z - i\hbar\hat{1}) + \hat{z}\hat{p}_z(\hat{y}\hat{p}_y - i\hbar\hat{1})] \\
&= \hat{y}^2\hat{p}_z{}^2 + \hat{z}^2\hat{p}_y{}^2 - (\hat{y}\hat{p}_y\hat{z}\hat{p}_z + \hat{z}\hat{p}_z\hat{y}\hat{p}_y) + i\hbar(\hat{y}\hat{p}_y + \hat{z}\hat{p}_z)
\end{aligned}$$

$$\begin{aligned}
\hat{L}_y{}^2 &= (\hat{z}\hat{p}_x - \hat{x}\hat{p}_z)(\hat{z}\hat{p}_x - \hat{x}\hat{p}_z) \\
&= \hat{z}^2\hat{p}_x{}^2 + \hat{x}^2\hat{p}_z{}^2 - (\hat{z}\hat{p}_z\hat{p}_x\hat{x} + \hat{x}\hat{p}_x\hat{p}_z\hat{z}) \\
&= \hat{z}^2\hat{p}_x{}^2 + \hat{x}^2\hat{p}_z{}^2 - (\hat{z}\hat{p}_z\hat{x}\hat{p}_x + \hat{x}\hat{p}_x\hat{z}\hat{p}_z) + i\hbar(\hat{z}\hat{p}_z + \hat{x}\hat{p}_x)
\end{aligned}$$

$$\hat{L}_z{}^2 = (\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x)$$
$$= \hat{x}^2\hat{p}_y{}^2 + \hat{y}^2\hat{p}_x{}^2 - (\hat{x}\hat{p}_x\hat{p}_y\hat{y} + \hat{y}\hat{p}_y\hat{p}_x\hat{x})$$
$$= \hat{x}^2\hat{p}_y{}^2 + \hat{y}^2\hat{p}_x{}^2 - (\hat{x}\hat{p}_x\hat{y}\hat{p}_y + \hat{y}\hat{p}_y\hat{x}\hat{p}_x) + i\hbar(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y)$$

Then we get

$$\hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2 = \hat{x}^2(\hat{p}_y{}^2 + \hat{p}_z{}^2) + \hat{y}^2(\hat{p}_z{}^2 + \hat{p}_x{}^2) + \hat{z}^2(\hat{p}_x{}^2 + \hat{p}_y{}^2)$$
$$- (\hat{y}\hat{p}_y\hat{z}\hat{p}_z + \hat{z}\hat{p}_z\hat{y}\hat{p}_y + \hat{z}\hat{p}_z\hat{x}\hat{p}_x + \hat{x}\hat{p}_x\hat{z}\hat{p}_z + \hat{x}\hat{p}_x\hat{y}\hat{p}_y + \hat{y}\hat{p}_y\hat{x}\hat{p}_x)$$
$$+ 2i\hbar(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z)$$

$$\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 = (\hat{x}^2 + \hat{y}^2 + \hat{z}^2)(\hat{p}_x{}^2 + \hat{p}_y{}^2 + \hat{p}_z{}^2)$$
$$= \hat{x}^2\hat{p}_x{}^2 + \hat{y}^2\hat{p}_y{}^2 + \hat{z}^2\hat{p}_z{}^2 + \hat{y}^2\hat{p}_z{}^2 + \hat{z}^2\hat{p}_y{}^2 + \hat{z}^2\hat{p}_x{}^2 + \hat{x}^2\hat{p}_z{}^2 + \hat{x}^2\hat{p}_y{}^2 + \hat{y}^2\hat{p}_x{}^2$$

$$(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 = (\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z)(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z)$$
$$= \hat{x}\hat{p}_x\hat{x}\hat{p}_x + \hat{y}\hat{p}_y\hat{y}\hat{p}_y + \hat{z}\hat{p}_z\hat{z}\hat{p}_z + \hat{x}\hat{p}_x\hat{y}\hat{p}_y + \hat{x}\hat{p}_x\hat{z}\hat{p}_z$$
$$+ \hat{y}\hat{p}_y\hat{x}\hat{p}_x + \hat{y}\hat{p}_y\hat{z}\hat{p}_z + \hat{z}\hat{p}_z\hat{x}\hat{p}_x + \hat{z}\hat{p}_z\hat{y}\hat{p}_y$$
$$= \hat{x}(\hat{x}\hat{p}_x - i\hbar\hat{1})\hat{p}_x + \hat{y}(\hat{y}\hat{p}_y - i\hbar\hat{1})\hat{p}_y + \hat{z}(\hat{z}\hat{p}_z - \hbar\hat{1})\hat{p}_z$$
$$+ \hat{x}\hat{p}_x\hat{y}\hat{p}_y + \hat{x}\hat{p}_x\hat{z}\hat{p}_z + \hat{y}\hat{p}_y\hat{x}\hat{p}_x + \hat{y}\hat{p}_y\hat{z}\hat{p}_z + \hat{z}\hat{p}_z\hat{x}\hat{p}_x + \hat{z}\hat{p}_z\hat{y}\hat{p}_y$$
$$= \hat{x}^2\hat{p}_x{}^2 + \hat{y}^2\hat{p}_y{}^2 + \hat{z}^2\hat{p}_z{}^2 - i\hbar(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z)$$
$$+ \hat{x}\hat{p}_x\hat{y}\hat{p}_y + \hat{x}\hat{p}_x\hat{z}\hat{p}_z + \hat{y}\hat{p}_y\hat{x}\hat{p}_x + \hat{y}\hat{p}_y\hat{z}\hat{p}_z + \hat{z}\hat{p}_z\hat{x}\hat{p}_x + \hat{z}\hat{p}_z\hat{y}\hat{p}_y$$

$$i\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} = i\hbar(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z),$$

where

$$[\hat{p}_x, \hat{x}] = -i\hbar\hat{1}, \qquad [\hat{p}_y, \hat{y}] = -i\hbar\hat{1}.$$

Thus we have

$$
\begin{aligned}
\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + i\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}} &= \hat{x}^2\hat{p}_x{}^2 + \hat{y}^2\hat{p}_y{}^2 + \hat{z}^2\hat{p}_z{}^2 + \hat{y}^2\hat{p}_z{}^2 + \hat{z}^2\hat{p}_y{}^2 + \hat{z}^2\hat{p}_x{}^2 \\
&\quad + \hat{x}^2\hat{p}_z{}^2 + \hat{x}^2\hat{p}_y{}^2 + \hat{y}^2\hat{p}_x{}^2 - (\hat{x}^2\hat{p}_x{}^2 + \hat{y}^2\hat{p}_y{}^2 + \hat{z}^2\hat{p}_z{}^2) \\
&\quad - (\hat{y}\hat{p}_y\hat{z}\hat{p}_z + \hat{z}\hat{p}_z\hat{y}\hat{p}_y + \hat{z}\hat{p}_z\hat{x}\hat{p}_x + \hat{x}\hat{p}_x\hat{z}\hat{p}_z + \hat{x}\hat{p}_x\hat{y}\hat{p}_y + \hat{y}\hat{p}_y\hat{x}\hat{p}_x) \\
&\quad + 2i\hbar(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z) \\
&= \hat{y}^2\hat{p}_z{}^2 + \hat{z}^2\hat{p}_y{}^2 + \hat{z}^2\hat{p}_x{}^2 + \hat{x}^2\hat{p}_z{}^2 + \hat{x}^2\hat{p}_y{}^2 + \hat{y}^2\hat{p}_x{}^2 \\
&\quad - (\hat{y}\hat{p}_y\hat{z}\hat{p}_z + \hat{z}\hat{p}_z\hat{y}\hat{p}_y + \hat{z}\hat{p}_z\hat{x}\hat{p}_x + \hat{x}\hat{p}_x\hat{z}\hat{p}_z + \hat{x}\hat{p}_x\hat{y}\hat{p}_y + \hat{y}\hat{p}_y\hat{x}\hat{p}_x) \\
&\quad + 2i\hbar(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z)
\end{aligned}
$$

Then we have

$$\hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2 = \hat{\boldsymbol{L}}^2 = \hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + i\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}$$

From this we get

$$
\begin{aligned}
\langle\boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle &= \langle\boldsymbol{r}|\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 + i\hbar(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})|\psi\rangle \\
&= r^2\langle\boldsymbol{r}|\hat{\boldsymbol{p}}^2|\psi\rangle - \langle\boldsymbol{r}|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2|\psi\rangle + i\hbar\langle\boldsymbol{r}|\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}|\psi\rangle
\end{aligned}
$$

where

$$
\begin{aligned}
\langle\boldsymbol{r}|\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2|\psi\rangle &= r^2\langle\boldsymbol{r}|\hat{\boldsymbol{p}}^2|\psi\rangle \\
&= -\hbar^2 r^2\nabla^2\langle\boldsymbol{r}|\psi\rangle
\end{aligned}
$$

and

$$
\begin{aligned}
-\langle\boldsymbol{r}|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2|\psi\rangle + i\hbar\langle\boldsymbol{r}|\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}|\psi\rangle &= -\left(\frac{\hbar}{i}\right)^2(\boldsymbol{r}\cdot\nabla)(\boldsymbol{r}\cdot\nabla)\langle\boldsymbol{r}|\psi\rangle + i\hbar\left(\frac{\hbar}{i}\right)(\boldsymbol{r}\cdot\nabla)\langle\boldsymbol{r}|\psi\rangle \\
&= -\left(\frac{\hbar}{i}\right)^2 r\frac{\partial}{\partial r}(r\frac{\partial}{\partial r})\psi(\boldsymbol{r}) + i\hbar\left(\frac{\hbar}{i}\right)(r\frac{\partial}{\partial r})\psi(\boldsymbol{r}) \\
&= \hbar^2(r\frac{\partial}{\partial r}r\frac{\partial}{\partial r} + r\frac{\partial}{\partial r})\psi(\boldsymbol{r}) \\
&= \hbar^2(r^2\frac{\partial^2}{\partial r^2} + 2r\frac{\partial}{\partial r})\psi(\boldsymbol{r})
\end{aligned}
$$

Here we note that

$$\langle \boldsymbol{r}|\hat{p}_r{}^2|\psi\rangle = -\hbar^2(\frac{\partial}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r})\psi(\boldsymbol{r}),$$ (which will be discussed later)

where $\hat{p}_r$ is the radial momentum in quantum mechanics. Then we get the expression

$$\langle \boldsymbol{r}|\hat{\boldsymbol{p}}^2|\psi\rangle = \frac{\langle \boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle}{r^2} + \langle \boldsymbol{r}|\hat{p}_r{}^2|\psi\rangle.$$

or

$$\boldsymbol{p}^2\psi(\boldsymbol{r}) = (p_r{}^2 + \frac{\boldsymbol{L}^2}{r^2})\psi(\boldsymbol{r})$$

(notation of the differential operator)

The Hamiltonian of the system is given by

$$\begin{aligned}\langle \boldsymbol{r}|\hat{H}|\psi\rangle &= \frac{1}{2\mu}\langle \boldsymbol{r}|\hat{\boldsymbol{p}}^2|\psi\rangle + V(|\boldsymbol{r}|)\langle \boldsymbol{r}|\psi\rangle \\ &= \frac{1}{2\mu}\langle \boldsymbol{r}|\hat{p}_r{}^2|\psi\rangle + \frac{\langle \boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle}{2\mu r^2} + V(|\boldsymbol{r}|)\langle \boldsymbol{r}|\psi\rangle\end{aligned}$$

or

$$H\psi(\boldsymbol{r}) = [\frac{1}{2\mu}p_r{}^2 + \frac{1}{2\mu r^2}\boldsymbol{L}^2 + V(r)]\psi(\boldsymbol{r})$$

The first term is the kinetic energy concerned with the radial momentum. The second term is the rotational energy. The third one is the potential energy.

((**Note**))

(i)

$$\langle \boldsymbol{r}|\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}|\psi\rangle = \boldsymbol{r}\cdot\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\psi\rangle = \frac{\hbar}{i}\boldsymbol{r}\cdot\nabla_r\psi(\boldsymbol{r}) = \frac{\hbar}{i}r\frac{\partial}{\partial r}\psi(\boldsymbol{r}),$$

(ii)

$$
\begin{aligned}
\langle \boldsymbol{r}|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2|\psi\rangle &= \langle \boldsymbol{r}|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})|\psi\rangle \\
&= \boldsymbol{r}\cdot\int\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\boldsymbol{r}'\rangle d\boldsymbol{r}'\langle \boldsymbol{r}'|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})|\psi\rangle \\
&= \boldsymbol{r}\cdot\int\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\boldsymbol{r}'\rangle d\boldsymbol{r}'\boldsymbol{r}'\cdot\langle \boldsymbol{r}'|\hat{\boldsymbol{p}}|\psi\rangle \\
&= \boldsymbol{r}\cdot\frac{\hbar}{i}\int\nabla_r\langle \boldsymbol{r}|\boldsymbol{r}'\rangle d\boldsymbol{r}'\boldsymbol{r}'\cdot\langle \boldsymbol{r}\cdot|\hat{\boldsymbol{p}}|\psi\rangle \\
&= \frac{\hbar}{i}\boldsymbol{r}\cdot\nabla_r\int\langle \boldsymbol{r}|\boldsymbol{r}'\rangle d\boldsymbol{r}'\boldsymbol{r}'\cdot\langle \boldsymbol{r}'\cdot|\hat{\boldsymbol{p}}|\psi\rangle \\
&= \frac{\hbar}{i}\boldsymbol{r}\cdot\nabla_r\int\delta(\boldsymbol{r}-\boldsymbol{r}')d\boldsymbol{r}'\boldsymbol{r}'\cdot\langle \boldsymbol{r}'|\hat{\boldsymbol{p}}|\psi\rangle \\
&= \frac{\hbar}{i}\boldsymbol{r}\cdot\nabla_r[\boldsymbol{r}\cdot\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\psi\rangle] \\
&= \frac{\hbar}{i}\boldsymbol{r}\cdot\nabla_r[\frac{\hbar}{i}\boldsymbol{r}\cdot\nabla_r\psi(\boldsymbol{r})] \\
&= \left(\frac{\hbar}{i}\right)^2(\boldsymbol{r}\cdot\nabla_r)(\boldsymbol{r}\cdot\nabla_r)\psi(\boldsymbol{r})
\end{aligned}
$$

or

$$
\langle \boldsymbol{r}|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2|\psi\rangle = \left(\frac{\hbar}{i}\right)^2(\boldsymbol{r}\cdot\nabla_r)(\boldsymbol{r}\cdot\nabla_r)\psi(\boldsymbol{r}).
$$

Using this relation $(\boldsymbol{r}\cdot\nabla_r)\psi(\boldsymbol{r}) = r\frac{\partial}{\partial r}\psi(\boldsymbol{r})$ twice, we get

$$
\langle \boldsymbol{r}|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2|\psi\rangle = \left(\frac{\hbar}{i}\right)^2(\boldsymbol{r}\cdot\nabla_r)(\boldsymbol{r}\cdot\nabla_r)\psi(\boldsymbol{r}) = -\hbar^2 r\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\psi(\boldsymbol{r}).
$$

(iii) Then we get the final form as

$$
\begin{aligned}
\frac{1}{r^2}\langle \boldsymbol{r}|(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2 - i\hbar(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})|\psi\rangle &= -\hbar^2\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\psi(\boldsymbol{r}) - \hbar^2\frac{1}{r}\frac{\partial}{\partial r}\psi(\boldsymbol{r}) \\
&= -\hbar^2(\frac{2}{r}\frac{\partial}{\partial r}+\frac{\partial^2}{\partial r^2})\psi(\boldsymbol{r})
\end{aligned}
$$

((**Mathematica**))

Proof of

$$\frac{1}{r^2}[\frac{\hbar}{i}(\boldsymbol{r}\cdot\nabla)\frac{\hbar}{i}(\boldsymbol{r}\cdot\nabla)\psi(\boldsymbol{r})-i\hbar\frac{\hbar}{i}(\boldsymbol{r}\cdot\nabla)\psi(\boldsymbol{r})]$$
$$=-\hbar^2(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r})\psi(\boldsymbol{r})$$

by using Mathematica.

```
Clear["Global`"]; ur = {1, 0, 0};
Gra := Grad[#, { r, θ, ϕ}, "Spherical"] &;
OP := (ℏ/ⅈ) r (ur.Gra[#]) &;

eq1 = (1/r^2) (Nest[OP, ψ[r, θ, ϕ], 2] - ⅈ ℏ OP[ψ[r, θ, ϕ]]) //
   Simplify
```

$$-\frac{\hbar^2\left(2\,\psi^{(1,0,0)}[r,\theta,\phi]+r\,\psi^{(2,0,0)}[r,\theta,\phi]\right)}{r}$$

2. Proof of $\hat{\boldsymbol{L}}^2=\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2-(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2+i\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}}$ (Sakurai)

The proof of the formula

$$\hat{\boldsymbol{L}}^2=\hat{\boldsymbol{r}}^2\hat{\boldsymbol{p}}^2-(\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}})^2+i\hbar\hat{\boldsymbol{r}}\cdot\hat{\boldsymbol{p}},$$

is given by Sakurai (Quantum mechanics) as follows.

$$\hat{\boldsymbol{L}}^2=\sum_i(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})_i(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}})_i$$
$$=\sum_i\sum_{jk}\varepsilon_{ijk}\hat{x}_j\hat{p}_k\sum_{lm}\varepsilon_{ilm}\hat{x}_l\hat{p}_m$$

We use the identity

$$\sum_i\varepsilon_{ijk}\varepsilon_{ilm}=\delta_{jl}\delta_{km}-\delta_{jm}\delta_{kl}.$$

Then we get

$$\hat{\boldsymbol{L}}^2 = \sum_{jklm} (\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl})\hat{x}_j \hat{p}_k \hat{x}_l \hat{p}_m$$
$$= \sum_{jk} (\hat{x}_j \hat{p}_k \hat{x}_j \hat{p}_k - \hat{x}_j \hat{p}_k \hat{x}_k \hat{p}_j)$$

Using the commutation relation

$$[\hat{x}_j, \hat{p}_k] = i\hbar\hat{1}\delta_{jk},$$

we have

$$\hat{\boldsymbol{L}}^2 = \sum_{jk} [\hat{x}_j (\hat{x}_j \hat{p}_k - i\hbar\delta_{jk})\hat{p}_k - \hat{x}_j \hat{p}_k (\hat{p}_j \hat{x}_k + i\hbar\hat{1}\delta_{jk})]$$
$$= \sum_{jk} (\hat{x}_j \hat{x}_j \hat{p}_k \hat{p}_k - 2i\hbar\delta_{jk}\hat{x}_j \hat{p}_k - \hat{x}_j \hat{p}_k \hat{p}_j \hat{x}_k)$$
$$= \sum_{jk} (\hat{x}_j \hat{x}_j \hat{p}_k \hat{p}_k - 2i\hbar\delta_{jk}\hat{x}_j \hat{p}_k - \hat{x}_j \hat{p}_j (\hat{x}_k \hat{p}_k - i\hbar\hat{1})$$
$$= \sum_{jk} (\hat{x}_j \hat{x}_j \hat{p}_k \hat{p}_k - \hat{x}_j \hat{p}_j \hat{x}_k \hat{p}_k) - 2i\hbar\sum_{jk}\delta_{jk}\hat{x}_j \hat{p}_k + i\hbar\sum_{jk}\hat{x}_j \hat{p}_j$$
$$= \sum_{jk} (\hat{x}_j \hat{x}_j \hat{p}_k \hat{p}_k - \hat{x}_j \hat{p}_j \hat{x}_k \hat{p}_k) - 2i\hbar\sum_{j}\hat{x}_j \hat{p}_j + 3i\hbar\sum_{j}\hat{x}_j \hat{p}_j$$
$$= \sum_{jk} \hat{x}_j \hat{x}_j \hat{p}_k \hat{p}_k - \sum_{jk}\hat{x}_j \hat{p}_j \hat{x}_k \hat{p}_k + i\hbar\sum_{j}\hat{x}_j \hat{p}_j$$

Then we obtain

$$\hat{\boldsymbol{L}}^2 = \hat{\boldsymbol{r}}^2 \hat{\boldsymbol{p}}^2 - (\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{p}})^2 + i\hbar\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{p}}.$$

3. Definition of the radial momentum operator in the quantum mechanics

(a) In classical mechanics, the radial momentum of the radius r is defined by

$$p_{rc} = \frac{1}{r}(\boldsymbol{r} \cdot \boldsymbol{p}).$$

(b) In quantum mechanics, this definition becomes ambiguous since the component of p and r do not commute. Since p_{r} should be Hermitian operator, we need to define as the radial momentum of the radius r is defined by

$$\hat{p}_r = \frac{1}{2}(\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}\cdot\hat{\boldsymbol{p}} + \hat{\boldsymbol{p}}\cdot\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}) .$$

Note that

$$\langle \boldsymbol{r}|\hat{p}_r|\psi\rangle = (-i\hbar)(\frac{\partial}{\partial r} + \frac{1}{r})\psi(\boldsymbol{r}) = (-i\hbar)\frac{1}{r}\frac{\partial}{\partial r} r\psi(\boldsymbol{r}) ,$$

$$\begin{aligned}
\langle r|\hat{p}_r{}^2|\psi\rangle &= (-i\hbar)\frac{1}{r}\frac{\partial}{\partial r} r(-i\hbar)\frac{1}{r}\frac{\partial}{\partial r} r\psi(\boldsymbol{r}) \\
&= -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2} r\psi(\boldsymbol{r}) \\
&= -\hbar^2(\frac{2}{r}\frac{\partial}{\partial r} + \frac{\partial}{\partial r^2})\psi(\boldsymbol{r})
\end{aligned}$$

((**Proof**))

$$\begin{aligned}
\langle \boldsymbol{r}|\hat{p}_r|\psi\rangle &= \frac{1}{2}\langle \boldsymbol{r}|\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}\cdot\hat{\boldsymbol{p}} + \hat{\boldsymbol{p}}\cdot\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|})|\psi\rangle \\
&= \frac{1}{2}\frac{\boldsymbol{r}}{|\boldsymbol{r}|}\cdot\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\psi\rangle + \frac{1}{2}\langle \boldsymbol{r}|\hat{\boldsymbol{p}}\cdot\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|})|\psi\rangle \\
&= \frac{1}{2}\boldsymbol{e}_r\cdot\frac{\hbar}{i}\nabla_r\psi(\boldsymbol{r}) + \frac{1}{2}\int\langle \boldsymbol{r}|\hat{\boldsymbol{p}}|\boldsymbol{r}'\rangle d\boldsymbol{r}'\cdot\langle \boldsymbol{r}'|\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|})|\psi\rangle \\
&= \frac{1}{2}\boldsymbol{e}_r\cdot\frac{\hbar}{i}\nabla_r\psi(\boldsymbol{r}) + \frac{\hbar}{2i}\int\nabla_r\langle \boldsymbol{r}|\boldsymbol{r}'\rangle d\boldsymbol{r}'\cdot\langle \boldsymbol{r}'|\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|})|\psi\rangle \\
&= \frac{1}{2}\boldsymbol{e}_r\cdot\frac{\hbar}{i}\nabla_r\psi(\boldsymbol{r}) + \frac{\hbar}{2i}\nabla_r\int\delta(\boldsymbol{r}-\boldsymbol{r}')d\boldsymbol{r}'\cdot\frac{\boldsymbol{r}'}{|\boldsymbol{r}'|}\langle \boldsymbol{r}'|\psi\rangle \\
&= \frac{\hbar}{2i}[\boldsymbol{e}_r\cdot\nabla\psi(\boldsymbol{r}) + \nabla\cdot[\frac{\boldsymbol{r}}{|\boldsymbol{r}|}\langle \boldsymbol{r}|\psi\rangle]
\end{aligned}$$

or simply, we get

$$
\begin{aligned}
\langle \boldsymbol{r}|\hat{p}_r|\psi\rangle &= \frac{\hbar}{2i}[\boldsymbol{e}_r\cdot\nabla\psi(\boldsymbol{r}) + \nabla\cdot[\frac{\boldsymbol{r}}{|\boldsymbol{r}|}\psi(\boldsymbol{r})] \\
&= \frac{\hbar}{2i}[\frac{\partial}{\partial r}\psi(\boldsymbol{r}) + (\frac{\partial}{\partial r}+\frac{2}{r})\psi(\boldsymbol{r})] \\
&= \frac{\hbar}{i}(\frac{\partial}{\partial r}+\frac{1}{r})\psi(\boldsymbol{r}) \\
&= \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}[r\psi(\boldsymbol{r})]
\end{aligned}
.
$$

Then we have

$$
p_r = \frac{\hbar}{i}(\frac{\partial}{\partial r}+\frac{1}{r}), \qquad \text{or} \qquad p_r = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r.
$$

(notation of the differential operator)
((**Note**))
(i)

$$
\boldsymbol{e}_r\cdot\nabla\psi = \frac{\partial}{\partial r}\psi,
$$

(ii)

$$
\begin{aligned}
\nabla\cdot[\frac{\boldsymbol{r}}{r}\psi] &= \frac{\partial}{\partial x}[\frac{x}{r}\psi(\boldsymbol{r})] + \frac{\partial}{\partial y}[\frac{y}{r}\psi(\boldsymbol{r})] + \frac{\partial}{\partial z}[\frac{z}{r}\psi(\boldsymbol{r})] \\
&= \frac{3}{r}\psi(\boldsymbol{r}) + x\frac{\partial}{\partial x}[\frac{1}{r}\psi(\boldsymbol{r})] + y\frac{\partial}{\partial y}[\frac{1}{r}\psi(\boldsymbol{r})] + z\frac{\partial}{\partial z}[\frac{1}{r}\psi(\boldsymbol{r})] \\
&= \frac{3}{r}\psi(\boldsymbol{r}) + (\boldsymbol{r}\cdot\nabla)[\frac{1}{r}\psi(\boldsymbol{r})] \\
&= \frac{3}{r}\psi(\boldsymbol{r}) + r\frac{\partial}{\partial r}[\frac{1}{r}\psi(\boldsymbol{r})] \\
&= \frac{3}{r}\psi(\boldsymbol{r}) + r[\frac{1}{r}\frac{\partial}{\partial r}\psi(\boldsymbol{r}) - \frac{1}{r^2}\psi(\boldsymbol{r})] \\
&= (\frac{\partial}{\partial r}+\frac{2}{r})\psi(\boldsymbol{r})
\end{aligned}
$$

((**Mathematica**))
Proof

$$\boldsymbol{e}_r \cdot \nabla \psi(\boldsymbol{r}) = \frac{\partial}{\partial r}\psi(\boldsymbol{r}), \qquad \nabla \cdot [\frac{\boldsymbol{r}}{|\boldsymbol{r}|}\psi(\boldsymbol{r})] = (\frac{\partial}{\partial r} + \frac{2}{r})\psi(\boldsymbol{r}).$$

by using Mathematica

```
Clear["Global`"]; ur = {1, 0, 0};
Gra := Grad[#, { r, θ, ϕ}, "Spherical"] &;
Diva := Div[#,  { r, θ, ϕ}, "Spherical"] &;

ur.Gra[ψ[r, θ, ϕ]] // Simplify
ψ^(1,0,0)[r, θ, ϕ]

Diva[ur ψ[r, θ, ϕ]] // Simplify
2 ψ[r, θ, ϕ]/r + ψ^(1,0,0)[r, θ, ϕ]
```

(c) The commutation relation:

$$[\hat{p}_r, |\hat{\boldsymbol{r}}|] = \frac{\hbar}{i}\hat{1},$$

or

$$\hat{p}_r|\hat{\boldsymbol{r}}| - |\hat{\boldsymbol{r}}|\hat{p}_r = \frac{\hbar}{i}\hat{1}. \qquad \text{(Commutation relation)}$$

((**Proof**))

$$\begin{aligned}
\langle \boldsymbol{r}|(\hat{p}_r|\hat{\boldsymbol{r}}| - |\hat{\boldsymbol{r}}|\hat{p}_r)|\psi\rangle &= \langle \boldsymbol{r}|\hat{p}_r|\hat{\boldsymbol{r}}||\psi\rangle - \langle \boldsymbol{r}||\hat{\boldsymbol{r}}|\hat{p}_r)|\psi\rangle \\
&= \int \langle \boldsymbol{r}|\hat{p}_r|\boldsymbol{r}'\rangle d\boldsymbol{r}'\langle \boldsymbol{r}'||\hat{\boldsymbol{r}}||\psi\rangle - r\langle \boldsymbol{r}|\hat{p}_r|\psi\rangle \\
&= \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r} r\int \delta(\boldsymbol{r}-\boldsymbol{r}')d\boldsymbol{r}'r'\langle \boldsymbol{r}'|\psi\rangle - r\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}[r\langle \boldsymbol{r}|\psi\rangle] \\
&= \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}[r^2\langle \boldsymbol{r}|\psi\rangle] - \frac{\hbar}{i}\frac{\partial}{\partial r}[r\langle \boldsymbol{r}|\psi\rangle]
\end{aligned}$$

or simply, we get

$$\langle \boldsymbol{r}|(\hat{p}_r|\hat{\boldsymbol{r}}|-|\hat{\boldsymbol{r}}|\hat{p}_r)|\psi\rangle = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}[r^2\psi(\boldsymbol{r})] - \frac{\hbar}{i}\frac{\partial}{\partial r}[r\langle \boldsymbol{r}|\psi\rangle]$$
$$= \frac{\hbar}{i}[2\psi(\boldsymbol{r}) + r\frac{\partial}{\partial r}\psi(\boldsymbol{r}) - r\frac{\partial}{\partial r}\psi(\boldsymbol{r}) - \psi(\boldsymbol{r})]$$
$$= \frac{\hbar}{i}\psi(\boldsymbol{r})$$

((**Mathematica**))

Commutation relation $\hat{p}_r|\hat{\boldsymbol{r}}|-|\hat{\boldsymbol{r}}|\hat{p}_r = \frac{\hbar}{i}\hat{1}$ in the spherical coordinate (Mathematica)

```
Clear["Global`"]; ur = {1, 0, 0};
Gra := Grad[#, {r, θ, ϕ}, "Spherical"] &;
Diva := Div[#, {r, θ, ϕ}, "Spherical"] &;
prc := (ℏ/ⅈ ur.Gra[#] &);

prc[ψ[r, θ, ϕ]]
-ⅈ ℏ ψ^(1,0,0)[r, θ, ϕ]

prq := ((-ⅈ ℏ)/2 ur .Gra[#] + (-ⅈ ℏ)/2 Diva[# ur]) &;

prq[ψ[r, θ, ϕ]] // Simplify
-(ⅈ ℏ (ψ[r, θ, ϕ] + r ψ^(1,0,0)[r, θ, ϕ]))/r
```

Commutation relation

```
prq[r ψ[r, θ, ϕ]] - r prq[ψ[r, θ, ϕ]] // Simplify
-ⅈ ℏ ψ[r, θ, ϕ]
```

4. In-coming and out-going spherical waves

The wave function of the spherical wave is given by

$$\psi(r) = \frac{e^{\pm ikr}}{r},$$

with the incoming spherical wave (-), and outgoing wave (+). Here we show that

$$
\begin{aligned}
p_r\psi &= \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{e^{\pm ikr}}{r}\right) \\
&= \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}(e^{\pm ikr}) \\
&= \pm\hbar k\frac{e^{\pm ikr}}{r} \\
&= \pm\hbar k\psi
\end{aligned},
$$

where $\psi(r)$ is the eigenket of the radial momentum p_r with the eigenvalue $\pm\hbar k$

((**Mathematica**))

```
Clear["Global`*"]; pr := ℏ/ⅈ 1/r D[r #, r] &;

ψ1 = Exp[ⅈ k r]/r; ψ2 = Exp[- ⅈ k r]/r;

pr[ψ1] // Simplify
```

$$\frac{e^{i k r} k \hbar}{r}$$

```
Nest[pr, ψ1, 2] // Simplify
```

$$\frac{e^{i k r} k^2 \hbar^2}{r}$$

```
pr[ψ2] // Simplify
```

$$-\frac{e^{-i k r} k \hbar}{r}$$

```
Nest[pr, ψ2, 2] // Simplify
```

$$\frac{e^{-i k r} k^2 \hbar^2}{r}$$

5. Hermitian operator

$$\langle \boldsymbol{r}|\hat{p}_r|\psi\rangle = (-i\hbar)(\frac{\partial}{\partial r}+\frac{1}{r})\psi(\boldsymbol{r}) = (-i\hbar)\frac{1}{r}\frac{\partial}{\partial r}r\psi(\boldsymbol{r}) .$$

We show that $\hat{p}_r$ is a Hermitian operator.

From the definition of the Hermite conjugate operator, we have in general,

$$\langle \psi_1|\hat{p}_r|\psi_2\rangle^* = \langle \psi_2|\hat{p}_r{}^+|\psi_1\rangle .$$

When $\hat{p}_r = \hat{p}_r{}^+$ (Hermitian), we get the relation

$$\langle \psi_1|\hat{p}_r|\psi_2\rangle^* = \langle \psi_2|\hat{p}_r|\psi_1\rangle .$$

((**Proof**))

$$\begin{aligned}
\langle \psi_1|\hat{p}_r|\psi_2\rangle &= \int d\boldsymbol{r}\langle \psi_1|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\hat{p}_r|\psi_2\rangle \\
&= \int d\Omega\int r^2 dr\langle \psi_1|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\hat{p}_r|\psi_2\rangle \\
&= \int d\Omega\int r^2 dr\,\psi_1^*(\boldsymbol{r})\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}[r\psi_2(\boldsymbol{r})] \\
&= \frac{\hbar}{i}\int d\Omega\int dr r\psi_1^*(\boldsymbol{r})\frac{\partial}{\partial r}[r\psi_2(\boldsymbol{r})] \\
&= -\frac{\hbar}{i}\int d\Omega\int dr r\psi_2(\boldsymbol{r})\frac{\partial}{\partial r}[r\psi_1^*(\boldsymbol{r})]
\end{aligned}$$

$$\begin{aligned}
\langle \psi_1|\hat{p}_r|\psi_2\rangle^* &= \frac{\hbar}{i}\int d\Omega\int dr r\psi_2^*(\boldsymbol{r})\frac{\partial}{\partial r}[r\psi_1(\boldsymbol{r})] \\
&= \frac{\hbar}{i}\int d\Omega\int r^2 dr\,\psi_2^*(\boldsymbol{r})\frac{1}{r}\frac{\partial}{\partial r}[r\psi_1(\boldsymbol{r})] \\
&= \langle \psi_2|\hat{p}_r|\psi_1\rangle
\end{aligned}$$

where Ω is an solid angle. $d\Omega = \sin\theta d\theta d\phi$. $d\boldsymbol{r} = r^2 d\Omega$.

6. The angular momentum in the position space

Here we note that in quantum mechanics, we have

$$\langle \boldsymbol{r}|\hat{\boldsymbol{L}}|\psi\rangle = \langle \boldsymbol{r}|\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}|\psi\rangle = \frac{\hbar}{i}\boldsymbol{r}\times\nabla\psi(\boldsymbol{r}),$$

and

$$\begin{aligned}
\langle \boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle &= r^2\langle \boldsymbol{r}|\hat{\boldsymbol{p}}^2|\psi\rangle - r^2\langle \boldsymbol{r}|\hat{p}_r{}^2|\psi\rangle \\
&= r^2[-\hbar^2\nabla^2\psi(\boldsymbol{r})] - r^2\left(\frac{\hbar}{i}\right)^2\frac{1}{r}\frac{\partial}{\partial r}r\frac{1}{r}\frac{\partial}{\partial r}[r\psi(\boldsymbol{r})] \\
&= \hbar^2[-r^2\nabla^2\psi(\boldsymbol{r}) + r^2\frac{\partial^2}{\partial r^2}[r\psi(\boldsymbol{r})]
\end{aligned}$$

or

$$\langle \boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle = \boldsymbol{L}^2\psi(\boldsymbol{r}) = \hbar^2\{-r^2\nabla^2\psi(\boldsymbol{r}) + r^2\frac{\partial^2}{\partial r^2}[r\psi(\boldsymbol{r})]\}$$

For simplicity, here, we use the differential operator for the angular momentum such that

$$\boldsymbol{L}\psi(r) = \frac{\hbar}{i}\boldsymbol{r}\times\nabla\psi(\boldsymbol{r}),$$

$$\boldsymbol{L}^2\psi(\boldsymbol{r}) = \langle \boldsymbol{r}|\hat{\boldsymbol{L}}^2|\psi\rangle = \hbar^2[-r^2\nabla^2\psi(\boldsymbol{r}) + r\frac{\partial^2}{\partial r^2}[r\psi(\boldsymbol{r})].$$

7. Angular momentum in the spherical coordinates

In the spherical coordinate, the unit vectors are given by

$$\boldsymbol{e}_r = \frac{\partial\boldsymbol{r}}{\partial s_r} = \frac{\partial\boldsymbol{r}}{\partial r} = \sin\theta\cos\phi\boldsymbol{e}_x + \sin\theta\sin\phi\boldsymbol{e}_y + \cos\theta\boldsymbol{e}_z,$$

$$\boldsymbol{e}_\theta = \frac{\partial\boldsymbol{r}}{\partial s_\theta} = \frac{1}{r}\frac{\partial\boldsymbol{r}}{\partial\theta} = \cos\theta\cos\phi\boldsymbol{e}_x + \cos\theta\sin\phi\boldsymbol{e}_y - \sin\theta\boldsymbol{e}_z,$$

$$\boldsymbol{e}_\phi = \frac{\partial\boldsymbol{r}}{\partial s_\phi} = \frac{1}{r\sin\theta}\frac{\partial\boldsymbol{r}}{\partial\phi} = -\sin\phi\boldsymbol{e}_x + \cos\phi\boldsymbol{e}_y,$$

where

$$ds_r = dr\,, \qquad ds_\theta = rd\theta\,, \qquad ds_\phi = r\sin\theta d\phi\,.$$

The gradient operator can be written as

$$\begin{aligned}\nabla &= \boldsymbol{e}_r\frac{\partial}{\partial s_r} + \boldsymbol{e}_\theta\frac{\partial}{\partial s_\theta} + \boldsymbol{e}_\phi\frac{\partial}{\partial s_\phi} \\ &= \boldsymbol{e}_r\frac{\partial}{\partial r} + \boldsymbol{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \boldsymbol{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\end{aligned}$$

where

$$\boldsymbol{r} = r\sin\theta\cos\phi\boldsymbol{e}_x + r\sin\theta\sin\phi\boldsymbol{e}_y + r\cos\theta\boldsymbol{e}_z\,,$$

or

$$\begin{pmatrix}\boldsymbol{e}_r \\ \boldsymbol{e}_\theta \\ \boldsymbol{e}_\phi\end{pmatrix} = A\begin{pmatrix}\boldsymbol{e}_x \\ \boldsymbol{e}_y \\ \boldsymbol{e}_z\end{pmatrix} = \begin{pmatrix}\sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ \cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta \\ -\sin\phi & \cos\phi & 0\end{pmatrix}\begin{pmatrix}\boldsymbol{e}_x \\ \boldsymbol{e}_y \\ \boldsymbol{e}_z\end{pmatrix},$$

or

$$\begin{pmatrix}\boldsymbol{e}_x \\ \boldsymbol{e}_y \\ \boldsymbol{e}_z\end{pmatrix} = A^T\begin{pmatrix}\boldsymbol{e}_r \\ \boldsymbol{e}_\theta \\ \boldsymbol{e}_\phi\end{pmatrix} = \begin{pmatrix}\sin\theta\cos\phi & \cos\theta\cos\phi & -\sin\phi \\ \sin\theta\sin\phi & \cos\theta\sin\phi & \cos\phi \\ \cos\theta & -\sin\theta & 0\end{pmatrix}\begin{pmatrix}\boldsymbol{e}_r \\ \boldsymbol{e}_\theta \\ \boldsymbol{e}_\phi\end{pmatrix},$$

where A^{T} is the transpose of the matrix A.

The angular momentum can be rewritten as

$$\begin{aligned}\boldsymbol{L}\psi &= \frac{\hbar}{i}\boldsymbol{r}\times\nabla\psi \\ &= \frac{\hbar}{i}r\boldsymbol{e}_r\times(\boldsymbol{e}_r\frac{\partial}{\partial r} + \boldsymbol{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \boldsymbol{e}_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi})\psi \\ &= \frac{\hbar}{i}r[(\boldsymbol{e}_r\times\boldsymbol{e}_\theta)\frac{1}{r}\frac{\partial}{\partial\theta} + (\boldsymbol{e}_r\times\boldsymbol{e}_\phi)\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi})\psi] \\ &= \frac{\hbar}{i}(\boldsymbol{e}_\phi\frac{\partial}{\partial\theta} - \boldsymbol{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})\psi\end{aligned}$$

The x-component of the angular momentum:

$$L_x = \boldsymbol{e}_x.\frac{\hbar}{i}(\boldsymbol{e}_\phi \frac{\partial}{\partial\theta} - \boldsymbol{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$$
$$= \frac{\hbar}{i}(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi})$$

where

$$\boldsymbol{e}_x.\boldsymbol{e}_\phi = -\sin\phi, \qquad \boldsymbol{e}_x.\boldsymbol{e}_\theta = \cos\theta\cos\phi$$

The y-component of the angular momentum:

$$L_y = \boldsymbol{e}_y.\frac{\hbar}{i}(\boldsymbol{e}_\phi \frac{\partial}{\partial\theta} - \boldsymbol{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$$
$$= \frac{\hbar}{i}(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi})$$

where

$$\boldsymbol{e}_y.\boldsymbol{e}_\phi = \cos\phi, \qquad \boldsymbol{e}_y\cdot\boldsymbol{e}_\theta = \cos\theta\sin\phi$$

The z-component of the angular momentum:

$$L_z = \boldsymbol{e}_z.\frac{\hbar}{i}(\boldsymbol{e}_\phi \frac{\partial}{\partial\theta} - \boldsymbol{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$$
$$= \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

where

$$\boldsymbol{e}_z.\boldsymbol{e}_\phi = 0, \qquad \boldsymbol{e}_z.\boldsymbol{e}_\theta = -\sin\theta$$

The raising operator:

$$L_x + iL_y = \hbar(i\sin\phi\frac{\partial}{\partial\theta} + i\cot\theta\cos\phi\frac{\partial}{\partial\phi}) + \hbar(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi})$$
$$= \hbar e^{i\phi}(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi})$$

The lowering operator:

$$L_x - iL_y = \hbar(i\sin\phi\frac{\partial}{\partial\theta} + i\cot\theta\cos\phi\frac{\partial}{\partial\phi}) - \hbar(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi})$$
$$= -\hbar e^{-i\phi}(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\phi})$$

The evaluation:

$$\begin{aligned}
\boldsymbol{L}^2 &= L_x{}^2 + L_y{}^2 + L_z{}^2 \\
&= -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}] \\
&= \hbar^2(-r^2\nabla^2 + \frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}) \\
&= \hbar^2(-r^2\nabla^2 + r\frac{\partial^2}{\partial r^2}r)
\end{aligned}$$

Note that

$$-\frac{r^2}{\hbar^2}p_r{}^2 = \frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) = r\frac{\partial^2}{\partial r^2}r\ .$$

where

$$p_r = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r\ , \qquad p_r{}^2 = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r\ .$$

Then we get

$$\frac{\boldsymbol{L}^2}{\hbar^2} = -r^2\nabla^2 + \frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) = -r^2\nabla^2 - \frac{r^2}{\hbar^2}p_r{}^2,$$

The Laplacian is expressed by

$$\nabla^2 = -\frac{1}{\hbar^2}(p_r{}^2 + \frac{\boldsymbol{L}^2}{r^2}).$$

or

$$\boldsymbol{p}^2 = p_r{}^2 + \frac{\boldsymbol{L}^2}{r^2}$$

The Hamiltonian of the free particle is given by

$$H = -\frac{\hbar^2}{2m}\nabla^2 = \frac{1}{2m}(p_r{}^2 + \frac{\boldsymbol{L}^2}{r^2}).$$

8. Eigenvalue problem for the Hamiltonian in the spherical coordinate

We have the expression for Hamiltonian H (as a differential operator) in the central-force problem by

$$\begin{aligned} H &= \frac{1}{2\mu}\boldsymbol{p}^2 + V(r) \\ &= \frac{1}{2\mu}p_r{}^2 + \frac{\boldsymbol{L}^2}{2\mu r^2} + V(r) \\ &= -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\boldsymbol{L}^2}{2\mu r^2} + V(r) \end{aligned} .$$

where

$$p_r{}^2 = -\frac{\hbar^2}{r}\frac{\partial^2}{\partial r^2}r = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}.$$

Note that

$$\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} = r\frac{\partial^2}{\partial r^2}r$$

In this case, the wavefunction is given by a separation form

$$\psi(\boldsymbol{r}) = R(r)Y_{lm}(\theta,\phi),$$

where $Y_{lm}(\theta,\phi)$ is the spherical harmonics, and it is the simultaneous eigenket of $\boldsymbol{L}^2$ and L_z,

$$\boldsymbol{L}^2 Y_{lm}(\theta,\phi) = \hbar^2 l(l+1)^2 Y_{lm}(\theta,\phi)\,, \qquad L_z Y_{lm}(\theta,\phi) = m\hbar^2 Y_{lm}(\theta,\phi)\,.$$

The radial wave function $R(r)$ is the eigenfunction of the Hamiltonian *H*,

$$\begin{aligned} HR(r) &= [-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r)]R(r) \\ &= [-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + V_{eff}(r)]\Phi(r) = E\Phi(r) \end{aligned}$$

where the effective potential $V_{\mathrm{eff}}(r)$ is defined as

$$V_{eff}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}\,.$$

((**Note**)) **Effective potential**

The effective potential (also known as effective potential energy) is a mathematical expression combining multiple (perhaps opposing) effects into a single potential. In classical mechanics it is defined as the sum of the 'opposing' centrifugal potential energy with the potential energy of a dynamical system. It is commonly used in calculating the orbits of planets (both Newtonian and relativistic) and in semi-classical atomic calculations, and often allows problems to be reduced to fewer dimensions.

9. Mathematica

Using Mathematica, we can easily calculate the above expression.

((**Method**))

(1) We need the relation between the unit vectors of the Cartesian coordinate and the unit vectors of the spherical coordinate.

(2) We need to define the operators of the angular momentum ($\boldsymbol{L}$, L_x, L_y, and L_z)

$\boldsymbol{L}$:

$$\boldsymbol{L} := \frac{\hbar}{i} Cross[\boldsymbol{r}, Grad[\#], \{r, \theta, \phi\}, "Spherical"'];$$

Lx

$$Lx := \boldsymbol{e}_x \cdot L[\#]\,\&$$

Ly

$$Ly := \boldsymbol{e}_y \cdot L[\#]\,\&$$

Lz

$$Lz := \boldsymbol{e}_r \cdot L[\#]\,\&$$

where

$\boldsymbol{r} = \{r,0,0\}$ for the spherical coordinate ($\boldsymbol{r} = r\boldsymbol{e}_r$)

and

$$\boldsymbol{e}_x = \sin\theta\cos\phi\boldsymbol{e}_r + \cos\theta\cos\phi\boldsymbol{e}_\theta - \sin\phi\boldsymbol{e}_\phi = \{\sin\theta\cos\phi, \cos\theta\cos\phi, -\sin\phi\}$$
$$\boldsymbol{e}_y = \sin\theta\sin\phi\boldsymbol{e}_r + \cos\theta\sin\phi\boldsymbol{e}_\theta + \cos\phi\boldsymbol{e}_\phi = \{\sin\theta\sin\phi, \cos\theta\sin\phi, \cos\phi\}$$
$$\boldsymbol{e}_z = \cos\theta\boldsymbol{e}_r - \sin\theta\boldsymbol{e}_\theta = \{\cos\theta, -\sin\theta, 0\}$$

or

```
ux = {Sin[θ] Cos[ϕ], Cos[θ] Cos[ϕ], -Sin[ϕ]};
uy = {Sin[θ] Sin[ϕ], Cos[θ] Sin[ϕ], Cos[ϕ]};
uz = {Cos[θ], -Sin[θ], 0};
ur = {1, 0, 0};

L := (-ⅈ ℏ (Cross[(ur r), Gra[#]]) &) // Simplify;
Lx := (ux.L[#] &) // Simplify;
Ly := (uy.L[#] &) // Simplify;
Lz := (uz.L[#] &) // Simplify;
```

(3) Use the above Mathematica program to calculate

$$Lx[Lx[\psi[r,\theta,\phi]] + Ly[Ly[\psi[r,\theta,\phi]] + Lz[Lz[\psi[r,\theta,\phi]]\,,$$

which is equivalent to

$$Nest[Lx,\psi[r,\theta,\phi],2] + Nest[Ly,\psi[r,\theta,\phi],2] + Nest[Ly,\psi[r,\theta,\phi],2].$$

((**Mathematica**))

```
Clear["Global`"];
ux = {Sin[θ] Cos[ϕ], Cos[θ] Cos[ϕ], -Sin[ϕ]};
uy = {Sin[θ] Sin[ϕ], Cos[θ] Sin[ϕ], Cos[ϕ]};
uz = {Cos[θ], -Sin[θ], 0}; ur = {1, 0, 0};
Lap := Laplacian[#, { r, θ, ϕ}, "Spherical"] &;
Gra := Grad[#, { r, θ, ϕ}, "Spherical"] &;
Diva := Div[#, {r, θ, ϕ}, "Spherical"] &;

L := (-ⅈ ℏ (Cross[(ur r), Gra[#]]) &) // Simplify;
Lx := (ux.L[#] &) // Simplify;
Ly := (uy.L[#] &) // Simplify;
Lz := (uz.L[#] &) // Simplify;
```

$$\text{prq} := \left(\frac{-i\hbar}{2}\,\text{ur}\,.\text{Gra}[\#] + \frac{-i\hbar}{2}\,\text{Diva}[\#\ \text{ur}]\right)\ \&;$$

```
prq[χ[r, θ, ϕ]] // Simplify
```

$$-\frac{i\hbar\left(\chi[r,\theta,\phi] + r\,\chi^{(1,0,0)}[r,\theta,\phi]\right)}{r}$$

```
eq1 = Nest[prq, χ[r, θ, ϕ], 2] // Simplify;

eq2 =
  1/r^2 (Lx[Lx[χ[r, θ, ϕ]]] + Ly[Ly[χ[r, θ, ϕ]]] +
      Lz[Lz[χ[r, θ, ϕ]]]) // FullSimplify;
eq12 = eq1 + eq2 // Simplify
```

$$-\frac{1}{r^2}\hbar^2\left(\text{Csc}[\theta]^2\chi^{(0,0,2)}[r,\theta,\phi]+\text{Cot}[\theta]\chi^{(0,1,0)}[r,\theta,\phi]+\chi^{(0,2,0)}[r,\theta,\phi]+2\,r\,\chi^{(1,0,0)}[r,\theta,\phi]+r^2\chi^{(2,0,0)}[r,\theta,\phi]\right)$$

```
eq3 = -ℏ^2 Lap[χ[r, θ, ϕ]] // Simplify
```

$$-\frac{1}{r^2}\hbar^2\left(\text{Csc}[\theta]^2\chi^{(0,0,2)}[r,\theta,\phi]+\text{Cot}[\theta]\chi^{(0,1,0)}[r,\theta,\phi]+\chi^{(0,2,0)}[r,\theta,\phi]+2\,r\,\chi^{(1,0,0)}[r,\theta,\phi]+r^2\chi^{(2,0,0)}[r,\theta,\phi]\right)$$

```
eq12 - eq3 // Simplify
```

0

REFERENCES

G.B. Arfken, H.J. Weber, and F.E. Harris, *Mathematical Methods for Physicists*, Seventh edition (Elsevier, New York, 2013).

F.S. Levin, *An Introduction to Quantum Theory* (Cambridge University Press 2002).

APPENDIX Commutation relation among p_r and r

$$p_r = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r\,,$$

$$p_r{}^2 = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r(\frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r)$$
$$= -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r$$
$$= -\frac{\hbar^2}{r}(2\frac{\partial}{\partial r} + r\frac{\partial^2}{\partial r^2})$$
$$= -\frac{\hbar^2}{r^2}(2r\frac{\partial}{\partial r} + r^2\frac{\partial^2}{\partial r^2})$$

or

$$p_r{}^2 = -\frac{\hbar^2}{r^2}(2r\frac{\partial}{\partial r} + r^2\frac{\partial^2}{\partial r^2}) = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}),$$

$$[p_r, r] = -i\hbar ,$$

$$[p_r, r^2] = -2i\hbar r ,$$

$$[p_r, r^n] = -ni\hbar r^{n-1},$$

$$[r, p_r{}^2] = 2i\hbar p_r ,$$

$$[r, p_r{}^3] = 3i\hbar p_r{}^2 ,$$

$$[p_r, \frac{1}{r}] = \frac{i\hbar}{r^2} ,$$

$$[p_r, \frac{1}{r^2}] = \frac{2i\hbar}{r^3} ,$$

$$[p_r{}^2, \frac{1}{r^2}] = -\frac{2\hbar^2}{r^4}(1 - 2r\frac{\partial}{\partial r}),$$

$$[p_r{}^2, \frac{1}{r}] = \frac{2\hbar^2}{r^2}\frac{\partial}{\partial r}.$$

((**Mathematica**))

```
Clear["Global`*"]; Pr = (1/r) (ℏ/ⅈ) D[r #, r] &;
```

```
Pr[Pr[f[r]]] // Simplify
```

$$-\frac{\hbar^2 (2 f'[r] + r f''[r])}{r}$$

```
Pr[r f[r]] - r Pr[f[r]] // Simplify
```

$-i \hbar f[r]$

```
Pr[r^2 f[r]] - r^2 Pr[f[r]] // Simplify
```

$-2 i r \hbar f[r]$

```
Pr[r^n f[r]] - r^n Pr[f[r]] // Simplify
```

$-i n r^{-1+n} \hbar f[r]$

```
r Nest[Pr, f[r], 2] - Nest[Pr, r f[r], 2] -
  2 ⅈ ℏ Pr[f[r]] // Simplify
```

0

```
r Nest[Pr, f[r], 3] - Nest[Pr, r f[r], 3] -
  3 ⅈ ℏ Pr[Pr[f[r]]] // Simplify
```

0

$$\text{Pr}\left[\frac{1}{r} f[r]\right] - \frac{1}{r}\,\text{Pr}[f[r]]\ \text{// Simplify}$$

$$\frac{i\,\hbar\,f[r]}{r^2}$$

$$\text{Pr}\left[\frac{1}{r^2} f[r]\right] - \frac{1}{r^2}\,\text{Pr}[f[r]]\ \text{// Simplify}$$

$$\frac{2\,i\,\hbar\,f[r]}{r^3}$$

$$\text{Nest}\left[\text{Pr}, \frac{1}{r^2} f[r], 2\right] - \frac{1}{r^2}\,\text{Nest}[\text{Pr}, f[r], 2]\ \text{//}$$
$$\text{Simplify}$$

$$-\frac{2\,\hbar^2\,(f[r] - 2\,r\,f'[r])}{r^4}$$

$$\text{Nest}\left[\text{Pr}, \frac{1}{r} f[r], 2\right] - \frac{1}{r}\,\text{Nest}[\text{Pr}, f[r], 2]\ \text{//}$$
$$\text{Simplify}$$

$$\frac{2\,\hbar^2\,f'[r]}{r^2}$$