Diatomic molecule with the freedom of translation and rotation

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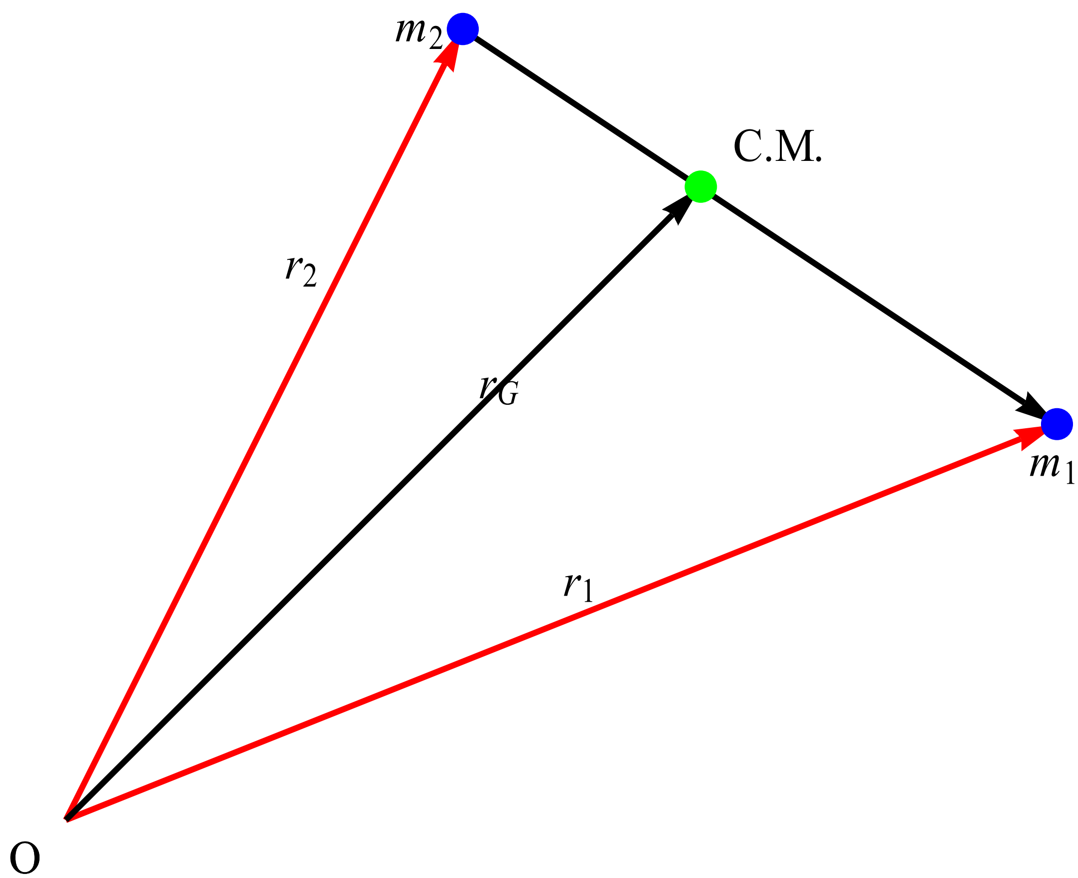
1. Motion of diatomic molecule: classical mechanics

We consider a molecules consisting of two particles. There is an interaction between two particles.



The Lagrangian is given by

$$L = \frac{1}{2} m_1 (\frac{d\boldsymbol{r}_1}{dt})^2 + \frac{1}{2} m_2 (\frac{d\boldsymbol{r}_2}{dt})^2 - V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|),$$

where the potential energy depends only on the relative distance, $|\boldsymbol{r}_1 - \boldsymbol{r}_2|$.

$$\boldsymbol{p}_1 = m_1 \frac{d\boldsymbol{r}_1}{dt}, \qquad \boldsymbol{p}_2 = m_2 \frac{d\boldsymbol{r}_2}{dt}.$$

Center of mass:

$$\boldsymbol{r}_G = \frac{m_1\boldsymbol{r}_1 + m_2\boldsymbol{r}_2}{m_1 + m_2}.$$

Relative coordinate:

$$\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2,$$

$$\boldsymbol{r}_1 = \boldsymbol{r}_G + \frac{m_2\boldsymbol{r}}{m_1 + m_2}, \qquad \boldsymbol{r}_2 = \boldsymbol{r}_G - \frac{m_1\boldsymbol{r}}{m_1 + m_2}.$$

The Lagrangian L can be written in terms of $\boldsymbol{r}_G$ and $\boldsymbol{r}$

$$L(\boldsymbol{r}, \dot{\boldsymbol{r}}, \boldsymbol{r}_G) = \frac{1}{2}m_1(\dot{\boldsymbol{r}}_G + \frac{m_2}{m_1 + m_2}\dot{\boldsymbol{r}})^2 + \frac{1}{2}m_2(\dot{\boldsymbol{r}}_G - \frac{m_1}{m_1 + m_2}\dot{\boldsymbol{r}})^2 - V(|\boldsymbol{r}|),$$

or

$$L(\boldsymbol{r}, \dot{\boldsymbol{r}}, \boldsymbol{r}_G) = \frac{1}{2}M\dot{\boldsymbol{r}}_G^{\ 2} + \frac{1}{2}\mu\dot{\boldsymbol{r}}^2 - V(|\boldsymbol{r}|)$$

where the total mass is defined by

$$M = m_1 + m_2,$$

and the reduced mass is defined by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}.$$

Lagrange equations:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\boldsymbol{r}}}\right) = \frac{\partial L}{\partial \boldsymbol{r}}, \qquad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\boldsymbol{r}}_G}\right) = \frac{\partial L}{\partial \boldsymbol{r}_G} = 0.$$

Since $L(\boldsymbol{r},\dot{\boldsymbol{r}},\boldsymbol{r}_G)$ is independent of $\boldsymbol{r}_G$, we find that the conjugate momentum

$$\boldsymbol{p}_G = \frac{\partial L}{\partial \dot{\boldsymbol{r}}_G} = M\dot{\boldsymbol{r}}_G = m_1\dot{\boldsymbol{r}}_1 + m_2\dot{\boldsymbol{r}}_2 = \boldsymbol{p}_1 + \boldsymbol{p}_2 ,$$

is a cyclic (time-independent) (which means the momentum conservation because of no external force). The conjugate momentum is given by

$$\boldsymbol{p} = \frac{\partial L}{\partial \dot{\boldsymbol{r}}} = \mu\dot{\boldsymbol{r}} = \frac{m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2}{m_1 + m_2} .$$

Note that

$$\dot{\boldsymbol{r}} = \dot{\boldsymbol{r}}_1 - \dot{\boldsymbol{r}}_2 = \frac{1}{m_1}\boldsymbol{p}_1 - \frac{1}{m_2}\boldsymbol{p}_2 = \frac{m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2}{m_1 m_2} ,$$

$$\boldsymbol{p} = \mu\dot{\boldsymbol{r}} = \frac{m_1 m_2}{m_1 + m_2}\frac{m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2}{m_1 m_2} = \frac{m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2}{m_1 + m_2} .$$

Since the momentum of the center of mass is given by

$$\boldsymbol{p}_G = \boldsymbol{p}_1 + \boldsymbol{p}_2 ,$$

we get

$$\boldsymbol{p}_1 = \boldsymbol{p} + \frac{m_1}{m_1 + m_2}\boldsymbol{p}_G , \qquad \boldsymbol{p}_2 = -\boldsymbol{p} + \frac{m_2}{m_1 + m_2}\boldsymbol{p}_G .$$

The Hamiltonian H can be written as

$$\begin{aligned} H &= \boldsymbol{p}_G \cdot \dot{\boldsymbol{r}}_G + \boldsymbol{p}\cdot\dot{\boldsymbol{r}} - L \\ &= \boldsymbol{p}_G \cdot \dot{\boldsymbol{r}}_G + \boldsymbol{p}\cdot\dot{\boldsymbol{r}} - [\frac{1}{2}M\dot{\boldsymbol{r}}_G^{\ 2} + \frac{1}{2}\mu\dot{\boldsymbol{r}}^2 - V(|\boldsymbol{r}|)] . \\ &= \frac{\boldsymbol{p}_G^{\ 2}}{2M} + \frac{\boldsymbol{p}^2}{2\mu} + V(|\boldsymbol{r}|) \end{aligned}$$

where

$$\dot{\boldsymbol{r}}_G = \frac{1}{M}\boldsymbol{p}_G, \qquad \dot{\boldsymbol{r}} = \frac{1}{\mu}\boldsymbol{p}$$

The total orbital angular momentum:

$$\begin{aligned}\boldsymbol{L}_T &= \boldsymbol{L}_1 + \boldsymbol{L}_2 \\ &= \boldsymbol{r}_1 \times \boldsymbol{p}_1 + \boldsymbol{r}_2 \times \boldsymbol{p}_2 \\ &= (\boldsymbol{r}_G + \frac{m_2\boldsymbol{r}}{m_1+m_2}) \times (\boldsymbol{p} + \frac{m_1}{m_1+m_2}\boldsymbol{p}_G) + (\boldsymbol{r}_G - \frac{m_1\boldsymbol{r}}{m_1+m_2}) \times (-\boldsymbol{p} + \frac{m_2}{m_1+m_2}\boldsymbol{p}_G)\end{aligned}$$

or

$$\boldsymbol{L}_T = \boldsymbol{L}_G + \boldsymbol{L}$$

with

$$\boldsymbol{L}_G = \boldsymbol{r}_G \times \boldsymbol{p}_G . \qquad \boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$$

2. Quantum Kepler problem

We now consider the quantum mechanics of the central force problem.

(i) The relative co-ordinate operator:

$$\hat{\boldsymbol{r}} = \hat{\boldsymbol{r}}_1 - \hat{\boldsymbol{r}}_2 ,$$

(ii) The relative momentum operator:

$$\hat{\boldsymbol{p}} = \frac{m_2\hat{\boldsymbol{p}}_1 - m_1\hat{\boldsymbol{p}}_2}{m_1+m_2} .$$

(iii) The co-ordinate operator for the center of mass:

$$\hat{\boldsymbol{r}}_G = \frac{m_1\hat{\boldsymbol{r}}_1 + m_2\hat{\boldsymbol{r}}_2}{m_1+m_2} .$$

(iv) The momentum operator for the center of mass:

$$\hat{\boldsymbol{p}}_G = \hat{\boldsymbol{p}}_1 + \hat{\boldsymbol{p}}_2 .$$

(v) The total angular momentum operator for the system:

$$\hat{\boldsymbol{L}}_T = \hat{\boldsymbol{L}}_G + \hat{\boldsymbol{L}} ,$$

with

$$\hat{\boldsymbol{L}}_G = \hat{\boldsymbol{r}}_G \times \hat{\boldsymbol{p}}_G .$$

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}} . \qquad \text{(internal angular momentum)}$$

The reduced mass is defined as

$$\mu = \frac{m_1 m_2}{m_1 + m_2} .$$

3. The commutation relation:

We assume that

$$[\hat{x}_{1i}, \hat{x}_{1j}] = 0 , \qquad [\hat{x}_{2i}, \hat{x}_{2j}] = 0 ,$$

$$[\hat{p}_{1i}, \hat{p}_{1j}] = 0 , \qquad [\hat{p}_{2i}, \hat{p}_{2j}] = 0 ,$$

We note that

$$[\hat{x}_{1i}, \hat{p}_{1j}] = i\hbar\delta_{ij} , \qquad [\hat{x}_{2i}, \hat{p}_{2j}] = i\hbar\delta_{ij} ,$$

for the same particle, and

$$[\hat{x}_{1i}, \hat{p}_{2j}] = 0 , \qquad [\hat{x}_{2i}, \hat{p}_{1j}] = 0 ,$$

$$[\hat{x}_{1i}, \hat{x}_{2j}] = 0 , \qquad [\hat{p}_{1i}, \hat{p}_{2j}] = 0 ,$$

for the different particles, where $i = x, y, z$, and $j = x, y, z$.

Based on the above relations, we discuss the commutation relations between $\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}, \hat{\boldsymbol{r}}_G, \hat{\boldsymbol{p}}_G$, as follows.

$$
\begin{aligned}
[\hat{x}_i, \hat{p}_j] &= [\hat{x}_{1i} - \hat{x}_{2i}, \frac{m_2 \hat{p}_{1j} - m_1 \hat{p}_{2j}}{m_1 + m_2}] \\
&= \frac{m_2}{m_1 + m_2}[\hat{x}_{1i}, \hat{p}_{1j}] + \frac{m_1}{m_1 + m_2}[\hat{x}_{2i}, \hat{p}_{2j}] \\
&= i\hbar \delta_{ij} \hat{1}
\end{aligned}
$$

$$
\begin{aligned}
[\hat{x}_i, \hat{p}_{Gj}] &= [\hat{x}_{1i} - \hat{x}_{2i}, \hat{p}_{1j} + \hat{p}_{2j}] \\
&= [\hat{x}_{1i}, \hat{p}_{1j}] - [\hat{x}_{2i}, \hat{p}_{2j}] \\
&= i\hbar \delta_{ij} \hat{1} - i\hbar \delta_{ij} \hat{1} \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
[\hat{x}_{Gi}, \hat{p}_{Gj}] &= [\frac{m_1 \hat{x}_{1i} + m_2 \hat{x}_{2i}}{m_1 + m_2}, \hat{p}_{1j} + \hat{p}_{2j}] \\
&= \frac{m_1}{m_1 + m_2}[\hat{x}_{1i}, \hat{p}_{1j}] + \frac{m_2}{m_1 + m_2}[\hat{x}_{2i}, \hat{p}_{2j}] \\
&= i\hbar \delta_{ij} \hat{1}
\end{aligned}
$$

$$
\begin{aligned}
[\hat{x}_{Gi}, \hat{p}_j] &= [\frac{m_1 \hat{x}_{1i} + m_2 \hat{x}_{2i}}{m_1 + m_2}, \frac{m_2 \hat{p}_{1j} - m_1 \hat{p}_{2j}}{m_1 + m_2}] \\
&= \frac{m_1 m_2}{m_1 + m_2}[\hat{x}_{1i}, \hat{p}_{1j}] - \frac{m_1 m_2}{m_1 + m_2}[\hat{x}_{2i}, \hat{p}_{2j}] \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
[\hat{p}_{Gi}, \hat{p}_j] &= [\hat{p}_{1i} + \hat{p}_{2i}, \frac{m_2 \hat{p}_{1j} - m_1 \hat{p}_{2j}}{m_1 + m_2}] \\
&= \frac{m_2}{m_1 + m_2}[\hat{p}_{1i}, \hat{p}_{1j}] - \frac{m_{12}}{m_1 + m_2}[\hat{p}_{2i}, \hat{p}_{2j}] \\
&= 0
\end{aligned}
$$

We note that the original Hamiltonian

$$
\hat{H} = \frac{1}{2m_1}\hat{\boldsymbol{p}}_1{}^2 + \frac{1}{2m_2}\hat{\boldsymbol{p}}_2{}^2 + V(|\hat{\boldsymbol{r}}_1 - \hat{\boldsymbol{r}}_2|),
$$

can be rewritten as

$$\hat{H} = \hat{H}_G + \hat{H}_{rel} = \frac{\hat{\boldsymbol{p}}_G^{\;2}}{2M} + \frac{\hat{\boldsymbol{p}}^2}{2\mu} + V(|\hat{\boldsymbol{r}}|).$$

4. Reduction of the two-body problem

We note that

$$[\hat{\boldsymbol{p}}_G, \hat{H}_{rel}] = 0,$$

and

$$[\hat{H}, \hat{\boldsymbol{p}}_G] = [\hat{H}_G + \hat{H}_{rel}, \hat{\boldsymbol{p}}_G] = [\hat{H}_{rel}, \hat{\boldsymbol{p}}_G] = 0.$$

Then $\hat{H}_{rel}$, $\hat{H}$, and $\hat{\boldsymbol{p}}_G$ can all be simultaneously diagonalized. In other words, there exists a simultaneous eigenstate $|\boldsymbol{p}_G, E_r\rangle$.

$$\hat{H}_G|\boldsymbol{p}_G, E_r\rangle = E_G|E_G, E_r\rangle, \qquad \hat{H}_{rel}|\boldsymbol{p}_G, E_r\rangle = E_r|\boldsymbol{p}_G, E_r\rangle,$$

and

$$\hat{H}|\boldsymbol{p}_G, E_r\rangle = (\hat{H}_G + \hat{H}_{rel})|\boldsymbol{p}_G, E_r\rangle = (E_G + E_r)|\boldsymbol{p}_G, E_r\rangle.$$

We note that

$$\hat{H}_G|\boldsymbol{p}_G\rangle = \frac{\boldsymbol{p}_G^{\;2}}{2M}|\boldsymbol{p}_G\rangle = E_G|\boldsymbol{p}_G\rangle,$$

where

$$E_G = \frac{\boldsymbol{p}_G^{\;2}}{2M}.$$

The wave function can be described by

$$|\psi\rangle = |\boldsymbol{p}_G\rangle \otimes |E_r\rangle = |\boldsymbol{p}_G\rangle|\psi_r\rangle,$$

where

$$\left|E_r\right\rangle = \left|\psi_r\right\rangle .$$

5. The representation of $\left|\boldsymbol{r}_G,\boldsymbol{r}\right\rangle = \left|\boldsymbol{r}_G\right\rangle \otimes \left|\boldsymbol{r}\right\rangle$

Based on the commutation relations,

$$[\hat{x}_{Gi},\hat{p}_{Gj}] = i\hbar\delta_{ij}\hat{1}, \qquad [\hat{x}_i,\hat{p}_j] = i\hbar\delta_{ij}\hat{1},$$

we can use the basis

$$\left|\boldsymbol{r}_G,\boldsymbol{r}\right\rangle = \left|\boldsymbol{r}_G\right\rangle \otimes \left|\boldsymbol{r}\right\rangle,$$

for both the center-of mass co-ordinate and relative co-ordinate, corresponding to the basis for the momentum basis

$$\left|p_G,\boldsymbol{p}\right\rangle = \left|\boldsymbol{p}_G\right\rangle \otimes \left|\boldsymbol{p}\right\rangle .$$

The transformation functions are defined by

$$\left\langle \boldsymbol{r}_G \middle| \boldsymbol{p}_G \right\rangle = \frac{1}{(2\pi\hbar)^{3/2}} \exp\!\left(\frac{i}{\hbar}\boldsymbol{p}_G\cdot\boldsymbol{r}_G\right),$$

and

$$\left\langle \boldsymbol{r} \middle| \boldsymbol{p} \right\rangle = \frac{1}{(2\pi\hbar)^{3/2}} \exp\!\left(\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}\right).$$

The wave function in the position representation can be described by

$$\left|\psi\right\rangle = \left|\boldsymbol{p}_G\right\rangle\left|E_r\right\rangle = \left|\boldsymbol{p}_G\right\rangle\left|\psi_r\right\rangle .$$

The representation of the wave function in the positional representation

$$\left\langle \boldsymbol{r}_G,\boldsymbol{r} \middle| \psi \right\rangle = \left\langle \boldsymbol{r}_G \middle| \boldsymbol{p}_G \right\rangle \left\langle r \middle| \psi_r \right\rangle = \frac{1}{(2\pi\hbar)^{3/2}} \exp\!\left(\frac{i}{\hbar}\boldsymbol{p}_G\cdot\boldsymbol{r}_G\right)\left\langle \boldsymbol{r} \middle| \psi_r \right\rangle .$$

6. Ehrenfest theorem for $\left\langle \hat{\boldsymbol{p}}_G \right\rangle$

We note that

$$[\hat{H}, \hat{\boldsymbol{p}}_G] = 0 .$$

From the Ehrenfest theorem, we have

$$\frac{d}{dt}\langle \hat{\boldsymbol{p}}_G \rangle = \frac{1}{i\hbar}\langle [\hat{\boldsymbol{p}}_G, \hat{H}] \rangle = 0 ,$$

leading to $\langle \hat{\boldsymbol{p}}_G \rangle$=constant of motion. For simplicity, we assume that

$$\hat{\boldsymbol{p}}_G = 0 .$$

The we have the final form of the Hamiltonian as

$$\hat{H} = \hat{H}_{rel} = \frac{\hat{\boldsymbol{p}}^2}{2\mu} + V(\hat{\boldsymbol{r}}) .$$

The Schrodinger equation is given by

$$[\frac{\hat{\boldsymbol{p}}^2}{2\mu} + V(\hat{\boldsymbol{r}})]|\psi_r\rangle = E_r|\psi_r\rangle$$

or

$$[-\frac{\hbar^2}{2\mu}\nabla_r{}^2 + V(\boldsymbol{r})]\langle \boldsymbol{r}|\psi_r\rangle = E_r\langle \boldsymbol{r}|\psi_r\rangle .$$

7. Radial momentum operator and angular momentum operator

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 $\hat{p}_r = \frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|} \cdot \hat{\boldsymbol{p}}$, where $\frac{\hat{\boldsymbol{r}}}{|\hat{\boldsymbol{r}}|}$ 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

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

as the radial momentum. This operator is Hermitian.

Definition of angular momentum

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

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

The proof of this is straightforward:

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

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

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

Then we get

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

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

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

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

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

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

where

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

and

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

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

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

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)

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

or simply

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

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

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

8. 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.

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

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

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

9. 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

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

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

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

(notation of the differential operator)

((**Note**))

(i)

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

(ii)

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

(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

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

10. 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. $d\Omega = \sin\theta d\theta d\phi$. $d\boldsymbol{r} = r^2 d\Omega$.

11. 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

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

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

12. 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

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

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:

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

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:

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

We note that

$$\begin{aligned} L_-L_+ &= (L_x - iL_y)((L_x + iL_y) \\ &= L_x{}^2 + L_y{}^2 + i[L_x, L_y] \\ &= \boldsymbol{L}^2 - L_z{}^2 - \hbar L_z \end{aligned}$$

and

$$\begin{aligned} L_+L_- &= (L_x + iL_y)((L_x - iL_y) \\ &= L_x{}^2 + L_y{}^2 - i[L_x, L_y] \\ &= \boldsymbol{L}^2 - L_z{}^2 + \hbar L_z \end{aligned}$$

Then we have

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

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

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

13. 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,

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

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)) Laplacian in the spherical co-ordinate

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

where

$$\frac{\boldsymbol{L}^2}{\hbar^2} = -\frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

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

---

14. Hamiltonian in the classical mechanics

Here we discuss the classical theory for the Hamiltonian of diatomic molecules. We use the spherical co-ordinate.

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

The Lagrangian is given by

$$L = \frac{1}{2}\mu(\dot{\boldsymbol{r}}\cdot\dot{\boldsymbol{r}}) - V(r) = \frac{1}{2}\mu(\dot{r}^2 + r^2\,\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2) - V(r)$$

where V is the potential energy which contains all the information and m is the reduced mass. The canonical momenta are defined by

$$p_r = \frac{\partial L}{\partial\dot{r}} = \mu\,\dot{r}, \qquad p_\theta = \frac{\partial L}{\partial\dot{\theta}} = \mu\,r^2\dot{\theta}, \qquad p_\phi = \frac{\partial L}{\partial\dot{\phi}} = \mu\,r^2\sin^2\theta\,\dot{\phi}$$

Thus the Hamiltonian for the relative motion can be derived as

$$\begin{aligned}
H_{rel} &= p_r\dot{r} + p_\theta\dot{\theta} + p_\phi\dot{\phi} - L \\
&= \mu(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2) - \frac{1}{2}\mu(\dot{r}^2 + r^2\,\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2) + V(r) \\
&= \frac{1}{2}\mu(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2) + V(r) \\
&= \frac{1}{2\mu}p_r^{\ 2} + \frac{1}{2}\mu r^2\left(\frac{p_\theta}{\mu r^2}\right)^2 + \frac{1}{2}\mu r^2\sin^2\theta\left(\frac{p_\phi}{\mu r^2\sin^2\theta}\right)^2 + V(r) \\
&= \frac{1}{2\mu}p_r^{\ 2} + V(r) + \frac{1}{2\mu r^2}(p_\theta^{\ 2} + \frac{p_\phi^{\ 2}}{\sin^2\theta})
\end{aligned}$$

So the resultant Hamiltonian is expressed by

$$H = \frac{\boldsymbol{P}_G{}^2}{2M} + H_{vib} + H_{rot}$$

where

$$H_G = \frac{\boldsymbol{P}_G{}^2}{2M} \qquad \text{(the motion of center of mass)}$$

$$H_{vib} = \frac{1}{2\mu} p_r{}^2 + V(r) = \frac{1}{2\mu} p_r{}^2 + \frac{1}{2}\mu\omega^2 r^2$$

(the simple harmonics due to the vibration)

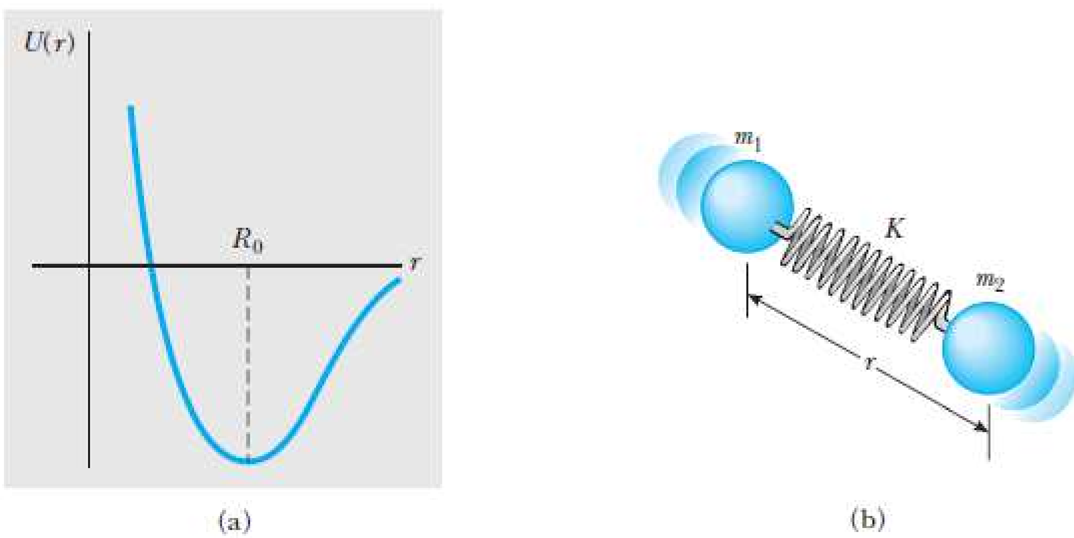


Fig. (a) A plot of the potential energy of a diatomic molecule versus atomic separation. The parameter $R0$ is the equilibrium separation of the atoms. (b) Model of a diatomic molecule whose atoms are bonded by an effective spring of force constant K. The fundamental vibration is along the molecular axis. (R. Serway, C.J. Moses, and C.A. Moyer, Modern Physics, 3rd edition (Thomson Brooks/Cole, 2005))

$$H_{rot} = \frac{1}{2\mu r^2}(p_\theta{}^2 + \frac{p_\phi{}^2}{\sin^2\theta}) = \frac{1}{2I}(p_\theta{}^2 + \frac{p_\phi{}^2}{\sin^2\theta})$$

(the rotation around the axis connecting two atoms)

where $I = \mu r^2$ is the moment of inertia and r is the distance between two atoms,

$$M = m_1 + m_2,$$

and the reduced mass is defined by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}.$$

15. Partition function (canonical ensemble)

The partition function is given by

$$Z_1 = Z_1(\mathrm{CM}) Z_1(\mathrm{vib}) Z_1(\mathrm{rot})$$

$$Z_1(\mathrm{CM}) = \frac{V}{(2\pi\hbar)^3}\left(\frac{2\pi M}{\beta}\right)^{3/2}$$

$$\begin{aligned}
Z_1(\mathrm{vib}) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_r \int_{-\infty}^{\infty} dr \exp(-\beta H_r) \\
&= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dp_r \int_{-\infty}^{\infty} dr \exp[-\beta(\frac{1}{2\mu} p_r{}^2 + \frac{1}{2}\mu\omega^2 r^2)] \\
&= \frac{1}{2\pi\hbar}\sqrt{\frac{2\pi\mu}{\beta}}\sqrt{\frac{2\pi}{\beta\mu\omega^2}} \\
&= \frac{1}{\hbar\beta\omega}
\end{aligned}$$

$$
\begin{aligned}
Z_1(\text{rot}) &= \frac{1}{(2\pi\hbar)^2}\int_0^{\pi} d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\phi \exp(-\beta H_r) \\
&= \frac{1}{(2\pi\hbar)^2}\int_0^{\pi} d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dp_\theta \int_{-\infty}^{\infty} dp_\phi \exp[-\frac{\beta}{2I}(p_\theta{}^2 + \frac{p_\phi{}^2}{\sin^2\theta})] \\
&= \frac{1}{(2\pi\hbar)^2}\int_0^{\pi} d\theta \int_0^{2\pi} d\phi \sqrt{\frac{2\pi I}{\beta}}\sqrt{\frac{2\pi I}{\beta}}\sin\theta \\
&= \frac{1}{(2\pi\hbar)^2}\frac{2\pi I}{\beta}\int_0^{\pi}\sin\theta\, d\theta \int_0^{2\pi} d\phi \\
&= \frac{1}{(2\pi\hbar)^2}\frac{2\pi I}{\beta}4\pi \\
&= \frac{2Ik_BT}{\hbar^2}
\end{aligned}
$$

Then the Helmholtz free energy per molecule is

$$
\ln Z_1 = \ln[Z_1(\text{CM})Z_1(\text{vib})Z_1(\text{rot})] = [\ln Z_1(\text{CM}) + \ln Z_1(\text{vib}) + Z_1(\text{rot})]]
$$

where

$$
\begin{aligned}
\text{In}[Z_1(CM)] &= \ln[\frac{V}{(2\pi\hbar)^3}\left(\frac{2\pi M}{\beta}\right)^{3/2} \\
&= \frac{3}{2}\ln(k_BT) + k_BT\ln\frac{V}{(2\pi\hbar)^3}(2\pi M)^{3/2}]
\end{aligned}
$$

$$
\ln Z_1(\text{vib}) = \ln[\frac{k_BT}{\hbar\omega}] = \ln(k_BT) - \ln(\hbar\omega)
$$

$$
\ln Z_1(\text{rot}) = \ln(\frac{2Ik_BT}{\hbar^2}) = \ln(k_BT) + k_BT\ln(\frac{2IT}{\hbar^2})
$$

Using the formula $E_1 = k_BT^2\frac{\partial}{\partial T}\ln Z_1$

$E_1(\text{C}M) = \frac{3}{2}k_BT$ (degree of freedom 3: three direction)

$E_1(\text{vib}) = k_BT$ (degree of freedom: 2; kinetic energy and potential energy))

$E_1(\text{rot}) = k_B T$

(degree of freedom: 2; rotation around axis perpendicular to the axis)

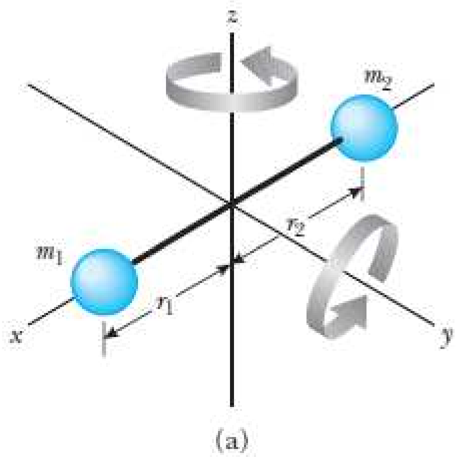


Fig. A diatomic molecule oriented along the x-axis has 2 rotational degrees of freedom, corresponding to rotation about the y- and z-axes. (R. Serway, C.J. Moses, and C.A. Moyer, Modern Physics, 3rd edition (Thomson Brooks/Cole, 2005))

From the equipartition of energy, we conclude that there are totally 7 freedoms in the diatomic molecule.

((**Note**)) **Equipartition of energy**

The theorem of equipartition of energy states that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion and that the energy is $k_B T/2$.

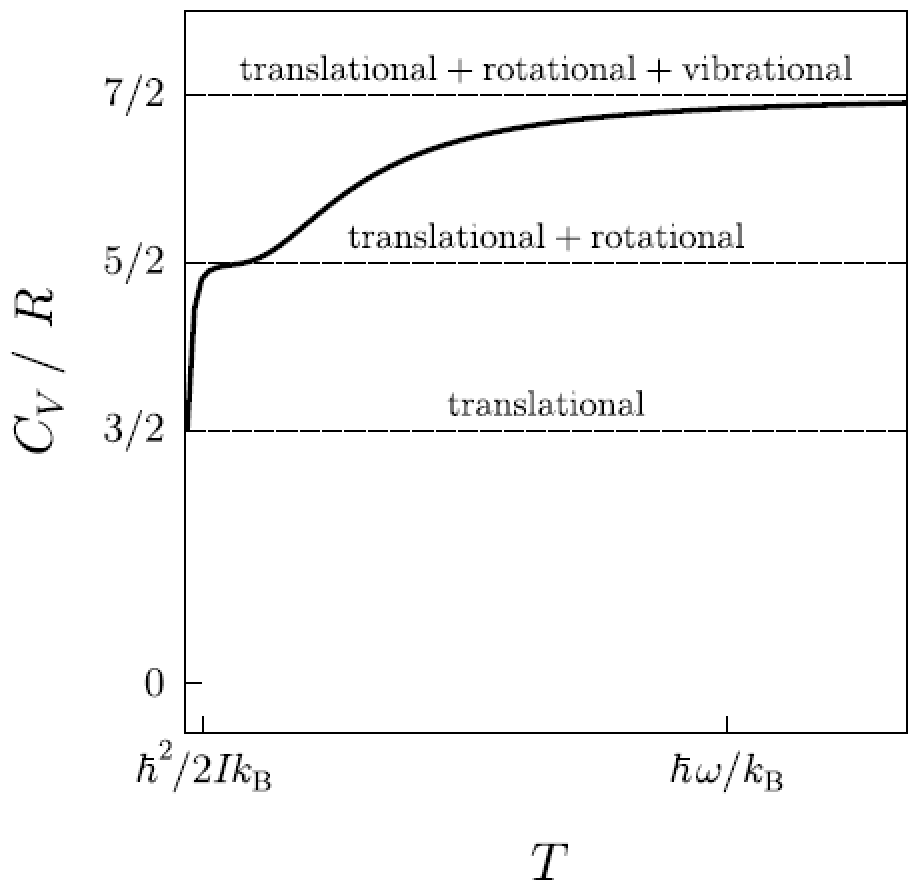


Fig. The molar heat capacity at constant volume of a diatomic gas as a function of temperature. (S.J. Blundell and K.M. Blundell, Concepts of thermal physics, Oxford, 2006).

16. Quantum mechanical treatment of rotation

In quantum mechanics, the rotation energy is given by

$$H(\text{rot}) = \frac{\boldsymbol{L}^2}{2I} = \frac{\hbar^2}{2I} l(l+1) \, .$$

where l = 0, 1, 2, 3, ….

Then the partition function is

$$Z_1(\text{rot}) = \sum_{l=0}^{\infty} (2l+1) \exp[-\frac{\beta\hbar^2}{2I} l(l+1)]$$

In the high temperature limit, this can be replaced by

$$
\begin{aligned}
Z_1(\mathrm{rot}) &= \int_0^\infty dx(2x+1)\exp[-\frac{\beta\hbar^2}{2I}x(x+1)] \\
&= \int_0^\infty dy\exp(-\frac{\beta\hbar^2}{2I}y) \\
&= \frac{2I}{\beta\hbar^2} \\
&= \frac{2Ik_B T}{\hbar^2}
\end{aligned}
$$

which agrees with the result obtained from the classical theory.

REFERENCE

M. Kardar, Statistical Physics of Particles (Cambridge, 2007).
M. Kardar: MIT 8.333 Statistical Mechanics I: Statistical Mechanics Part I
Fall 2013
https://www.youtube.com/playlist?list=PLUl4u3cNGP60gl3fdUTKRrt5t_GPx2sRg