Lecture 11

Quantum rigid rotor

Study Goal of This Lecture

- Classical rigid rotpr
- Angular momentum
- Quantum rigid rotor:
  Schrödinger equation, spherical coordinate and eigenfunctions

11.1 Classical Rigid Rotor

So far we have restricted ourself to 1-D problem. Now we are ready to go on to treat more complex problems in 3-D and beyond. Before we solve the hydrogen atom problem, we must understood quantum rotation first.

Consider a particle rotates around a fixed axis, the radius is fixed and we called this kind of system a rigid rotor. The system should be described by the angular momentum

$$\vec{L} = \vec{r} \times \vec{p}, \tag{11.1}$$

and the kinetic energy is

$$\hat{T} = \frac{1}{2} m\omega^2 = \frac{\vec{L}^2}{2I}, \text{ where I is moment of inertia.} \tag{11.2}$$

Again, for many particle system, the rotation can be seperated from the center-of-mass motion and described in reduced coordinate.

For example, a rigid diatomic molecule:

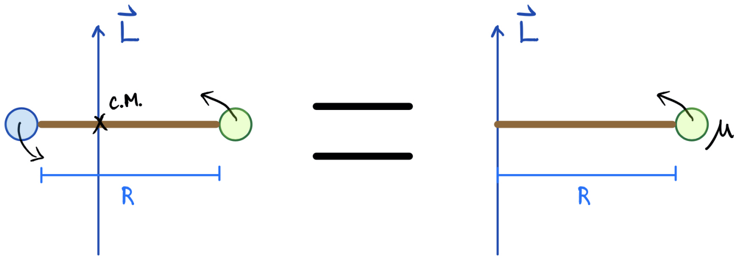

Figure 11.1: Transform to the reduced coordinate.

with reduced mass $\mu = \frac{m_1 m_2}{m_1+m_2}$, so

$$T = \frac{\vec{L}^2}{2I} = \frac{\vec{L}^2}{2\mu R^2}. \tag{11.3}$$

Now we return to consider $\vec{L}$. It is a vector, defined as:

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\hat{i} + (zp_x - xp_y)\hat{j} + (xp_y - yp_x)\hat{k}. \tag{11.4}$$

Therefore,

$$\vec{L} = L_x\hat{i} + L_y\hat{j} + L_z\hat{k} \text{ and } \vec{L}^2 = L_x^2 + L_y^2 + L_z^2. \tag{11.5}$$

11.2 Quantum Rigid Rotor

11.2.1 Angular Momentum Operator

In quantum mechanics, we use the corresponding principle and obtain

Note $\left[y, \frac{\partial}{\partial y}\right] = 0$

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{L}^2}{2\mu\hat{R}^2} = \frac{\hat{L}^2}{2\mu\hat{R}^2} = \frac{\hat{L}^2}{2I}, \tag{11.6}$$

$$\hat{L} = \hat{L}_x\hat{i} + \hat{L}_y\hat{j} + \hat{L}_z\hat{k}, \tag{11.7}$$

$$\hat{L}_x = \hat{y}\hat{p_z} - \hat{z}\hat{p_y} = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}), \tag{11.8}$$

$$\hat{L}_y = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}), \tag{11.9}$$

$$\hat{L}_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}). \tag{11.10}$$

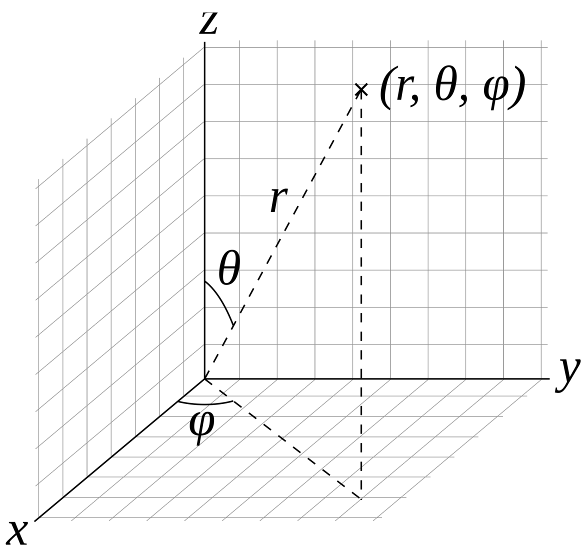

Figure 11.2: Spherical coordinate.

11.2.2 Spherical Coordinate

For rotation motions, these operators are most conveniently studied in spherical coordinate:

$$|\vec{r}| = r \, : \text{ fixed.} \tag{11.11}$$

$$\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ y &= r\cos\theta \end{aligned} \tag{11.12}$$

to transform operators from Cartesian Coordinate, we need:

$$\begin{aligned} \cos\theta &= \frac{z}{r} = \frac{z}{\sqrt{x^2+y^2+z^2}}, \\ \tan\phi &= \frac{y}{x}. \end{aligned} \tag{11.13}$$

Therefore, we want to write $\hat{L}_x, \hat{L}_y, \hat{L}_z$ in spherical coordinates. We know how to rewrite x, y, z, but how about the operator $\frac{\partial}{\partial x}$? $\rightarrow$ the chain rule!

$$\frac{\partial}{\partial x} = \left(\frac{\partial\theta}{\partial x}\right)_{y,z}\frac{\partial}{\partial\theta} + \left(\frac{\partial\phi}{\partial x}\right)_{y,z}\frac{\partial}{\partial\phi} \ , \tag{11.14}$$

and

$$\frac{\partial}{\partial x}\cos\theta = -\sin\theta\Big(\frac{\partial\theta}{\partial x}\Big)_{y,z} = \frac{\partial}{\partial x}[\frac{z}{\sqrt{x^2+y^2+z^2}}]$$
$$\begin{aligned} &= \frac{z}{(x^2+y^2+z^2)^{\frac{3}{2}}} \times \frac{-1}{2} \times 2x \\ &= -\frac{1}{r^3} \times x \times z \\ &= -\frac{1}{r^3} \times r\sin\theta\cos\phi \times r\cos\theta. \end{aligned} \tag{11.15}$$

$$\therefore \Big(\frac{\partial\theta}{\partial x}\Big)_{y,z} = \frac{1}{r}\cos\theta\cos\phi. \tag{11.16}$$

We can similarly prove: by $\frac{\partial}{\partial x}\tan\phi$, that

$$\Big(\frac{\partial\phi}{\partial x}\Big)_{y,z} = -\frac{1}{r} \times \frac{\sin\phi}{\sin\theta}. \tag{11.17}$$

$$\therefore \hat{L}_x = i\hbar\Big[\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\Big] \tag{11.18}$$

Also

$$\hat{L}_y = -i\hbar\Big[\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\Big], \tag{11.19}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}, \tag{11.20}$$

and

$$\hat{L}^2 = -\hbar^2\Big[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big]. \tag{11.21}$$

Nota that $[\hat{L}_x, \hat{L}_y]$, $[\hat{L}_y, \hat{L}_z]$, $[\hat{L}_z, \hat{L}_x] \neq 0$ and $[\hat{L}^2, \hat{L}_{x,y,z}] = 0$.

11.2.3 Spherical Harmonic

Thus, the Schrödinger equation:

$$\hat{H}\psi = E\psi,\ \hat{H} = \frac{\hat{L}^2}{2I}\ . \tag{11.22}$$

$$\therefore -\frac{\hbar^2}{2I}\Big[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big]\psi(\theta,\phi) = E\psi(\theta,\phi). \tag{11.23}$$

The solution are well known in mathematics, they are the spherical harmonic. They are denoted as $Y_l^m(\theta,\phi)$ and are simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

Why does it require two quantum number to describe the wavefunction?
$\rightarrow$ Because there are two variables (degree of freedoms).

$$\hat{L}^2 Y_l^m(\theta,\phi) = l(l+1)\hbar^2 Y_l^m(\theta,\phi),\ \text{with}\ l = 0, 1, 2, \cdots\ , \tag{11.24}$$

l is angular momentum quantum number.

$$\hat{L}_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi), \text{ with } m = -l, -l+1, \cdots, 0, \cdots, l-1, l \quad , \tag{11.25}$$

m is magnetic quantum number.

So, the energy levels of a rigid rotor is

Energy only depends on l.

$$E_l = \frac{\hbar^2}{2I} l(l+1) = \frac{\hbar}{2I} J(J+1), \text{ where } l, J = 0, 1, 2, \cdots . \tag{11.26}$$

J is often used in spectroscopy.

So what is $Y_l^m(\theta, \phi)$ function?

Note that each energy level has $2l+1$-fold degeneracy!(Due to for all $m = -l, -l+1, \cdots, 0, \cdots, l-1, l$ Y_l^m states have the same energy.) One should think that for a state $Y_l^m(\theta, \phi)$, the amplitude of angular momentum is

$$|\vec{L}| = \sqrt{l(l+1)}\hbar, \tag{11.27}$$

and the projection on the rotational axis z is

$$|L_z| = m\hbar. \tag{11.28}$$

Of course $|L_z|$ must smaller than $|\vec{L}|$, so $m = -l, -l+1, \cdots, 0, \cdots, l-1, l$, alway $< \sqrt{l(l+1)}$. This is summarized by the figure, for example for $l = 2$, there are five m states: $m = \pm 2, \pm 1, 0$. Each represented by a vector with length $= \sqrt{l(l+1)}\hbar = \sqrt{b}\hbar$ and z-projection $m\hbar$ precessing along z.

Note the quantization conditions. All five states has the same energy. The first few spherical harmonics will be given later and they are also listed on Silbey's Table 9.2.

11.2.4 Uncertainty of Quantum Rigid Rotor

Let's spend some time on the uncertainty of spherical harmonics: Conceptually, given a quantized ratotaional energy level, one determined l rotational energy:

$$E_l = \frac{\hbar}{2I} l(l+1), \tag{11.29}$$

but the direction is not determined, i.e. there are degenerate states with the same energy, this preserves the uncertainty in the system.

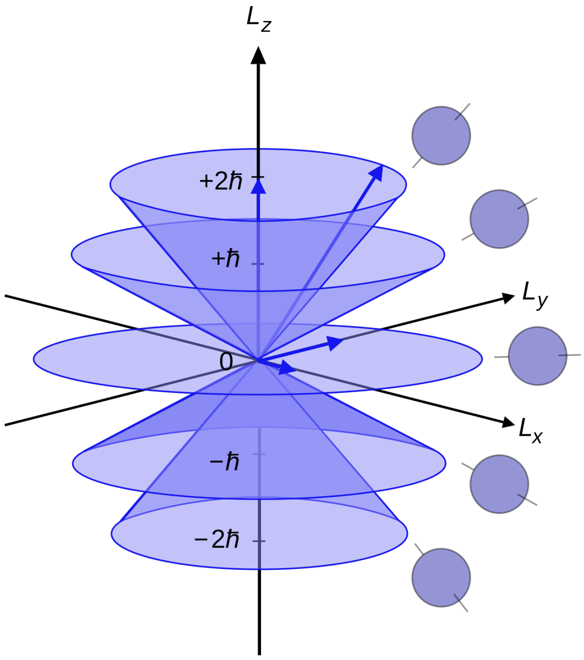

Figure 11.3: Graphical summary of spherical harmonics.

11.3 The First Few Spherical Harmonics

The first few spherical harmonics:

$$Y_0^0 = (\tfrac{1}{4\pi})^{\frac{1}{2}}, \tag{11.30}$$

$$Y_1^0 = (\tfrac{3}{4\pi})^{\frac{1}{2}} \cos\theta, \tag{11.31}$$

$$Y_1^{-1} = (\tfrac{3}{8\pi})^{\frac{1}{2}} \sin\theta e^{-i\phi}, \tag{11.32}$$

$$Y_1^1 = (\tfrac{3}{8\pi})^{\frac{1}{2}} \sin\theta e^{i\phi}. \tag{11.33}$$

Let's look on some features of those spherical harmonics function:

- For Y_0^0, the rotation energy is "0". However, it does not violate the uncertainty principle because this state has an wavefunctions that gives "equal", "uniform" probability density in θ and ϕ. This is quite different to the case of harmonic oscillator.

- We find the complex number in wavefunction. Practically, we will do superposition to obtain:

$$
\begin{aligned}
p_x &= \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}), \\
p_y &= \frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1}), \\
p_z &= Y_1^0.
\end{aligned} \tag{11.34}
$$

These are p orbitals in hydrogen atom!

Note that, just like the eigenfunctions of harmonic oscillator, we do not need to know the explicit forms of $Y_l^m(\theta, \phi)$, we only need to know that:

$$\int Y_l^m(\theta,\phi) Y_{l'}^{m'}(\theta,\phi) d\tau = \delta_{l,l'} \cdot \delta_{m,m'}. \tag{11.35}$$

11.4 More on Magnetic Quantum Number

The emergence of the magnetic quantum number provides useful insights and is analogous to the giving of l, so we will study it a little more, recall:

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}. \tag{11.36}$$

To find eigenfunctions $\Rightarrow$ $T(\phi)$

$$-i\hbar \frac{\partial}{\partial \phi} T(\phi) = b \cdot T(\phi), \tag{11.37}$$

$$\therefore T(\phi) = A e^{\frac{-ib\phi}{\hbar}}. \tag{11.38}$$

If $T(\phi)$ is a single-valued function, we must have $T(\phi) = T(\phi + 2\pi) \Leftarrow$ the same after rotating one round.

Cylic boundary condition.

Derivation of eigenfunction of $\hat{L}_z$

Since $T(\phi) = T(\phi + 2\pi)$,

$$A e^{\frac{ib\phi}{\hbar}} = A e^{\frac{ib(\phi+2\pi)}{\hbar}} = A e^{\frac{ib\phi}{\hbar}} e^{\frac{i2\pi b}{\hbar}}, \tag{11.39}$$

$$e^{\frac{ib2\pi}{\hbar}} = 1, \ \cos\frac{2\pi b}{\hbar} + i \sin\frac{2\pi b}{\hbar} = 1. \tag{11.40}$$

Therefore

$$\frac{2\pi b}{\hbar} = 2\pi m, \ m = 0, \pm 1, \pm 2, \cdots, \ b = m\hbar, \tag{11.41}$$

$$T(\phi) = \frac{1}{\sqrt{2\pi}} e^{-im\phi}. \tag{11.42}$$

11.4.1 Physical Meaning

- "Measured" angular momentum along on axis equals to integer of $\hbar$!
- For rotation about an axis, i.e. on a plane, or rotation in two directions

$$\hat{H}_{2D} = \frac{\hat{L}_z^2}{2I} \Rightarrow \hat{H}_{2D} T(\phi) = \frac{1}{2I}(m\hbar)^2 T(\phi),\ m = 0, \pm 1, \pm 2, \cdots, \tag{11.43}$$

  for $m \neq 0$ state, the energy has two-fold degenerarcy.

Why it has two-fold degenerarcy?

Still, we do not explain why $l = 0, 1, 2, \cdots$ and why $\hat{L}^2$ has eigenvalues of $l(l+1)\hbar^2$. But a physical way to understand this is to recognize that: For $\langle \hat{L}^2 \rangle$ and $\langle \hat{L}_z^2 \rangle$, if $\langle \hat{L}^2 \rangle = \langle \hat{L}_z^2 \rangle$,then $\langle \hat{L}_x \rangle = \langle \hat{L}_y \rangle = 0$, everything is determined. Therefore, if $\hat{L}^2 = l(l+1)\hbar^2$, the maximal $\langle \hat{L}_z^2 \rangle$ is when $m = \pm l$.