A. Physics of Classical Rotations

- We consider the motion of two masses \( m_1 \) and \( m_2 \) connected by a rigid, massless “bond” of length \( r \). This entity is called a rigid rotor. It is a model for the rotational dynamics of diatomic molecules, and it is a simple illustration of how rotational motions are quantized.

- Before we consider how to quantize rotations, we introduce some basic concepts on rotational motions from classical physics.

- Consider a mass \( m \) moving in a circular orbit of radius \( r \). Assume the mass moves with constant velocity \( v \). See figure below.

\[ \omega = \frac{d\phi}{dt} \]  

(7.1)

where \( \phi \) is the angle traced out as \( r \) changes direction.

- The relationship between \( v \) and \( \omega \) can be obtained as follows. Assume as a result of the motion of the mass on a circular path with linear velocity \( v \), in a short time \( \Delta t \) the angle changes by \( \Delta \phi \). As shown in the figure the particle covers a linear distance \( \Delta s \) on the orbit. We have:
The kinetic energy of the particle is now

\[ K = \frac{p^2}{2m} = \frac{\mu v^2}{2} = \frac{\mu r^2 \omega^2}{2} = \frac{I \omega^2}{2} \]  

(7.3)

• The term \( I = \mu r^2 \) is called the moment of inertia. We will discuss it in detail later.

• We can also express the energy \( K \) in terms of the angular momentum. The angular momentum is defined in terms of the cross product between the position vector \( \mathbf{r} \) and the linear momentum vector \( \mathbf{p} \):

\[ \mathbf{L} = \mathbf{r} \times \mathbf{p} \]

\[ = pr \sin \theta = pr = \mu vr \]  

(7.4)

where the angle \( \theta \) between \( \mathbf{p} \) and \( \mathbf{r} \) is ninety degrees for circular motion.

• As a cross product, the angular momentum vector \( \mathbf{L} \) is perpendicular to the plane defined by the \( \mathbf{r} \) and \( \mathbf{p} \) vectors.

- We can use equation 7.4 to obtain an expression for the kinetic energy in terms of the angular momentum \( \mathbf{L} \):

\[ K = \frac{p^2}{2\mu} = \frac{L^2}{2\mu r^2} = \frac{L^2}{2I} \]  

(7.5)

- The moment of inertia is derived as follows. For two masses \( m_1 \) and \( m_2 \):

\[ I = m_1 r_1^2 + m_2 r_2^2 \]  

(7.6)

where \( r_1 \) and \( r_2 \) are the distances of \( m_1 \) and \( m_2 \) from the center of mass, respectively where,

\[ r_{1,2} = \frac{m_{2,1}}{m_1 + m_2} r \]  

(7.7)
• Putting 7.7 into 7.6 we obtain $I = \mu r^2$ where $\mu = \frac{m_1 m_2}{m_1 + m_2}$

B. Quantum Planar Rigid Rotor

• Suppose a diatomic molecule rotates in such a way that the vibration of the bond is unaffected by the rotation. Molecular rotation is not naturally treated in Cartesian coordinates so we change to spherical coordinates

\[ x = r \cos \varphi \sin \theta; \quad y = r \sin \varphi \sin \theta; \quad z = r \cos \theta \]  

(7.8)

See the figure below for the graphical relationship between the two coordinate systems:

• For simplicity, assume the rigid rotor is confined to a plane. This is not a terribly realistic model for molecular rotations, but it does illustrate an application of Schroedinger’s equation that can be worked out fairly easily.

• For a planar rigid rotor we set the angle $\theta$ at a constant value of 90 degrees. We imagine that the origin is the center of mass of the rigid rotor and length of the rotor is $r$ and at the point P is located a reduced mass $\mu$. Rotation occurs in the x-y plane around the z axis. As rotation occurs the angle $\varphi$ changes. The notation $L_z$ refers to the fact that because the rotation is around the z axis the angular momentum vector is parallel to the z axis. Schroedinger’s equation is:

\[ \frac{p^2}{2\mu} \psi(\varphi) = \frac{L_z^2}{2I} \psi(\varphi) = E\psi(\varphi) \]  

(7.9)
We define \( \hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} = -i \hbar \frac{\partial}{\partial \phi} \) so that \( \hat{L}_z^2 = -\hbar^2 \frac{d^2}{d\phi^2} \) and Schrödinger’s equation becomes:

\[
-\frac{\hbar^2}{2I} \frac{d^2 \psi(\phi)}{d\phi^2} = E\psi(\phi)
\]

(7.10)

The solution is:

\[
\psi(\phi) = A_+ e^{ik\phi} + A_- e^{-ik\phi} = \psi_+(\phi) + \psi_-(\phi)
\]

(7.11)

where \( k^2 = \frac{2IE}{\hbar^2} \)

We require that because the rotor is indistinguishable when it is oriented at \( \phi \) versus \( \phi + 2\pi \):

\[
\psi(\phi) = \psi(\phi + 2\pi)
\]

or \( A_+ e^{ik\phi} + A_- e^{-ik\phi} = A_+ e^{i(k+2\pi)\phi} + A_- e^{-i(k+2\pi)\phi} \)

(7.12)

For this to occur we require that \( e^{i2\pi k} = 1 \), which will only occur if \( k = 0, \pm 1, \pm 2, \pm 3 \ldots \) Because \( k \) is positive and negative we need only a single function to describe the wave function, which can now be normalized:

\[
1 = \int_0^{2\pi} \psi^*(\phi)\psi(\phi) d\phi = A_+^2 \int_0^{2\pi} e^{-ik\phi} e^{ik\phi} d\phi = A_+^2 \int_0^{2\pi} d\phi = 2\pi A^2
\]

(7.13)

\[
A = \frac{1}{\sqrt{2\pi}}
\]

We substitute \( \psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{ik\phi} \) into Schrödinger’s equation 7.10 and obtain the energy quantization condition:

\[
E_k = \frac{\hbar^2 k^2}{2I}
\]

(7.14)

where \( k = 0, \pm 1, \pm 2, \pm 3 \ldots \)

Because \( E_k = \frac{L^2}{2I} \), equation 7.14 implies that the angular momentum around the z axis is quantized according to

\[
|L_z| = k\hbar
\]

(7.15)

B. Rigid Rotor: Two Dimensions

A more realistic model has a rigid linear molecule with moment of inertia \( I \) rotating through two angular dimensions, designated by \( \theta \) and \( \phi \). Using the transformation (7.4) and assuming that \( r \) is constant, Schrödinger’s equation becomes

\[
\frac{1}{2I} \left( \frac{p_{\theta}^2}{\sin^2 \theta} + \frac{p_{\phi}^2}{\sin^2 \phi} \right) \Psi(\theta, \phi) = \frac{L^2}{2I} \Psi(\theta, \phi) = E \Psi(\theta, \phi)
\]

(7.16)
where it can be shown that  \[ p^{2}_{\phi} = -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \]  and  \[ p^{2}_{\psi} = L^{2}_{z} = -\hbar^2 \frac{\partial^2}{\partial \phi^2} \]

- Therefore \( L^{2} \) is the total angular momentum:
\[
L^{2} = -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{\hbar^2}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}
\]

(7.17)

- Note because the rotor is rigid \( r \) is a constant and so all derivatives with respect to \( r \) vanish. The problem becomes two dimensional and the wave function that is obtained by solving (7.16) has the form…
\[
\Psi(\theta, \phi) = \Theta(\theta) \Phi(\phi)
\]

(7.18)

- One dimensional problems like the particle in the one dimensional box have a single quantum number \( n \). The particle in a three dimensional box has three quantum numbers \( n_{x}, n_{y}, n_{z} \). Accordingly the rigid rotor has two quantum numbers \( l \) and \( m \). The dependence of the wave functions on \( l \) and \( m \) is
\[
\Psi_{l,m}(\theta, \phi) = \Theta_{l,m}(\theta) \Phi_{m}(\phi)
\]

(7.19)

- Schrodinger’s equation can be solved to get the energy and the wave functions.

- The energy is a function of \( l \) only:  \( E_{l} = \frac{L^{2}_{z}}{2I} = \frac{\hbar^2}{2I} (l + 1) \)

- The total angular momentum is therefore quantized according to  \( L^{2} = \hbar^2 (l + 1) \)

- The quantum number \( l \) has values \( l=0,1,2,3,4,\ldots \)

- Because \( L^{2}_{z} \) also appears in the Schrodinger equation \( L_{z} \) is quantized exactly as in the planar rigid rotor:  \( L^{2}_{z} = \hbar^2 m^2 \)

- For a given value of \( l \), \( m \) runs from \(-l\) to \(+l\), a total of \( 2l+1 \) values. Because the energy is dependent only on \( l \), there will be \( 2l+1 \) wavefunctions corresponding to different values of \( m \), that will have this energy. Each rotational level will be \( 2l+1 \) degenerate.

- All wave functions  \( \Phi_{m}(\phi) = \frac{\epsilon^{l,m}_{\phi}}{\sqrt{2\pi}} = \frac{1}{\sqrt{2\pi}} (\cos m\phi + i \sin m\phi) \). The following table gives the wavefunctions for \( l=0,1,2 \).

<table>
<thead>
<tr>
<th>( l )</th>
<th>( m )</th>
<th>( \Theta_{l,m}(\theta) )</th>
<th>( \sqrt{2\pi} \times \Phi_{m}(\phi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>( \sqrt{\frac{\pi}{2}} \cos \theta )</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>( \sqrt{\frac{\pi}{2}} \sin \theta )</td>
<td>( e^{\pm ip} )</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( \sqrt{\frac{\pi}{2}} (3 \cos^2 \theta - 1) )</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>( \sqrt{\frac{\pi}{4}} \sin \theta \cos \theta )</td>
<td>( e^{\pm ip} )</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>( \sqrt{\frac{\pi}{16}} \sin^2 \theta )</td>
<td>( e^{\pm 2ip} )</td>
</tr>
</tbody>
</table>
Note that we finally have a complex wave function. Now for \( I = 1 \) and \( m = 1 \) we obtain
\[
\Psi_{1,1} (\theta, \varphi) = \Theta_{1,1} (\theta) \Phi_1 (\varphi) = \sqrt{\frac{3}{4\pi}} \sin \theta \times e^{i\varphi}
\]
\[
\therefore \Psi_{1,1} (\theta, \varphi) = \Theta_{1,1} (\theta) \Phi^*_1 (\varphi) = \sqrt{\frac{3}{4\pi}} \sin \theta \times e^{-i\varphi}
\]
\[
\therefore \Psi_{1,1} (\theta, \varphi) \times \Psi_{1,1} (\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \sin \theta \times e^{i\varphi} \times \sqrt{\frac{3}{4\pi}} \sin \theta \times e^{-i\varphi} = \frac{3}{8\pi} \sin^2 \theta
\]

Complex wave functions can be expressed as linear combinations that are real:
\[
\Psi_+ = A (\Psi_{1,1} (\theta, \varphi) + \Psi_{1,-1} (\theta, \varphi)) = A \sqrt{\frac{3}{4\pi}} \sin \theta \times e^{i\varphi} + A \sqrt{\frac{3}{4\pi}} \sin \theta \times e^{-i\varphi}
\]
\[
= A \sqrt{\frac{3}{4\pi}} \sin \theta (e^{i\varphi} + e^{-i\varphi}) = A \sqrt{\frac{3}{2\pi}} \sin \theta \cos \varphi
\]

Then normalize:
\[
1 = 4 \pi \int_0^{2\pi} d\varphi \cos^2 \varphi \int_0^{\pi} d\theta \sin \theta = \frac{3}{2\pi} A^2 (\pi) (\frac{1}{4}) = 2A^2
\]
\[
\therefore A = \frac{1}{\sqrt{2}} \quad \text{and} \quad \Psi_+ = \frac{1}{\sqrt{2}} (\Psi_{1,1} (\theta, \varphi) + \Psi_{1,-1} (\theta, \varphi)) = \frac{1}{4} \sqrt{\frac{3}{2\pi}} \sin \theta \cos \varphi
\]

Probability Integrals:
\[
\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta \Psi_{1,1} (\theta, \varphi) \times \Psi^*_{1,1} (\theta, \varphi) = \frac{1}{8\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin^3 \theta = \frac{1}{8} \int_0^{\pi} d\theta \sin^3 \theta = \frac{1}{4} \left( 2 + \frac{1}{3} (-2) \right) = 1
\]

Probability that rotor lies between \( \varphi = 0 \) and \( \pi/2 \) and \( \theta = 0 \) and \( \pi/2 \) and
\[
\frac{\pi}{2} = \frac{1}{8\pi} \int_0^{\pi/2} d\varphi \int_0^{\pi/2} d\theta \sin^3 \theta = \frac{1}{16} \int_0^{\pi/2} d\theta \sin^3 \theta = \frac{1}{16} \left( \frac{1}{2} \right) = \frac{1}{32}
\]

This result could be obtained by just reasoning that the \( \varphi \) integral covers \( 1/4 \) of the total range while the \( \theta \) integral covers \( 1/2 \) of the total range. Because the wave function is normalized the result must be \( 1/4 \times 1/2 = 1/8 \).