The Rigid Rotor and Rotational Spectroscopy

2 particle problem that we want

to reduce to a 1 particle problem (easier to solve)

to do this we must choose an appropriate

Coordinate System and adjust the Hamiltonian

The System can be divided

into two parts:

1. Translation of the whole

   System

2. Internal/Relative motion:

   (a) Vibrations

   (b) Rotations

\[ H_{\text{total}} = H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} \]

\[ H_{\text{trans}} \quad \text{modeled like}\]

\[ H_{\text{rot}} \quad \text{modeled with}\]

\[ H_{\text{vib}} \quad \text{either}\]

\[ V = \frac{1}{2} k x^2 \quad \text{harmonic}\]

\[ V = \frac{1}{2} k x^2 + \text{other terms} \quad \text{or anharmonic} \]

Rigid Rotor

Internal Coordinates

\[ I = m_1 l_1^2 + m_2 l_2^2 = \mu l^2 \]

where \( \mu \) is the reduced mass:

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

Center of mass defined as

\[ m_1 l_1 = m_2 l_2 \]

Using moment of Inertia:

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]
Instead of tracking both \((x_1, y_1, z_1)\) \& \((x_2, y_2, z_2)\) it becomes much easier to switch to Spherical coordinates and track the center of mass.

\[
\text{Notes: } \frac{d}{dr} = \text{translation of entire molecule} \\
\frac{d}{dr} = \text{change of internal bond length} \\
\frac{d}{dr} = 0 \text{ for rigid rotor}
\]

\[\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{1}{r^2 \sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d}{d \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{d^2}{d \phi^2}
\]

Hamiltonian:

\[H = \hat{T} + \hat{V}\]

\[\hat{T} = -\frac{\hbar^2}{2M} \nabla^2\]

Recall \(I = M \ell^2\) \(\Rightarrow M = \frac{I}{\ell^2}\)

\[\hat{T} = -\frac{\hbar^2}{2(\ell^2)} \nabla^2\]

Where

\[\nabla^2 = \frac{1}{r^2 \sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d}{d \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{d^2}{d \phi^2}\]

Note the \(\ell^2\) cancel and we are left with

\[\hat{A}_{\text{rot}} = -\frac{\hbar^2}{2I} \left( \frac{1}{\sin \theta} \frac{d}{d \theta} \left( \sin \theta \frac{d}{d \theta} \right) + \frac{1}{\sin^2 \theta} \frac{d^2}{d \phi^2} \right)\]
Schroedinger Eq

\[-\frac{\hbar^2}{2m} \left[ \frac{1}{\sin \theta} \frac{d}{d \theta} (\sin \theta \frac{d}{d \theta}) + \frac{1}{\sin^2 \theta} \frac{d^2}{d \phi^2} \right] Y(\theta, \phi) = E Y(\theta, \phi)\]

Wavefunctions called Spherical Harmonics

Energies

\[E_J = \frac{\hbar^2}{2m} J(J+1) = B J(J+1)\]

where \(B = \frac{\hbar^2}{2m}\)

\(J = 0, 1, 2, 3, \ldots\)

Each energy level has a degeneracy \(g_J = 2J+1\)

Spherical Harmonics (wavefunctions)

\[Y_j^m(\theta, \phi) = i^m \sqrt{\frac{(2J+1)(J-|m|)!}{4\pi(J+|m|)!}} P_j^{|m|}(\cos \theta) e^{im\phi}\]

\(J = 0, 1, 2, 3, \ldots\)

\(m = 0, \pm 1, \pm 2, \ldots, \pm J\)

\(m\) depends on \(J\) (also determines the number of degeneracies)

Table 6.5 has the first few Spherical Harmonics

\[Y_0^0 = \frac{1}{\sqrt{4\pi}} \quad Y_1^0 = (\frac{3}{4\pi})^{1/2} \cos \theta\]
Purely Rotation

Selection Rule: $\Delta J = \pm 1$

$E_J = \frac{\hbar^2}{2I} J(J+1)$

$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{I} (J+1) = \frac{\hbar^2}{4\pi^2 I} (J+1)$ \hspace{1cm} J = 0, 1/2, ...

Since $\Delta E = \hbar \nu_{obs}$ then frequency of observed transition

$\nu_{obs} = \frac{\hbar}{4\pi^2 I} (J+1)$

Define $B = \frac{\hbar}{8\pi^2 I}$ to be the rotational constant.

then \hspace{1cm} $\nu_{obs} = 2B(J+1)$

$B = \frac{\hbar}{8\pi^2 CI}$ \hspace{1cm} $\nu_{obs} = 2B(J+1)$

Note: for a pure rotation transitions are equally spaced (theoretically!)
Experimentally, the spacing between transitions are not equal \( \rightarrow \) Bond length have a slight distortion from rotations

\[
E_j = \tilde{B}J(J+1) - \tilde{B}J^2(J+1)^2
\]

where \( \tilde{B} = \) centrifugal distortion const.

**Angular momentum Operator**

Classically,

\[
\mathbf{L} = I \mathbf{\omega}
\]

Quantum mechanically

Since \( I = \frac{L^2}{2I} \)

\[
\hat{L}^2 = -\hbar^2 \nabla^2
\]

\[
\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2
\]

\[
\begin{align*}
\hat{L}_x &= y\hat{P}_z - z\hat{P}_y = -i\hbar (y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}) \\
\hat{L}_y &= z\hat{P}_x - x\hat{P}_z = -i\hbar (z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}) \\
\hat{L}_z &= x\hat{P}_y - y\hat{P}_x = -i\hbar (x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})
\end{align*}
\]

Polar

\[
\begin{align*}
\hat{L}_x &= -i\hbar (-\sin \phi \frac{\partial}{\partial \phi} - \cos \theta \cos \phi \frac{\partial}{\partial \phi}) \\
\hat{L}_y &= -i\hbar (\cos \phi \frac{\partial}{\partial \phi} - \cos \theta \sin \phi \frac{\partial}{\partial \phi}) \\
\hat{L}_z &= -i\hbar \frac{\partial}{\partial \phi}
\end{align*}
\]