Chapter 7. A Quantum Mechanical Model for the Vibration and Rotation of Molecules

Harmonic oscillator:

Hooke’s law:

\[ F = -kx, \text{ } x \text{ is displacement} \]

Harmonic potential:

\[ V(x) = -\int F dx = \frac{1}{2}kx^2 \]

\( k \) is force constant:

\[ k = \frac{d^2V}{dx^2}\bigg|_{x=0} \quad \text{(curvature of } V \text{ at equilibrium)} \]

Newton’s equation:

\[ m \frac{d^2x}{dt^2} = F = -kx \quad \text{(diff. eqn)} \]

Solutions:

\[ x = Asin\omega t, \quad \text{(position)} \]

\[ \omega = (k/m)^{1/2} \quad \text{(vibrational frequency)} \]
Verify:

\[
lhs = m \frac{d^2 A \sin \omega t}{dt^2} = mA \omega \frac{d}{dt} \cos \omega t = -mA \omega^2 \sin \omega t
\]

\[
= -m \frac{k}{m} A \sin \omega t = -kx = rhs
\]

Momentum:

\[
p = m \frac{dx}{dt} = m \omega A \cos \omega t
\]

Energy:

\[
E = \frac{p^2}{2m} + V
\]

\[
= \frac{(m \omega A \cos \omega t)^2}{2m} + \frac{1}{2} k (A \sin \omega t)^2
\]

\[
= \frac{m \omega^2 A^2}{2} \left[ (\cos \omega t)^2 + (\sin \omega t)^2 \right]
\]

\[
= \frac{m \omega^2 A^2}{2} = \frac{kA^2}{2}
\]

When \( \omega t = 0 \), \( x = 0 \) and \( p = p_{\text{max}} = m \omega A \)
When \( \omega t = \pi/2 \), \( p = 0 \) and \( x = x_{\text{max}} = A \)

Energy conservation is maintained by oscillation between kinetic and potential energies.
Schrödinger equation for harmonic oscillator:

\[
\left[ -\hbar^2 \frac{d^2}{2m \, dx^2} + \frac{1}{2} kx^2 \right] \Psi = E \Psi
\]

Energy is quantized:

\[
E_{\nu} = \left( \nu + \frac{1}{2} \right) \hbar \omega \quad \nu = 0, 1, ...
\]

where the vibrational frequency

\[
\omega = \left( \frac{k}{m} \right)^{1/2}
\]

Restriction of motion leads to uncertainty in \( x \) and \( p \), and quantization of energy.

Wavefunctions:

\[
\Psi_{\nu}(x) = N_{\nu} H_{\nu}(y) e^{-y^2/2}
\]

where

\[
y = \alpha x, \quad \alpha = \left( \frac{mk}{\hbar^2} \right)^{1/4}
\]

Normalization factor
\[
N_\nu = \left( \frac{\alpha}{\sqrt{\pi} 2^\nu \nu!} \right)^{1/2}
\]

\(H_\nu(y)\) is the Hermite polynomial

\[H_0(y) = 1\]
\[H_1(y) = 2y\]
\[H_2(y) = 4y^2 - 2\]

\[\ldots\]
\[H_{\nu+1} = 2yH_\nu - 2\nu H_{\nu-1}\]  
(recursion relation)

Let’s verify for the ground state

\[\Psi_0(x) = N_0 e^{-\alpha^2 x^2 / 2}\]

\[
\text{lhs} = N_0 \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right] e^{-\alpha^2 x^2 / 2}
\]
\[
= N_0 \left[ -\frac{\hbar^2}{2m} d \left( e^{-\alpha^2 x^2 / 2}(-\alpha^2 x) \right) + \frac{1}{2} kx^2 e^{-\alpha^2 x^2 / 2} \right]
\]
\[
= N_0 \left[ -\frac{\hbar^2}{2m} \left( e^{-\alpha^2 x^2 / 2}(-\alpha^2)^2 + e^{-\alpha^2 x^2 / 2}(-\alpha^2) \right) + \frac{1}{2} kx^2 e^{-\alpha^2 x^2 / 2} \right]
\]
\[
= N_0 \left[ \frac{k}{2} - \frac{\hbar^2 \alpha^4}{2m} \right] x^2 \frac{\hbar^2 \alpha^2}{2m} e^{-\alpha^2 x^2 / 2}
\]

Note that
\[ \alpha = \left( \frac{mk}{\hbar^2} \right)^{1/4} \]

It is not difficult to prove that the first term is zero, and the second term as \( \hbar \omega/2 \).

\[ \text{rhs} = \frac{1}{2} \hbar \omega N_0 e^{-\alpha^2 x^2/2} \]

So, \( \text{rhs} = \text{lhs} \), it is a solution.

One can also show normalization:

\[ \int_{-\infty}^{\infty} |\Psi_0|^2 dx = N_0^2 \int_{0}^{\infty} e^{-\alpha^2 x^2} dx = \frac{\alpha}{\sqrt{\pi}} \cdot 2 \sqrt{\frac{\pi}{4\alpha^2}} = 1 \]

where we have taken advantage of the even symmetry of the Gaussian

\[ e^{-a(-x)^2} = e^{-ax^2} \]

and used the integral formula

\[ \int_{0}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{4a}} \]

For higher states, the wavefunctions are essentially the product of a Gaussian and a polynomial:
The Gaussian is always an even function, but the polynomial can either be even \( f(-x) = f(x) \) or odd \( f(-x) = -f(x) \). As a result, the wavefunctions are either even or odd, depending on \( \nu \).

Properties of the oscillator

i. **Zero point energy** \( (\nu = 0) \)

\[
E_0 = \frac{1}{2} \hbar \omega
\]  

(quantum effect)

Even at 0 K, there is still vibration.

ii. **Orthonormality:**

\[
\int_{-\infty}^{\infty} \Psi_{\nu}^* \Psi_{\nu'} dx = \delta_{\nu \nu'}
\]

iii. **Average displacement**

\[
\int_{-\infty}^{\infty} \Psi_{\nu}^* (x) x \Psi_{\nu} (x) dx = 0
\]
No matter if $\Psi_\nu(x)$ is even or odd, $|\Psi_\nu(x)|^2$ is even, and thus the integrant is odd. Integration of an odd function in $[-\infty, \infty]$ is always zero.

iv. **Average momentum**

$$\int\limits_{-\infty}^{\infty} \Psi_\nu^*(x) \left( \frac{\hbar}{i} \frac{d}{dx} \right) \Psi_\nu(x) dx = 0$$

Because the derivative of an even function is an odd function, and vice versa.

v. **Nodes**

The $\nu$ state has $\nu - 1$ nodes (due to Hermite polynomial)

vi. **Energy separation**

$$\Delta E = E_{\nu+1} - E_\nu = \left( (\nu + 1 + 1/2) - (\nu + 1/2) \right) \hbar \omega = \hbar \omega$$

(equal separation).

vii. **Tunneling**

Wavefunction penetrates into classically forbidden regions. A quantum phenomenon.

Example: A harmonic oscillator has a force constant of 475 N/m and a mass of $1.61 \times 10^{-27}$ kg. Calculate the ZPE and the photon frequency needed to bring the oscillator from ground state to the first excited state.
\[ \omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{475 N/m}{1.61 \times 10^{-27} \text{kg}}} = 5.43 \times 10^{14} \text{s}^{-1} \]

\[ (N/m = \text{kg/s}^2) \]

\[ E_0 = \frac{1}{2} \hbar \omega = 0.5 \times 1.054 \times 10^{-34} \text{Js} \times 5.43 \times 10^{14} \text{s}^{-1} \]
\[ = 2.86 \times 10^{-20} \text{J} \]

\[ \Delta E = \hbar \omega = 2E_0 = 5.72 \times 10^{-20} \text{J} \]

\[ \nu = \frac{\Delta E}{\hbar} = \frac{5.72 \times 10^{-20} \text{J}}{6.626 \times 10^{-34} \text{Js}} = 8.63 \times 10^{13} \text{s}^{-1} \]
\[ = 3476 \text{nm} \]

\[ (\nu \lambda = c) \]

Example: The IR spectrum of $\text{H}^{35}\text{Cl}$ is dominated by a peak at 2886 cm$^{-1}$. Calculate the force constant of the molecule.

Reduced mass

\[ \mu = \frac{1 \times 35}{1 + 35} = 0.97 \text{amu} \times 1.66 \times 10^{-27} \text{kg/amu} = 1.61 \times 10^{-27} \text{kg} \]

\[ \omega = 2\pi \nu = 2\pi c \tilde{\nu} \]
\[ = 2 \times 3.14 \times 3.0 \times 10^{10} \text{cm/s} \times 2886 \text{cm}^{-1} = 5.43 \times 10^{14} \text{s}^{-1} \]

\[ k = \mu \omega^2 = 1.61 \times 10^{-27} \text{kg} \times (5.43 \times 10^{14} \text{s}^{-1})^2 \]
\[ = 475 \text{kg/s}^2 = 475 \text{N/m} \]
What about DCl?

\[
\mu = \frac{2 \times 35}{2 + 35} = 1.89 \text{amu} \times 1.66 \times 10^{-27} \text{kg/amu} = 3.14 \times 10^{-27} \text{kg}
\]

\[\propto 2 \mu_{\text{HCl}}\]

\[
\omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{475 \text{kg/s}^2}{3.14 \times 10^{-27} \text{kg}}} = 3.89 \times 10^{14} \text{s}^{-1} \propto \frac{1}{\sqrt{2}} \omega_{\text{HCl}}
\]

\[
\tilde{v} = \frac{\omega}{2 \pi c} = \frac{3.89 \times 10^{14} \text{s}^{-1}}{2 \times 3.14 \times 3.0 \times 10^{10} \text{cm/s}} = 2063 \text{cm}^{-1} \propto \frac{1}{\sqrt{2}} \tilde{v}_{\text{HCl}}
\]

Isotope effect is important to assign spectral lines.

**Rigid rotors**

Angular momentum vector

\[
\vec{l} = \vec{r} \times \vec{p} = I \vec{\omega}
\]

(r fixed)

where the angular velocity and moment of inertia are

\[
\omega = \frac{d\theta}{dt}, \quad I = \mu r^2
\]

The rotational energy (classical):

\[
E = \frac{l^2}{2I}
\]
Schrödinger eqn. for 2D motion:

\[- \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \Psi = E \Psi\]

Use polar coordinate system \((x = r \cos \phi, y = r \sin \phi)\), it becomes for 2D rigid rotor:

\[- \frac{\hbar^2}{2I} \frac{d^2 \Psi}{d\phi^2} = E \Psi\]

General solution:

\[\Psi_m(\phi) = \left( \frac{1}{2\pi} \right)^{1/2} e^{im\phi}, \quad m = \pm \left( \frac{2IE}{\hbar^2} \right)^{1/2}\]

Cyclic boundary condition:

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

So,

\[\Psi(\phi + 2\pi) = Ne^{im(\phi+2\pi)} = Ne^{i2m\pi} e^{im\phi}\]

\[= N(e^{i\pi})^{2m} e^{im\phi} = (-1)^{2m} \Psi(\phi)\]

2\(m\) has to be even integers, i.e.

\[m = 0, \pm 1, \pm 2, \ldots\]
Quantization

\[ E_m = \frac{m^2 \hbar^2}{2I} \]  

(2D)

Angular momentum:

\[ l_z = m\hbar \]

(quantized angular momentum)

Angular momentum operator

\[ \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \]

\[ = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \]

\(\Psi\) is a common eigenfunction of both operators:

\[ \hat{L}_z \Psi = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \left[ \left( \frac{1}{2\pi} \right)^{1/2} e^{im\phi} \right] = \frac{im}{i} \left( \frac{1}{2\pi} \right)^{1/2} e^{im\phi} = m\hbar \Psi \]

\[ \hat{H} \Psi = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \left[ \left( \frac{1}{2\pi} \right)^{1/2} e^{im\phi} \right] = \frac{(m\hbar)^2}{2I} \Psi \]

Uncertainty principle (just like \(p\) and \(x\))

\[ \Delta l_z \Delta \phi \geq \hbar / 2 \]
3D rotors:

Spherical coordinates:

\[ x = r \sin \theta \cos \phi \]
\[ y = r \sin \theta \sin \phi \]
\[ z = r \cos \theta \]
\[ d\tau = dx dy dz = r^2 \sin \theta dr d\theta d\phi \]

Hamiltonian:

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 \]
\[ = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \]
\[ = -\frac{\hbar^2}{2m r} \frac{1}{r^2} \frac{\partial}{\partial r} r + \frac{\hat{L}^2}{2mr^2} \]

The differential operator \( \nabla^2 \) is called Laplacian.

If \( r \) is fixed, the 3D rigid rotor Hamiltonian:

\[ \hat{H} = \frac{\hat{L}^2}{2I} \]  
(rigid rotor)

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

Schrödinger eqn.

\[ \frac{\hat{L}^2}{2I} \Psi = E \Psi \]

The solution is the spherical harmonics:

\[ \Psi(\theta, \phi) = Y_l^m(\theta, \phi) = N_{lm} P_l^{|m|}(\cos \theta) \Phi_m(\phi) \]

where

\[ N_{lm} = \sqrt{\frac{(2l + 1) (l - |m|)!}{2 (l + |m|)!}} \]

\[ \Phi_m(\phi) = \left( \frac{1}{2\pi} \right)^{1/2} e^{im\phi} \quad (2D \text{ rotor}) \]

and \( P_l^{|m|}(\cos \theta) \) is the associated Legendre function.

The quantization of two angular coordinates leads to two quantum numbers:

\[ l = 0, 1, 2, ... \]
\[ m = 0, \pm 1, \pm 2, ..., \pm l \quad (2l + 1) \]
Rotational energy (3D rotor)

\[ E_l = \frac{l(l + 1)\hbar^2}{2I} \]

Since \( E \) is independent of \( m \), each \( l \) level is \( 2l + 1 \) degenerate, which can be removed by an external field (Zeeman effect).

When \( m = 0 \), \( P_l^{|m|}(\cos \theta) \) becomes the Legendre polynomial:

- \( P_0(\cos \theta) = 1 \)
- \( P_1(\cos \theta) = \cos \theta \)
- \( P_2(\cos \theta) = (3\cos^2 \theta - 1)/2 \)
- …

For \( m \neq 0 \)

\[ P_l^{|m|}(\cos \theta) = \sin^{|m|}\theta \frac{d^{|m|}}{d \cos \theta^{|m|}} P_l(\cos \theta) \]

Examples of spherical harmonics:

- \( Y_0^0 \propto 1 \)
- \( Y_1^0 \propto \cos \theta \)
- \( Y_1^\pm1 \propto \sin \theta \sqrt{\frac{1}{2\pi}} e^{\pm i\phi} \)
- \( Y_2^0 \propto \frac{1}{2} \left( 3\cos^2 \theta - 1 \right) \)
They are eigenfunctions for both $\hat{L}^2$ and $\hat{L}_z$:

$$\hat{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi)$$
$$\hat{L}_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi)$$

Verification for $\Psi = Y_l^0 \propto \cos \theta$

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

$$= -\hbar^2 \left[ 0 + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( -\sin^2 \theta \right) \right]$$

$$= \frac{\hbar^2}{\sin \theta} (2 \sin \theta \cos \theta) = 2\hbar^2 \Psi$$

$$\hat{H} \Psi = \frac{\hat{L}^2}{2I} \Psi = \frac{2\hbar^2}{2I} \Psi$$

$$\hat{L}_z \Psi = -\frac{\hbar}{i} \frac{\partial}{\partial \phi} \cos \theta = 0\hbar \Psi$$

The spherical harmonics are orthonormal

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi Y_l^m(\theta, \phi) Y_l^{m'}(\theta, \phi)^* = \delta_{ll'} \delta_{mm'}$$

Note the volume element and ranges.
Spherical harmonics have nodes due to Legendre functions.

For $Y_1^0 \propto \cos \theta$, the angular node can be determined by

$$\cos \theta = 0, \quad \theta = 90^\circ$$

**Vector model:**

The angular momentum can be considered as a vector $\vec{L}$. In quantum mechanics, it is quantized in

i. magnitude: $|\vec{L}| = \sqrt{l(l+1)\hbar}$

ii. orientation: $L_z = m\hbar$

Only certain directions of $\vec{L}$ are allowed.

Example ($l = 1, m_i = 0, \pm 1$):

Example: Calc. amplitude of $L, L_z$ and $E$ for a rotor with $I = 4.6 \times 10^{-48}$ kg m$^2$ and $l = 1$. 
\[ L = \sqrt{l(l+1)}\hbar = \sqrt{2} \times 1.055 \times 10^{-34} \, Js = 1.49 \times 10^{-34} \, Js \]

\[ L_z = m_l\hbar = 0, \pm 1.055 \times 10^{-34} \, Js \quad \text{(3-fold degen.)} \]

The angle between \( \vec{L} \) and the z-axis for \( m_l = 1 \):

\[ \cos \gamma = \frac{L_z}{L} = \frac{1}{\sqrt{2}}, \quad \gamma = 45^\circ \]

\[ E = \frac{L^2}{2I} = \frac{(1.49 \times 10^{-34} \, Js)^2}{2 \times (4.6 \times 10^{-48} \, kgm^2)} = 2.4 \times 10^{-21} \, J \]

Example. A 3D rotor absorbs at 11 cm\(^{-1} \). Calculate its moment of inertia.

\[ \Delta E = E_1 - E_0 = \frac{(2 - 0)\hbar^2}{2I} \]

\[ \Delta E = h\nu = hc\tilde{\nu} \]

so

\[ I = \frac{\hbar^2}{hc\tilde{\nu}} = \frac{\hbar}{2\pi c \tilde{\nu}} \]

\[ = \frac{1.05 \times 10^{-34} \, Js}{2 \times 3.14 \times 3.0 \times 10^{10} \, cm/s \times 11 \, cm^{-1}} \]

\[ = 5.06 \times 10^{-47} \, kgm^2 \]