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

Harmonic oscillator:

Hooke's law:

$F = -kx$, x is displacement

Harmonic potential:

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

k is force constant:

$$k = \left.\frac{d^2V}{dx^2}\right|_{x=0} \qquad \text{(curvature of } V \text{ at equilibrium)}$$

Newton's equation:

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

Solutions:

$x = A\sin\omega t$, (position)

$\omega = (k/m)^{1/2}$ (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 $p = p_{max} = m\omega A$
When $\omega t = \pi/2,\ p = 0$ and $x = x_{max} = A$

Energy conservation is maintained by oscillation between kinetic and potential energies.

Schrödinger equation for harmonic oscillator:

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

Energy is quantized:

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right)\hbar\omega \qquad\qquad \upsilon = 0, 1, \ldots$$

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:

$$\Psi_\upsilon(x) = N_\upsilon H_\upsilon(y) e^{-y^2/2}$$

where

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

Normalization factor

$$N_\upsilon = \left(\frac{\alpha}{\sqrt{\pi}\, 2^\upsilon \upsilon!} \right)^{1/2}$$

$H_\upsilon(y)$ is the <u>Hermite polynomial</u>

$$H_0(y) = 1$$
$$H_1(y) = 2y$$
$$H_2(y) = 4y^2 - 2$$
$$\ldots$$
$$H_{\upsilon+1} = 2yH_\upsilon - 2\upsilon H_{\upsilon-1} \qquad \text{(recursion relation)}$$

Let's verify for the ground state

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

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

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 $\hbar\omega/2$.

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

So, $rhs = lhs$, it is a solution.

One can also show normalization:

$$\int_{-\infty}^{\infty} |\Psi_0|^2 dx = N_0^2 2\int_0^{\infty} e^{-\alpha^2 x^2} dx = \frac{\alpha}{\sqrt{\pi}} 2\sqrt{\frac{\pi}{4\alpha^2}} = 1$$

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 υ.

<u>Properties of the oscillator</u>

i. <u>Zero point energy</u> ($\upsilon = 0$)

$$E_0 = \frac{1}{2}\hbar\omega \qquad \text{(quantum effect)}$$

Even at 0 K, there is still vibration.

<u>ii. Orthonormality</u>:

$$\int_{-\infty}^{\infty} \Psi_\upsilon^* \Psi_{\upsilon'} dx = \delta_{\upsilon\upsilon'}$$

iii. <u>Average displacement</u>

$$\int_{-\infty}^{\infty} \Psi_\upsilon^*(x) x \Psi_\upsilon(x) dx = 0$$

No matter if $\Psi_\upsilon(x)$ is even or odd, $\left|\Psi_\upsilon(x)\right|^2$ is even, and thus the integrant is odd. Integration of an odd function in $[-\infty,\infty]$ is always zero.

iv. <u>Average momentum</u>

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

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

<u>v. Nodes</u>

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

<u>vi. Energy separation</u>

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

(equal separation).

vii. <u>Tunneling</u>

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 1.61×10^{-27} kg. Calculate the ZPE and the photon frequency needed to bring the oscillator from ground state to the first excited state.

$$\omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{475N/m}{1.61\times10^{-27}kg}} = 5.43\times10^{14}s^{-1}$$

$$(N/m = kg/s^2)$$

$$E_0 = \frac{1}{2}\hbar\omega = 0.5\times1.054\times10^{-34}Js\times5.43\times10^{14}s^{-1}$$
$$= 2.86\times10^{-20}J$$

$$\Delta E = \hbar\omega = 2E_0 = 5.72\times10^{-20}J$$

$$\nu = \frac{\Delta E}{h} = \frac{5.72\times10^{-20}J}{6.626\times10^{-34}Js} = 8.63\times10^{13}s^{-1}$$
$$= 3476nm$$

$$(\nu\lambda = c)$$

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

Reduced mass

$$\mu = \frac{1\times35}{1+35} = 0.97amu\times1.66\times10^{-27}kg/amu = 1.61\times10^{-27}kg$$

$$\omega = 2\pi\nu = 2\pi c\tilde{\nu}$$
$$= 2\times3.14\times3.0\times10^{10}cm/s\times2886cm^{-1} = 5.43\times10^{14}s^{-1}$$

$$k = \mu\omega^2 = 1.61\times10^{-27}kg\times\left(5.43\times10^{14}s^{-1}\right)^2$$
$$= 475kg/s^2 = 475N/m$$

What about DCl?

$$\mu = \frac{2\times 35}{2+35} = 1.89 amu \times 1.66\times 10^{-27} kg/amu = 3.14\times 10^{-27} kg$$
$$\propto 2\mu_{HCl}$$

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

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

Isotope effect is important to assign spectral lines.

Rigid rotors

Angular momentum vector

$$\vec{l} = \vec{r}\times\vec{p} = I\vec{\omega} \qquad (r \text{ fixed})$$

where the angular velocity and moment of inertia are

$$\omega = \frac{d\theta}{dt}, \qquad I = \mu r^2$$

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:

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

Cyclic boundary condition:

$$\Psi(\phi) \ = \ \Psi(\phi + 2\pi)$$

So,

$$\Psi(\phi + 2\pi) = Ne^{im(\phi+2\pi)} = Ne^{i2m\pi}e^{im\phi}$$
$$= N(e^{i\pi})^{2m}e^{im\phi} = (-1)^{2m}\Psi(\phi)$$

$2m$ has to be even integers, i.e.

$$m \ = \ 0,\ \pm 1,\ \pm 2,\ ...$$

Quantization

$$E_m = \frac{m^2\hbar^2}{2I} \qquad \text{(2D)}$$

Angular momentum:

$$l_z = m\hbar \qquad \text{(quantized angular momentum)}$$

Angular momentum operator

$$\begin{aligned}\hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \\ &= \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}\frac{\partial}{\partial \phi}\end{aligned}$$

Ψ is a common eigenfunction of both operators:

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

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

Uncertainty principle (just like p and x)

$$\Delta l_z \Delta\phi \geq \hbar/2$$

<u>3D rotors:</u>

<u>Spherical coordinates</u>:

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$
$$d\tau = dxdydz = r^2\sin\theta drd\theta d\phi$$

Hamiltonian:

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

The differential operator ∇^2 is called Laplacian.

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

$$\hat{H} = \frac{\hat{L}^2}{2I} \qquad \text{(rigid rotor)}$$

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 <u>spherical harmonics</u>:

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

where

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

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

and $P_l^{|m|}(\cos\theta)$ is the <u>associated Legendre function</u>.

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

$l = 0, 1, 2, \ldots$
$m = 0, \pm1, \pm2, \ldots, \pm l$ $\qquad$ $(2l+1)$

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 <u>Legendre polynomial</u>:

$$P_0(\cos\theta) = 1$$
$$P_1(\cos\theta) = \cos\theta$$
$$P_2(\cos\theta) = \left(3\cos^2\theta - 1\right)/2$$
$$\ldots$$

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:

$$Y_0^0 \propto 1$$
$$Y_1^0 \propto \cos\theta$$
$$Y_1^{\pm 1} \propto \sin\theta \sqrt{\frac{1}{2\pi}} e^{\pm i\phi}$$
$$Y_2^0 \propto \frac{1}{2}\left(3\cos^2\theta - 1\right)$$

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 $\Psi = Y_1^0 \propto \cos\theta$

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

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

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

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

$$\cos\theta = 0, \qquad \theta = 90^{\circ}$$

<u>Vector model</u>:

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

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

ii. orientation: $L_z = m\hbar$

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

Example (l = 1, m_l = 0, ±1):

Example: Calc. amplitude of L, L_z and E for a rotor with I = 4.6x10^{-48} kg m^2 and l = 1.

$$L = \sqrt{l(l+1)}\hbar = \sqrt{2} \times 1.055 \times 10^{-34}\, Js = 1.49 \times 10^{-34}\, Js$$

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

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

$$\cos\gamma = \frac{L_z}{L} = \frac{1}{\sqrt{2}}, \qquad \gamma = 45^{\circ}$$

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

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

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

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

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