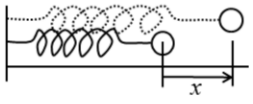
5. The Harmonic Oscillator and the Rigid Rotator: Two spectroscopic Models

- Harmonic Oscillator ⟶ Vibrational spectra (Force constants of molecules)
- Rigid Rotator ⟶ Rotational spectra (Bond lengths)

Classical { oscillator ⇒ quantum mechanical representation of energy; rotor }

5-1 A Harmonic Oscillator Obeys Hook's Law.



$f = -kx$

k: force constant

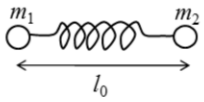
$$x(t) = C_1 \sin \omega t + C_2 \sin \omega t$$
$$= C \exp[i(\omega t - \phi)]$$
$$= \sqrt{\frac{k}{m}}$$

$$V(x) = -\int f(x)\,dx$$
$$= \frac{k}{2}x^2 + V(0)$$

$$K = \frac{kA^2}{2}\sin^2 \omega t,\quad V = \frac{kA^2}{2}\cos^2 \omega t,\quad E = K + V = \frac{kA^2}{2}$$

5-2 The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule.

Two particles connected with a spring



$$\begin{cases} m_1 \dfrac{\mathrm{d}x_1}{\mathrm{d}t^2} = k(x_2 - x_1 - l_0) \\ m_2 \dfrac{\mathrm{d}x_1}{\mathrm{d}t^2} = -k(x_2 - x_1 - l_0) \end{cases}$$

centroid coordinate

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$(m_1 + m_2)\frac{\mathrm{d}^2 X}{\mathrm{d}t^2} = 0$$

relative coordinate

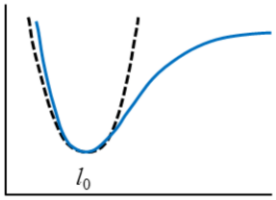
$$x = x_2 - x_1 - l_0$$

$$\frac{m_1 m_2}{m_1 + m_2}\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} + kx = 0$$

$$x = C\exp[i(\omega t - \phi)]$$

$$\omega = \sqrt{\frac{k}{\mu}} \qquad \left(\mu = \frac{m_1 m_2}{m_1 + m_2}\right)$$

5-3 The Harmonic Oscillator Approximation Results from the Expansion of an Internuclear Potential Around its Minimum.



Taylor expansion

$$V(l) = V(l0) + \frac{\mathrm{d}V}{\mathrm{d}l^2}(l - l_0) + \frac{1}{2!}\frac{\mathrm{d}^2 V}{\mathrm{d}l^2}(l - l_0)^2 + \cdots$$

$$V(x) = \frac{1}{2}kx^2 + \underline{\frac{1}{6}\gamma x^3 + \cdots}$$

anharmonic terms
(→ Chapter 13)

5-4 The Energy levels of a Quantum-Mechanical Harmonic Oscillator is $E_v = \hbar\omega\left(v+\frac{1}{2}\right)$, where v = 0, 1, 2, ...

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi(x)=E\psi(x), \qquad V(x)=\frac{1}{2}kx^2$$

$$E_v=\hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right) \qquad E_0=\hbar\omega\left(0+\frac{1}{2}\right)=\frac{1}{2}\hbar\omega$$

$$=\hbar\omega\left(v+\frac{1}{2}\right) \qquad \text{zero-point energy}$$

5-5 The Harmonic Oscillator Accounts for the Infrared Spectrum of a Diatomic Molecule.

$$E_v=\hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right) \qquad v=0,1,2,\cdots$$

$$\Delta E=h\nu_{\text{obs}} \qquad \Delta v=\pm 1$$

$$=E_{v+1}-E_v=\hbar\sqrt{\frac{k}{\mu}}$$

$$\nu_{\text{obs}}=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \left(\tilde{\nu}_{\text{obs}}=\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}\right)$$

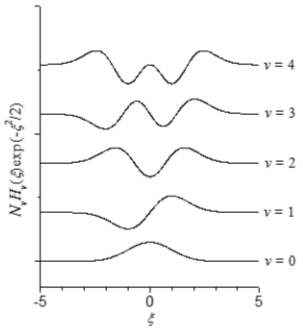
Compound	k / N m^{-1}	$\tilde{\nu}$ / cm^{-1}
H_2	510	4401
D_2	527	2990
$H^{35}Cl$	478	2886
$^{16}O_2$	1142	1556
$^{14}N_2$	2243	2330
$^{12}C^{16}O$	1857	2143

5-6 The Harmonic-Oscillator Wave Functions Involve Hermite Polynominals.

$$\psi_v(x) = N_v H_v(\sqrt{\alpha}x)\exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}, \quad N_v = \frac{1}{\sqrt{2^v v!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\left.\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \\ H_3(\xi) &= 8\xi^3 - 12\xi \\ &\vdots \end{aligned}\right\} \quad \frac{dH_v(\xi)}{d\xi} = 2vH_{v-1}(\xi)$$



$$\int \psi_v^*(x)\psi_{v'}(x)\,dx = \delta_{vv'} \quad \text{orthonormalized}$$

5-7 Hermit Polynominals are Either Even or Odd Functions.

$$\psi_v(-x) = \begin{cases} \psi_v(x) & (v:\text{even}) \\ -\psi_v(x) & (v:\text{odd}) \end{cases}$$

Average of the position

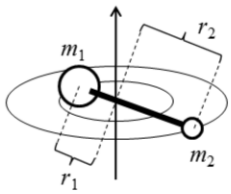
$$\langle x\rangle = \int \psi_v^*(x)\,x\,\psi_v(x)\,dx = 0$$

Average of the momentum

$$\langle p\rangle = \int \psi_v^*(x)\left(-i\hbar\frac{d}{dx}\right)\psi_v(x)\,dx = 0$$

5-8 The Energy Levels of a Rigid Rotator is $E = \hbar^2 J(J+1)/2I$.

Rigid-rotator model: bond length holds unchanged during rotation.



$$v_1 = 2\pi r_1 \nu_{rot} = r_1\omega,\ v_2 = 2\pi r_2 \nu_{rot} = r_2\omega$$

$$K = \frac{1}{2} m_1 v_1^{\ 2} + \frac{1}{2} m_2 v_2^{\ 2} = \frac{1}{2} I\omega^2$$

$$I = m_1 r_1^{\ 2} + m_2 r_2^{\ 2} = \frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2 \equiv \mu r^2$$

Angular momentum $L = I\omega$

Kinetic Energy $K = \dfrac{L^2}{2I}$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r^2\frac{\partial^2}{\partial r^2}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)\right\}$$

$$= -\frac{\hbar^2}{2\mu}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r^2\frac{\partial^2}{\partial r^2}\right)\right\} + \frac{\hat{L}^2}{2I}$$

$\hat{L}^2 Y(\theta,\varphi) = \hbar^2 J(J+1) Y(\theta,\varphi)$ $\qquad$ $Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$: spherical harmonics

5-8 The Energy Levels of a Rigid Rotator is $E = \hbar^2 J(J+1)/2I$. (cont.)

l	m	$\Theta_{l,m}(\theta)$	$\Phi_m(\varphi)$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
1	0	$\frac{\sqrt{3}}{\sqrt{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$
1	± 1	$\sqrt{3}\sin\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i\varphi)$
2	0	$\frac{\sqrt{5}}{2\sqrt{2}}(3\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}$
2	± 1	$\frac{\sqrt{30}}{2\sqrt{2}}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i\varphi)$
2	± 2	$\frac{\sqrt{30}}{4\sqrt{2}}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i2\varphi)$
3	0	$\frac{\sqrt{7}}{2\sqrt{2}}(5\cos^3\theta - 3\cos\theta)$	$\frac{1}{\sqrt{2\pi}}$
3	± 1	$\frac{\sqrt{21}}{4\sqrt{2}}\sin\theta(5\cos^2\theta - 1)$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i\varphi)$
3	± 2	$\frac{\sqrt{210}}{4\sqrt{2}}\sin^2\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i2\varphi)$
3	± 3	$\frac{\sqrt{35}}{4\sqrt{2}}\sin^3\theta$	$\frac{1}{\sqrt{2\pi}}\exp(\pm i3\varphi)$

5-9 The Rigid Rotator is a Model for a Rotating Diatomic Molecule.

Selection rule among rotation levels: $\Delta J = \pm 1$

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

$$= \frac{\hbar^2}{I}(J+1), \qquad J = 0,1,2,\cdots$$

I of diatomic molecule is 10^{-45}~10^{-46} kg m^2

$\Rightarrow$ $\nu = 10^{10}$~10^{11} Hz (microwave region)

$$\nu = 2B(J+1), \quad J = 0,1,2,\cdots$$

$$B = \frac{h}{8\pi^2 I}, \quad \tilde{B} = \frac{h}{8\pi^2 cI}$$

B: rotational constant

Microwave absorption spectra show serial peaks at $2B$ intervals.