

## Quantization of Vibrational Energy

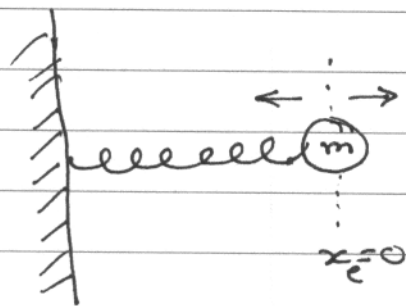
As a result of Born-Oppenheimer approximation, the vibrational wave function is separable from the rotational wave function:

$$\begin{aligned}\Psi_{\text{tot}} &= \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{rot}} \\ &= \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{rot}}\end{aligned}$$

And

$$\bar{E}_{\text{tot}} = \bar{E}_{\text{elec}} + \bar{E}_{\text{vib}} + \bar{E}_{\text{rot}}$$

Consider a spring model of a particle with mass  $m$ . This is called "harmonic oscillator" model and can be solved quantum mechanically.



Potential energy function can be expressed with Taylor's series about  $x_e$ :

$$\begin{aligned}V(x) &= \sum_i \frac{1}{i!} \left( \frac{\partial^i V}{\partial x^i} \right)_{x_e} x^i \\ &= V_0 + \frac{1}{1!} \left( \frac{\partial V}{\partial x} \right)_{x_e} x + \frac{1}{2!} \left( \frac{\partial^2 V}{\partial x^2} \right)_{x_e} x^2 + \dots\end{aligned}$$

At equilibrium ( $x_e$ )  $V$  is at minimum, thus

$$\left( \frac{\partial V}{\partial x} \right)_{x_e} = 0; \text{ and hence}$$

$$V(x) = \frac{1}{2} \left( \frac{\partial^2 V}{\partial x^2} \right)_{x_e} x^2 + \frac{1}{6} \left( \frac{\partial^3 V}{\partial x^3} \right)_{x_e} x^3 + \dots$$

↑  
 $k$

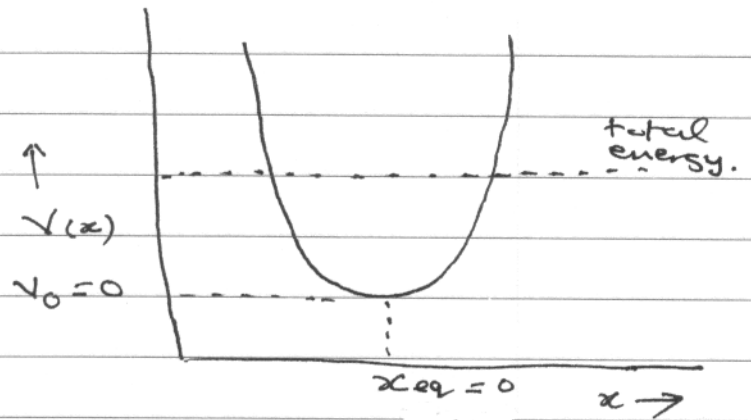
Anharmonicity

We retain only the first term for harmonic oscillator problem :

$$V(x) = \frac{1}{2} k x^2 ; \text{ where } k = \left( \frac{\partial^2 V}{\partial x^2} \right)_{x_e}$$

$k$  is known as force constant.

When  $V$  is plotted versus  $x$ , a parabolic curve results



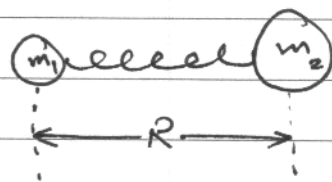
For a harmonic oscillator:

$$E_{tot} = E_{kinetic} + E_{pot}$$

$$= \frac{1}{2} m v^2 + \frac{1}{2} k x^2$$

For a diatomic molecule with masses  $m_1$  and  $m_2$ ,  $\mu$  is used

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



$$x = R - R_e$$

where  $R_e$  is the internuclear distance at equilibrium.

Schrödinger equation for one-dimensional harmonic oscillator is given by:

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right) \psi = E \psi$$

Solving this equation gives:

$$\begin{aligned} E_v &= h\nu \left( v + \frac{1}{2} \right) \\ &= hc\bar{\nu} \left( v + \frac{1}{2} \right) \end{aligned} \quad \left. \begin{array}{l} \nu \text{ is the vibrational} \\ \text{quantum number} \\ \nu = 0, 1, 2, \dots \end{array} \right\}$$

$\nu$ , the vibration frequency, is given by:

$$\nu = \sqrt{\frac{k}{\mu}} \frac{1}{2\pi}$$

As one would expect, the frequency (harmonic oscillation) of a two-particle system increases with increase of  $k$ .  $k$  is a measure of the stiffness (or strength) of the spring (or bond).

Also,  $\nu$  decreases with the increase of  $\mu$  or mass.

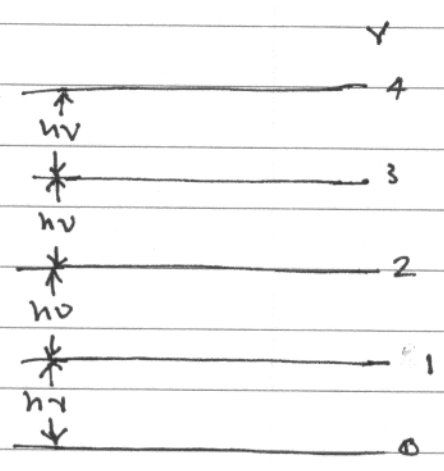
Also, since  $\omega = 2\pi\nu$  (Angular frequency)

$$\nu = \frac{\omega}{2\pi}$$

$$\text{Then } E_v = h \left( \frac{\omega}{2\pi} \right) \left( v + \frac{1}{2} \right)$$

$$E_v = h\nu \left( v + \frac{1}{2} \right)$$

The energy levels associated to the vibrational motion are separated by  $h\nu$ .



From the harmonic oscillator potential energy curve, one can see that at  $v=0$  level a minimum vibrational energy a molecule can have is  $\frac{1}{2} h\nu$ .

$$E_0 = h\nu \left( 0 + \frac{1}{2} \right)$$

$$E_0 = \frac{1}{2} h\nu$$

Even at absolute zero, a minimum vibrational energy a molecule will have is  $\frac{1}{2} h\nu$  because of the uncertainty principle.

$$\Delta p \Delta x \approx h/2$$

There is a vibrational wave function,  $\Psi_v$ , associated to each value of vibrational energy. The general form of  $\Psi_v$  is

$$\Psi_v = \underbrace{\left( 2^v v! \pi^{1/2} \right)^{-1/2}}_{\text{Normalization factor } (N_v)} \underbrace{H_v}_{\text{Hermite polynomial}} e^{-\frac{(4\pi^2\nu\mu/h)(R-R_e)^2}{2}}$$

A quantity  $y$  can be defined:

$$y = (4\pi^2 \nu \mu / h)^{1/2} (R - R_e)$$

$$\therefore \Psi_v = N_v H_v(y) e^{-y^2/2}$$