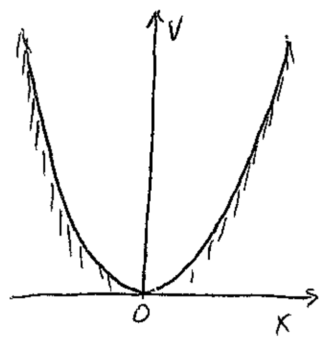
Vibrational Motion

Vibration motions of a molecule can be modeled by a set of harmonic oscillators. Furthermore, harmonic oscillator is one of a few problems for which we can solve exactly in quantum mechanics.

Harmonic oscillator



Let consider a particle of mass m undergoes harmonic motion corresponding to a potential energy

$$V = \frac{1}{2} k x^2 \qquad (28,1)$$

The Schrödinger equation for this system is

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \frac{1}{2} k x^2 \Psi = E\Psi \qquad (28,2)$$

by substitution of variable

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

and

$$\varepsilon = \frac{E}{\frac{1}{2}\hbar\omega} \quad \text{where} \quad \omega = \sqrt{\frac{k}{m}}$$

Equation (28,2) becomes

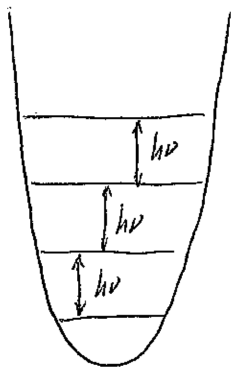
$$\frac{d^2\Psi}{dy^2} + (\varepsilon - y^2)\Psi = 0 \qquad (28,3)$$

This equation was first solved by Hermite and we will not solve it here !!! However, we will examine important features of the solution.

Energy

The energy of a harmonic oscillator is quantized.

$$\boxed{\begin{aligned} E_v &= (v+\tfrac{1}{2})\hbar\omega \\ \omega &= \sqrt{\frac{k}{m}} \end{aligned}} \quad \text{with } v = 0,1,2,\ldots \qquad (29.1)$$



$$\Delta E = E_n - E_{n-1} = \hbar\omega = h\nu$$

∴ The energy levels are uniform spacing.

The harmonic oscillator has the zero-point energy, E_0

$$\boxed{E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu} \qquad (29.2)$$

Similar to the particle in a box, the zero-point of energy is a consequence of the uncertainty principle: The position of the particle is not completely uncertain (confined within the harmonic potential), thus its momentum cannot be exactly zero.

Wavefunction

The wavefunction for a harmonic oscillator in the n quantum ~~number~~ state is

$$\psi_n = N_n H_n(y) e^{-y^2/2} \qquad (29.3)$$

where N_n is the normalization constant and $H_n(y)$ is the Hermite polynomial

$$H_0 = 1$$
$$H_1 = 2y$$
$$H_2 = 4y^2 - 2$$
$$\vdots$$
$$H_{n+1} = 2yH_n - 2nH_{n-1} \qquad \text{(recursive relation)}$$

and

$$\int_{-\infty}^{\infty} H_n H_{n'} e^{-y^2} dy = \begin{cases} 0 & \text{if } n \neq n' \\ \sqrt{\pi}\, 2^n n! & \text{if } n = n' \end{cases}$$

Recall earlier we set $y = \frac{x}{\alpha}$, the groundstate wavefunction is then given by

$$\psi_0 = N_0 \, e^{-x^2/2\alpha^2}$$

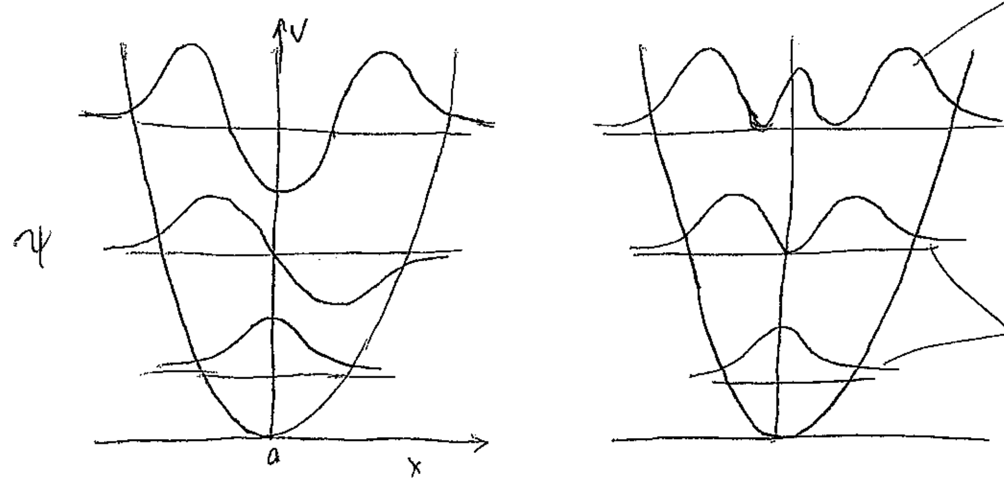
and the probability density $\psi_0^2 = N_0^2 \, e^{-x^2/\alpha^2}$

To find N_0, we set

$$\int_{-\infty}^{\infty} \psi_0^2 \, dx = 1$$

$$N_0^2 \int_{-\infty}^{\infty} e^{-x^2/\alpha^2} dx = \alpha N_0^2 \int_{-\infty}^{\infty} e^{-y^2} dy = \alpha N_0^2 \pi^{1/2} = 1$$

$$\Rightarrow \quad N_0 = \sqrt{\frac{1}{\alpha \pi^{1/2}}} = \sqrt{\left(\frac{mk}{\hbar^2 \pi^2}\right)^{1/4}} = \left(\frac{4mk}{h^2}\right)^{1/8}$$



probability is larger near the end of the path, because classically the particle is slow down and spend more time in these regions.

classical forbidden region (tunneling)

Use one of the quantum mechanics postulates for the average value of a mechanical properties

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, dv}{\int \psi^* \psi \, dv}$$

you can show that $\langle x \rangle = 0$ and $\langle x^2 \rangle = (n+1/2)\left(\frac{\hbar^2}{mk}\right)^{1/2}$

Having shown these, we can calculate the average potential energy of the oscillator in the n quantum state

$$\langle V \rangle = \frac{1}{2} k \langle x^2 \rangle = \frac{1}{2} k \left(n+\frac{1}{2}\right)\left(\frac{\hbar^2}{mk}\right)^{1/2} = \frac{1}{2}\left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{k}{m}} = \frac{1}{2}\left(n+\frac{1}{2}\right)\hbar\omega$$

$$= \frac{1}{2} E_n$$

Since the total energy of the system is the sum of the kinetic and potential energies, therefore

$$\langle V \rangle = \langle K \rangle = \frac{1}{2} E_n$$

This is a special case of the virial theorem which states that if the potential energy has the form $V = ax^b$ then its average potential and kinetic energies are related by

$$2\langle K \rangle = b \langle V \rangle$$