Chapter 7 – Vibrations and Rotations
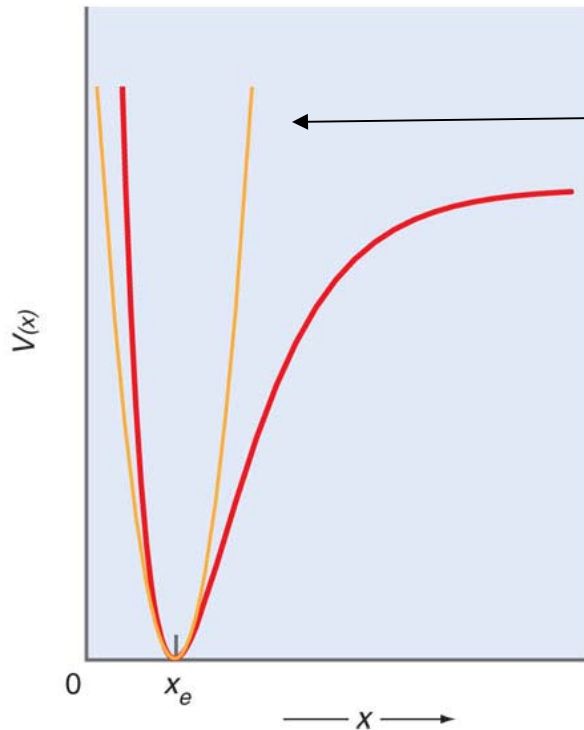
translation – particle in box
rotation – rigid rotor
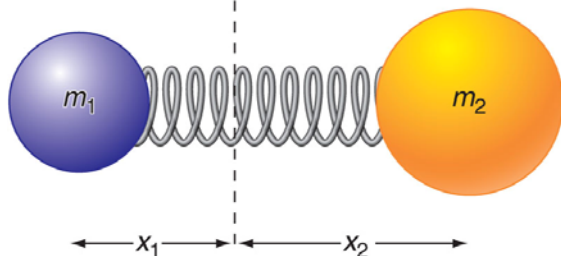vibration – harmonic oscillator

harmonic potential: $V(x) = \dfrac{1}{2}kx^2$, k = force constant

true potential

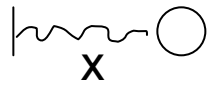actually, we generally use the of variable $x' = (x - x_e)$ so

$$V(x') = \frac{1}{2}kx'^2$$

$$x' = 0 \quad \Rightarrow \quad x = x_e$$

Diatomic molecule

center of mass coordinates

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$ ← reduced mass

for vibration what matters is the separation between the atoms

true potential can be written as a Taylor series

$$V(x) = V(x_e) + \frac{dV}{dx}\Big|_{x_e}(x - x_e)$$

$$+ \frac{1}{2}\frac{d^2V}{dx^2}\Big|_{x_e}(x - x_e)^2$$

$$+ \frac{1}{6}\frac{d^3V}{dx^3}\Big|_{x_e}(x - x_e)^3 + \ldots$$

$$\frac{dV}{dx}\Big|_{x=x_e} = 0$$

choose V(x$_e$) to be the zero of energy

$$V(x) = \frac{1}{2}\frac{d^2V}{dx^2}(x - x_e)^2 + \ldots$$

$$= \frac{1}{2}k(x - x_e)^2 + \ldots$$

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

Schrodinger Eq. for 1D harmonic oscillator

Note: $e^{-\frac{1}{2}\alpha x^2}$ is a solution

$$\frac{d}{dx}e^{-\frac{\alpha}{2}x^2} = -\alpha x e^{-\frac{\alpha}{2}x^2}$$

$$\frac{d}{dx}\left[-\alpha x e^{-\frac{\alpha}{2}x^2}\right] = (-\alpha + \alpha^2 x^2)e^{-\frac{\alpha}{2}x^2}$$

Do you see why this solves the equation?

$e^{+\frac{\alpha}{2}x^2}$ also solves the differential equation. But we reject it.

Why?

The general form of the wavefuction is

$$\psi_n = A_n H_n\left(\alpha^{\frac{1}{2}}x\right)e^{-\frac{\alpha}{2}x^2}, \quad n = 0,1,2,...$$

$H_n(\alpha^{1/2}x):$

Hermite polynomials

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

$$A_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha}{2}x^2}$$

$$\psi_1 = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\frac{\alpha}{2}x^2}$$

$$\psi_2 = \left(\frac{\alpha}{4\pi}\right)^{1/4}\left(2\alpha x^2 - 1\right)e^{-\frac{\alpha}{2}x^2}$$

$\psi_0, \psi_2, \psi_4,...$ even

$\psi_1, \psi_3, \psi_5,...$ odd

$$\psi_3 = \left(\frac{\alpha^3}{9\pi}\right)^{1/4}\left(2\alpha x^3 - 3x\right)e^{-\frac{\alpha}{2}x^2}$$
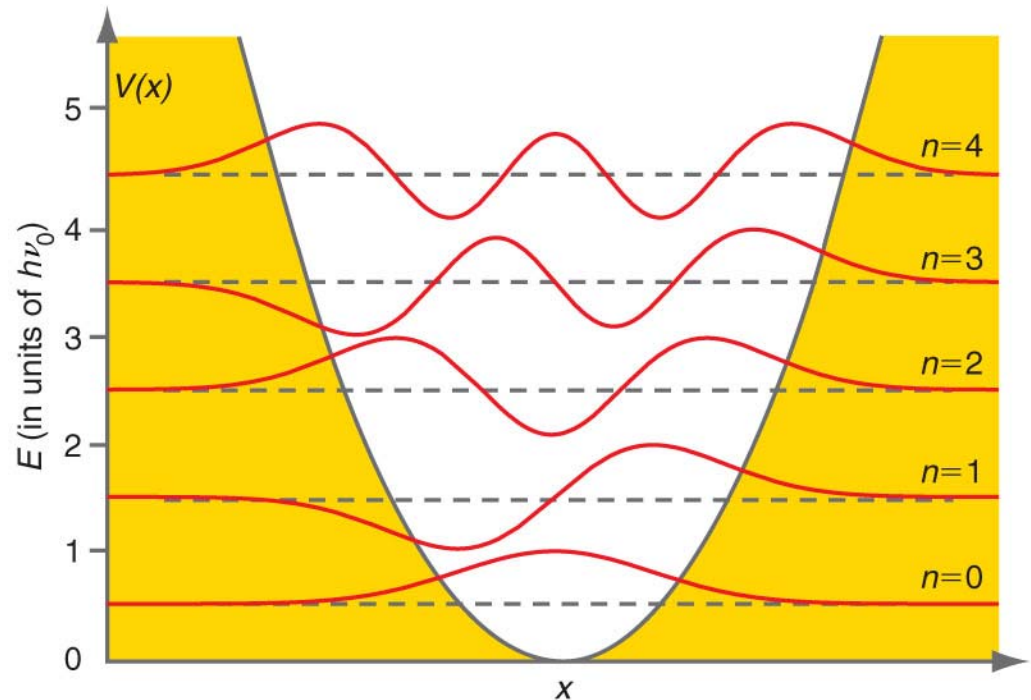
even function f(-x) = f(x)
odd function f(-x) = f(x)

$$E_n = \hbar\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right) = \hbar\omega\left(n+\frac{1}{2}\right) = h\upsilon\left(n+\frac{1}{2}\right), \quad n = 0,1,2,...$$

quantization due to requiring $\psi \rightarrow 0$ as $x \rightarrow \pm\infty$

$$\langle E_{KE}\rangle = \langle E_{PE}\rangle = \frac{h\upsilon}{2}\left(n+\frac{1}{2}\right)$$

As *n* becomes large, there is a high probability of finding the oscillator near the classical turning points

← velocity → 0

← maximum velocity

Classical situation

Similar situation for the classical oscillator

short-hand nomenclature

$$\langle n|\hat{A}|m\rangle = \int \psi_n^* \hat{A} \psi_m dx$$

$$\langle 0|x|0\rangle = 0$$

The integral $\langle n|x|0\rangle$ is the transition moment for going from state ψ_0 to ψ_n.

$$\langle 1|x|1\rangle = 0$$

Transition probability

$$\langle 1|0\rangle = 0$$

$$\propto |\langle n|x|0\rangle|^2$$

integral non zero only if $n = 1$

$$\langle 1|x|0\rangle \neq 0$$

Later, we will see that it is also essential that the dipole moment is changing.