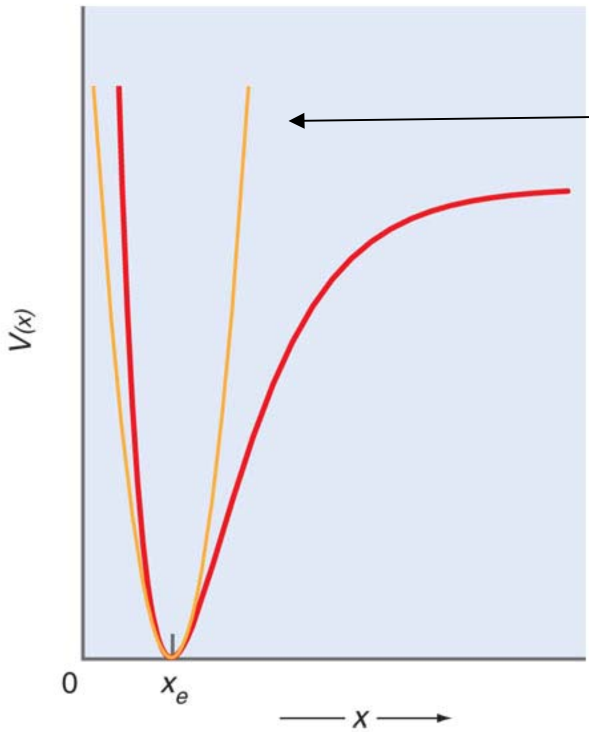
Chapter 2 – Vibrations

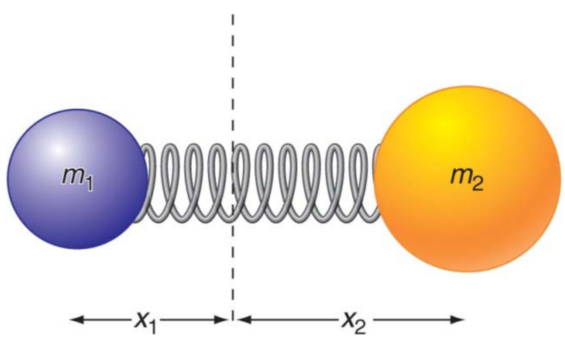
translation	–	particle in box
rotation	–	rigid rotor
vibration	–	harmonic oscillator



harmonic potential: $V(x) = \frac{1}{2}k\left(x - x_e\right)^2,$

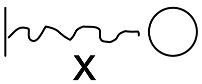
true potential

k = force constant



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

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

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

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

choose $V(x_e)$ to be the zero of energy

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

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

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

With a shift of the origin, we can replace $x - x_e$ with x

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

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, since it $\rightarrow \infty$ as x $\rightarrow \pm\infty$.

The general form of the wavefuction is

$$\psi_n = N_n H_n(\alpha x) e^{-\frac{\alpha^2}{2}x^2}, \quad n = 0,1,2,\ldots$$

$H_n(\alpha x)$: Hermite Polynomials

Adopting the convention Of the text

$$\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/4}$$

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

Note: Atkins' use of α^2 instead of α.

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

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

$$\psi_2 = \left(\frac{\alpha}{8\pi^{1/2}}\right)^{1/2} \left(4\alpha^2 x^2 - 2\right) e^{-\frac{\alpha^2}{2}x^2}$$

$$\psi_3 = \left(\frac{\alpha}{48\pi^{1/2}}\right)^{1/2} \left(8\alpha^3 x^3 - 12\alpha x\right) e^{-\frac{\alpha^2}{2}x^2}$$

Text: $z = \alpha x$

$\psi_0, \psi_2, \psi_4, \ldots$ even

$\psi_1, \psi_3, \psi_5, \ldots$ odd

even function f(-x) = f(x)
odd function f(-x) = -f(x)

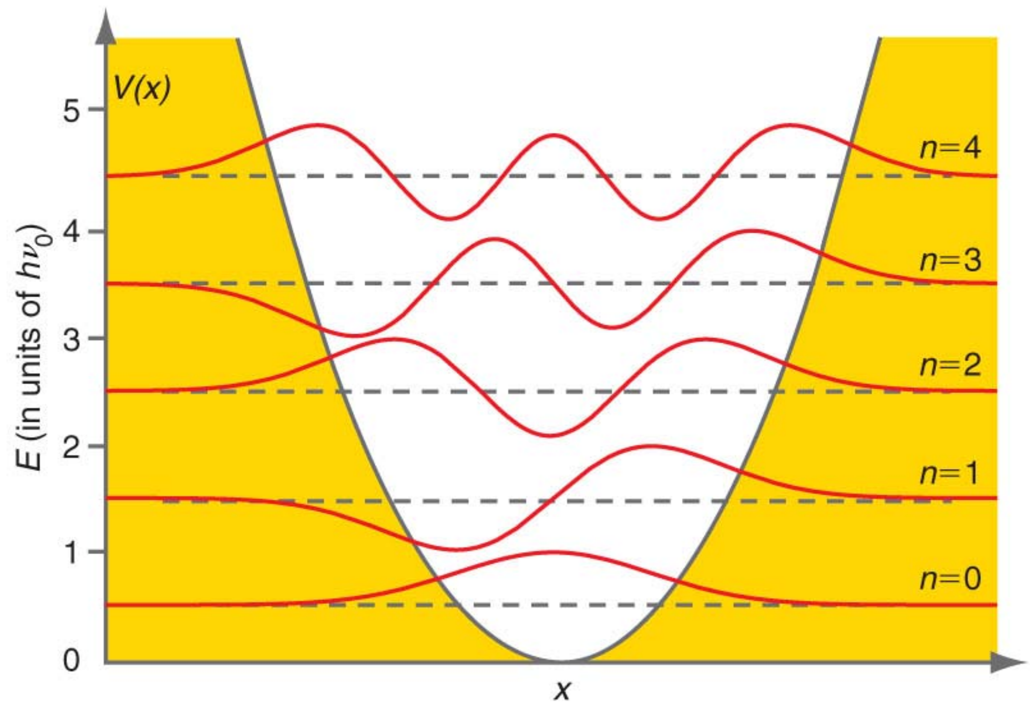
$$E_n = \hbar\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right) = \hbar\omega\left(n+\frac{1}{2}\right) = h\upsilon\left(n+\frac{1}{2}\right), \quad n = 0,1,2,\ldots$$

ω = √k/μ

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

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

For the harmonic oscillator

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

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

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

Follows from the properties of even/odd functions

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

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

integral non zero only if *n* = 1

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

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

Some useful relations

Orthogonality: $$\int_{-\infty}^{\infty} H_{\mathrm{v}}(z) H_{\mathrm{v}'}(z) e^{-z^2} dz = \delta_{\mathrm{v},\mathrm{v}'}$$

Recursion Relation: $$H_{\mathrm{v}+1} = 2zH_{\mathrm{v}} - 2\mathrm{v}H_{\mathrm{v}-1}$$

$$\langle \mathrm{v}+1 | x | \mathrm{v} \rangle = \sqrt{\frac{\hbar}{2\mu\omega}} \left(\mathrm{v} + \frac{1}{2} \right)^{1/2}$$

$$\langle \mathrm{v}-1 | x | \mathrm{v} \rangle = \sqrt{\frac{\hbar}{2\mu\omega}} \ \mathrm{v}^{1/2}$$

$$\langle \mathrm{v}+1 | p_x | \mathrm{v} \rangle = i \left(\frac{\hbar\mu\omega}{2} \right)^{1/2} \left(\mathrm{v} + \frac{1}{2} \right)^{1/2}$$

$$\langle \mathrm{v}-1 | p_x | \mathrm{v} \rangle = -i \left(\frac{\hbar\mu\omega}{2} \right)^{1/2} \mathrm{v}^{1/2}$$

$$\langle E_k \rangle = \langle E_p \rangle$$

← This is a consequence of the virial theorem