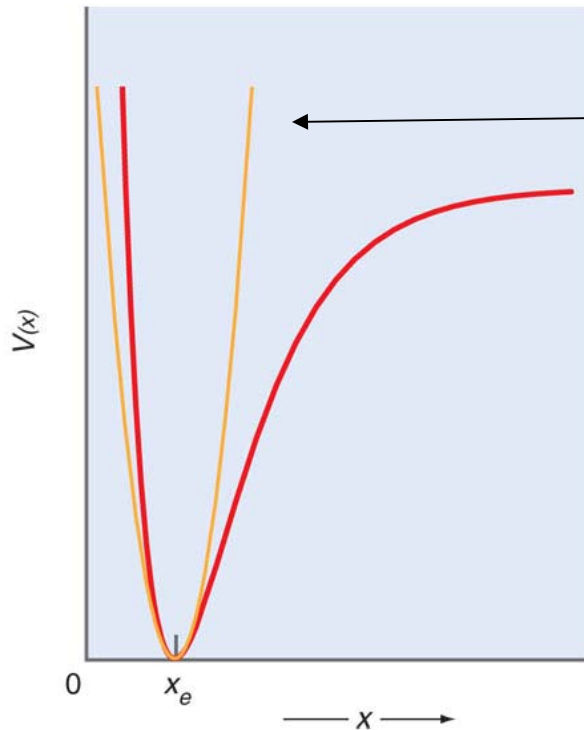


Chapter 2 – Vibrations

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

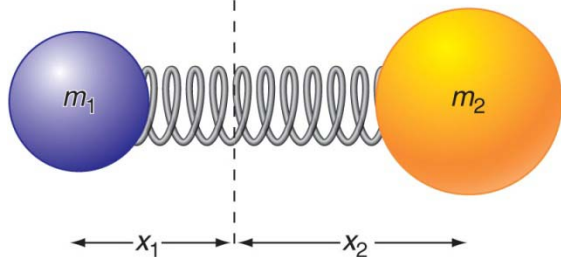


harmonic potential:

$$V(x) = \frac{1}{2}k(x - x_e)^2,$$

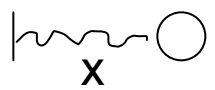
true potential

k = force constant



Diatomic molecule

center of mass coordinates


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

for vibration what matters is the separation between the atoms

true potential can be written as a Taylor series

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

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

$$+ \frac{1}{6} \left. \frac{d^3V}{dx^3} \right|_{x_e} (x - x_e)^3 + \dots$$

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

$$\left. \frac{dV}{dx} \right|_{x=x_e} = 0$$

$$V(x) = \frac{1}{2} \left. \frac{d^2V}{dx^2} \right|_{x_e} (x - x_e)^2 + \dots$$

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

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 wavefunction is

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

Adopting the convention
Of the text

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

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

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

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

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

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

Text: $z = \alpha x$

$H_n(\alpha x)$: Hermite
Polynomials

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

$\psi_0, \psi_2, \psi_4, \dots$ even

$\psi_1, \psi_3, \psi_5, \dots$ odd

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

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

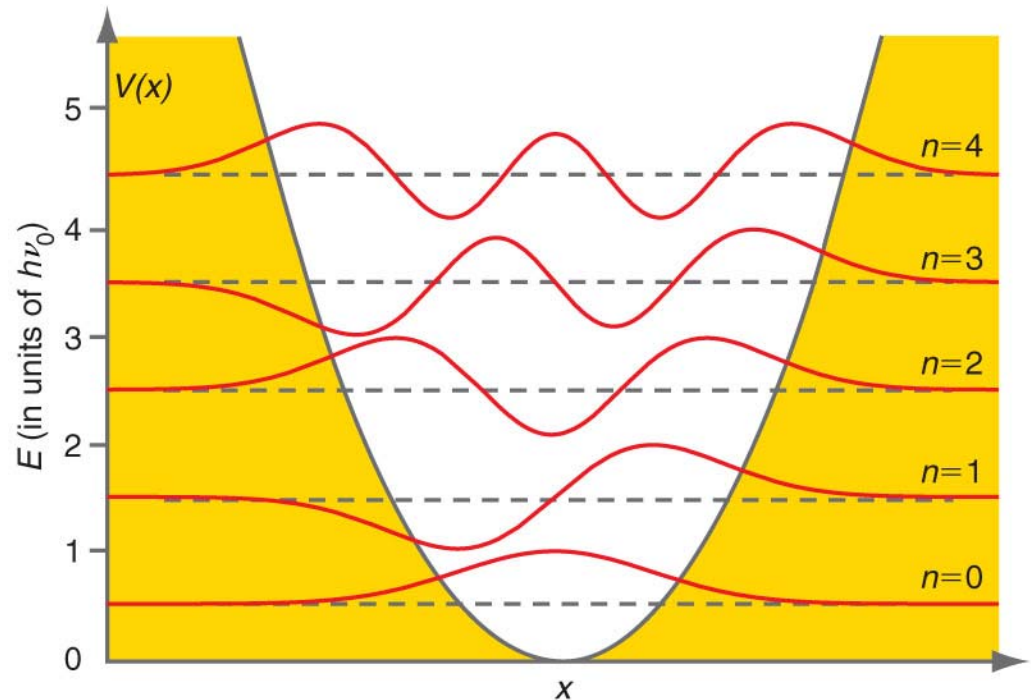
$$E_n = \hbar \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right) = \hbar \omega \left(n + \frac{1}{2} \right) = h\nu \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots$$

$$\omega = \sqrt{k/\mu}$$

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

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

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



← velocity $\rightarrow 0$
 ← maximum velocity

Classical
situation

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

For the harmonic oscillator

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

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

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

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

Follows from the
properties of
even/odd functions

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

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

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

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

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

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

$$\langle E_k \rangle = \langle E_p \rangle \leftarrow \text{This is a consequence of the virial theorem}$$