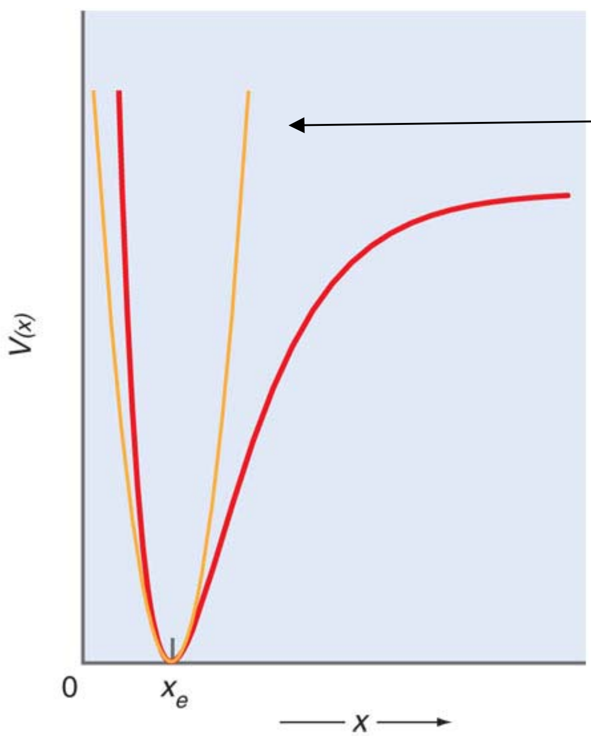
Chapter 7 – Vibrations and Rotations

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



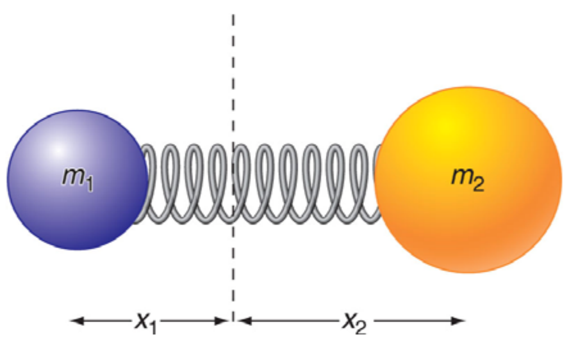
harmonic potential: $V(x) = \frac{1}{2}kx^2$, k = force constant

true potential

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

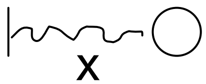
$$V(x') = \frac{1}{2}kx'^2$$

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

Hermite polynomials

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

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

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

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

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

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

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

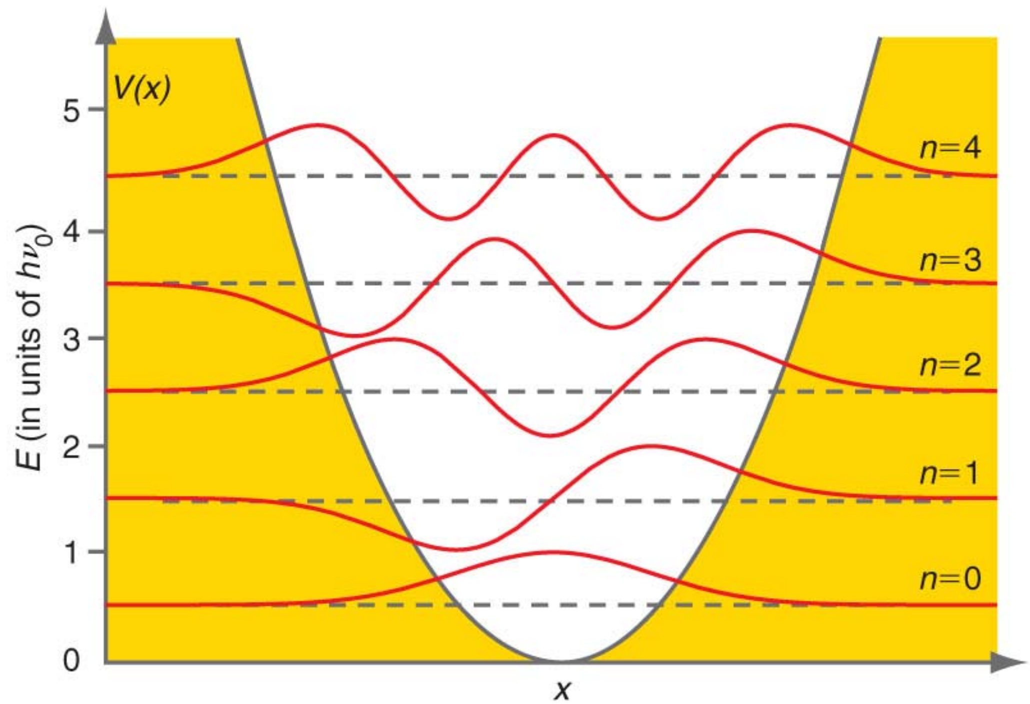
$$E_n = \hbar\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right) = \hbar\omega\left(n+\frac{1}{2}\right) = h\upsilon\left(n+\frac{1}{2}\right), \quad n = 0,1,2,\ldots$$

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

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

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

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



From Engel

← velocity → 0

← maximum velocity

Classical situation

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

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

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

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

short-hand nomenclature

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

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

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

integral is non zero only if *n* = 1

Δ±

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

Chapter 7, continued

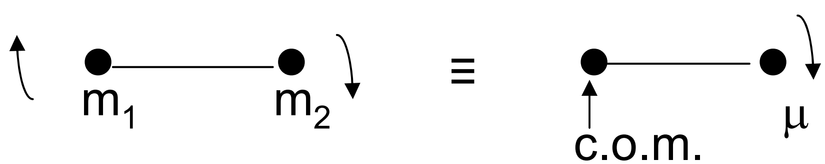
Rotation in 2 dimensions

$H_{total} = H_{trans}(r_{cm}) + H_{vib}(\tau_{internal}) + H_{rot}(\theta, \phi)$

$E_{total} = E_{trans} + E_{vib} + E_{rot}$

$\psi_{tot} = \psi_{trans}\, \psi_{vib}\, \psi_{rot}$

separation of variables



V(x,y) = 0 everywhere

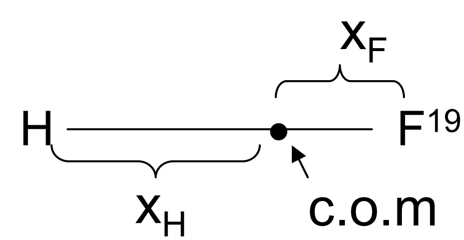
$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)_{r=r_0} = E\psi$$

fixed radius

reduced mass

$$\frac{1}{\mu} = \frac{1}{m_1} = \frac{1}{m_2}$$

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



$$x_H + x_F = .9168\text{Å}$$

$$x_H m_H = x_F m_F$$

$$x_F = .0458\text{Å}$$

$$x_H = .8710\text{Å}$$

Switch to polar coordinates: (x, y) $\rightarrow$ (r, ϕ)

$$\frac{-\hbar^2}{2\mu r_0^2}\frac{d^2\Phi}{d\phi^2} = E\Phi \longrightarrow \Phi = e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \ldots$$

$$0 \le \phi \le 2\pi$$

$$e^{im(\phi+2\pi)} = e^{im\phi} \quad \Rightarrow \quad e^{im2\pi} = 1$$

$$e^{im2\pi} = \cos 2\pi m + i \sin 2\pi m = 1 \quad \Rightarrow \quad m = 0, \pm 1, \pm 2, \ldots$$

$$E = \frac{\hbar^2 m^2}{2\mu r_0^2} = \frac{\hbar^2 m^2}{2I}$$

$I = \mu r_0^2 =$ moment of inertia

quantization due to boundary condition $\Phi(0) = \Phi(2\pi)$

Note: there is no zero-point energy. Why?

Classically $E = \frac{|\vec{\ell}|^2}{2I} = \frac{1}{2} I\omega^2$

$\vec{\ell} =$ angular momentum

All energies possible

angular momentum in z direction: $\vec{\ell}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$

$$\vec{\ell}_z \Phi = \frac{\hbar}{i}\frac{1}{\sqrt{2\pi}}\frac{d}{d\phi} e^{im\phi} = m\hbar\Phi$$

$P(\phi)d\phi = \frac{d\phi}{2\pi}$, all ϕ values equally probable
angular momentum in z direction precisely defined

$\vec{\ell}_z$, $\hat{\phi}$ do **not** commute