Classical Harmonic Oscillator

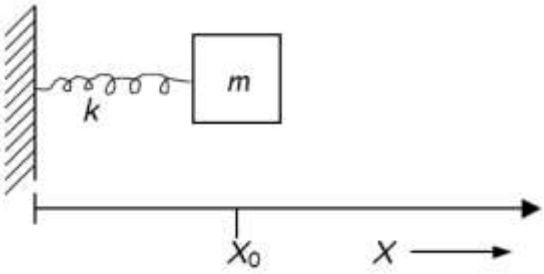

Figure 5.1: Classical Harmonic Oscillator

Hooke's Law

$$f = -kx = -k\left(x - x_{eq}\right)$$

$$f = ma = -kx$$

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$$

General solutions

$$x(t) = A\sin\omega t + B\cos\omega t \qquad \omega = \sqrt{k/m}$$

$$x(t) = C\sin(\omega t + \phi)$$

Initial conditions:

$x\ (t = 0) = x_0\,,\quad v_0 = 0$ spring stretched to x_0 and released at time $t = 0$. This gives,

$$x(t) = x_0\cos\omega t$$

Mass and spring (spring is assumed massless) oscillate with frequency $\omega = \sqrt{k/m}$

Energy of H.O.

Kinetic Energy

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}m\left(\omega^2 x_0^2\sin^2\omega t\right) = \frac{1}{2}k\,x_0^2\sin^2\omega t$$

Potential Energy (U) is given by $f(x) = -dU/dx$

$$PE = U = -\int f(x)dx = k\int x\,dx = \frac{1}{2}kx^2 = \frac{1}{2}k\,x_0^2\cos^2\omega t$$

$$Total\ Energy = KE + PE = \frac{1}{2}\ kx_0^2$$

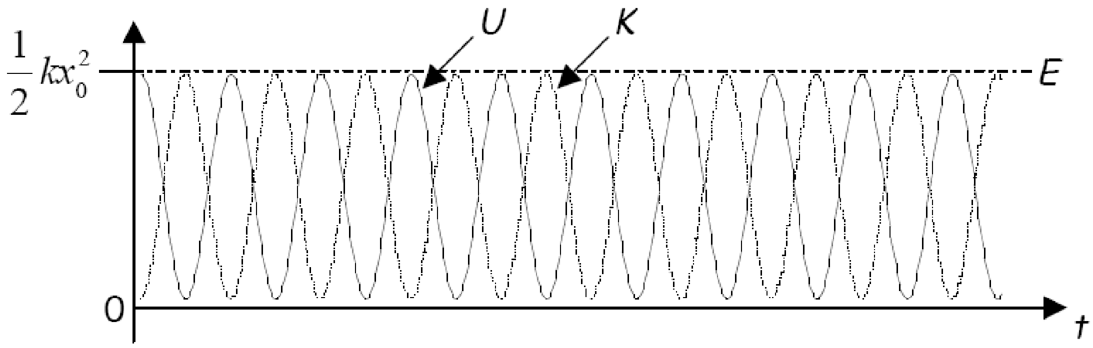

Figure 5.2: KE, PE and Total energy

Small displacements - diatomic molecule

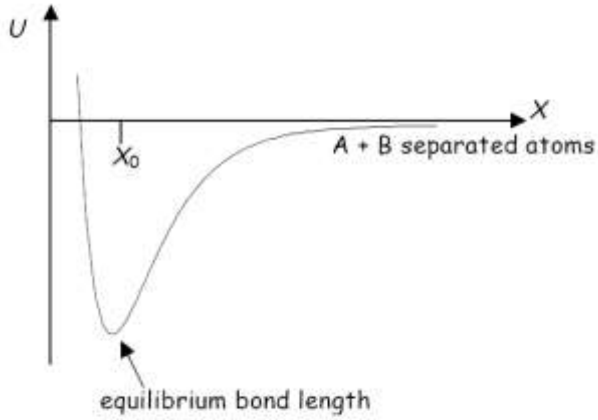

Figure 5.3: PE as a function of the distance

Expand $U(x)$about the mean position x_e

$$U(x) = \ U(x_e) + \left\{\frac{dU}{dx}\bigg|_{x=x_e} (x - x_e)\right\} + \left\{\frac{1}{2}\frac{d^2U}{dx^2}\bigg|_{x=x_e} (x - x_e)^2\right\} + \left\{\frac{1}{3.2}\frac{d^3U}{dx^3}\bigg|_{x=x_e} (x - x_e)^3\right\} + \cdots$$

Since the zero of potential can be defined as per our choice, lets fix $U(x_e) = 0$.

We could shift the origin to the equilibrium position

$$U(x) = \ \left\{\frac{dU}{dx}\bigg|_{x=0} x\right\} + \left\{\frac{1}{2}\frac{d^2U}{dx^2}\bigg|_{x=0} x^2\right\} + \left\{\frac{1}{3.2}\frac{d^3U}{dx^3}\bigg|_{x=0} x^3\right\} + \ \ldots$$

The first term goes to zero at equilibrium

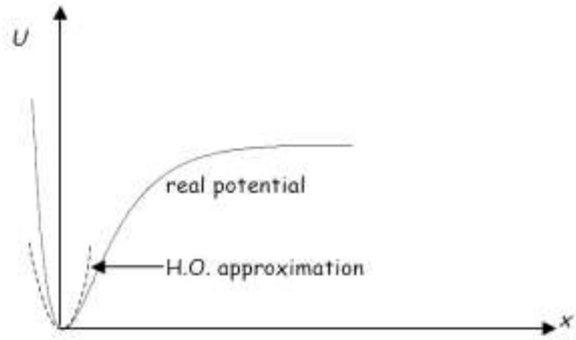

Figure 5.4: H. O. approximation

For small displacements only the second term is significant enough

$$U(x) = \frac{1}{2}\frac{d^2U}{dx^2}\bigg|_{x=0} x^2 \qquad or \quad U(x) = \frac{1}{2}kx^2$$

Center of mass and reduced mass coordinates

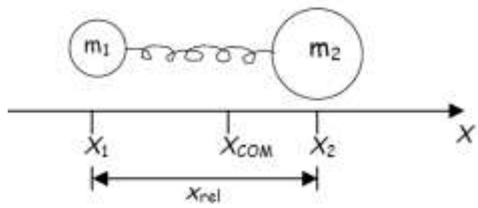

Figure 5.5: Center of mass (l_0 is the undisturbed length)

For particle 1, $m_1\frac{d^2x_1}{dt^2} = k(x_2 - x_1 - l_0)$ and for particle 2, $m_2\frac{d^2x_2}{dt^2} = -k(x_2 - x_1 - l_0)$

The forces are equal and opposite, $\frac{d^2}{dt^2}(m_1x_1 + m_2x_2) = 0$

Define the center of mass coordinate, $X = \frac{m_1x_1+m_2x_2}{m_1+m_2} = \frac{m_1x_1+m_2x_2}{M}$

Then, $M\frac{d^2X}{dt^2} = 0$ (The COM moves uniformly in time with constant momentum)

The relative motion of the two bodies is important, $x = x_2 - x_1 - l_0$ is the relative coordinate

This gives, $\frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2} = -\frac{k}{m_2}x - \frac{k}{m_1}x$ (from the above equations by dividing with the respective m)

$\frac{d^2}{dt^2}(x_2 - x_1) = -k\left(\frac{1}{m_1} + \frac{1}{m_2}\right)x = -\frac{k}{\mu}x$ (μ is the reduced mass)

Gives, $\mu\frac{d^2x}{dt^2} + kx = 0$ (A two body problem gets reduced to a one body problem

$$E_{vib} = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}kx^2$$

Solve this problem quantum mechanically.

Schrödinger equation

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

No longer are we dealing with constant coefficients

Try a solution - wild guess !!! (Gaussian function) → $f(x) = e^{-\frac{\alpha x^2}{2}}$

$$\frac{d^2 f}{dx^2} = -\alpha\exp\left(-\frac{\alpha x^2}{2}\right) + \alpha^2 x^2 \exp\left(-\frac{\alpha x^2}{2}\right) = -\alpha^2 f + \alpha^2 x^2 f$$

$$\frac{d^2 f}{dx^2} + \alpha f - \alpha^2 x^2 f = 0$$

which matches the S. E. if , $\alpha = \frac{2\mu E}{\hbar^2}$ $\quad and \quad \alpha^2 = \frac{\mu k}{\hbar^2} \quad and \;\; E = \frac{1}{2}\,\hbar\omega$

Normalize the wavefunction to get

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

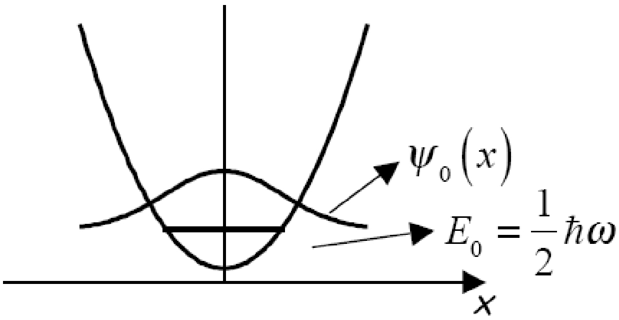

Figure 5.6: Lowest eigenfunction for H.O.
Symmetric function. Even function. No nodes.

What about other eigenfunctions and eigenvalues?

$\boldsymbol{\psi_v(x) = N_v H_v(y) e^{-y^2/2}}$ $\qquad$ $\boldsymbol{y^2 = \alpha x^2}$ $\qquad$ $\boldsymbol{\alpha^2 = (\mu k/\hbar^2)}$ $\qquad$ $\boldsymbol{N_v = \frac{1}{2^v\, v!}\left(\frac{\alpha}{\pi}\right)^{1/4}}$

Atkin's notation$\boldsymbol{\psi_v(x) = N_v H_v(y) e^{-y^2/2}}$ $\qquad$ $\boldsymbol{y^2 = \frac{x}{\alpha}}$ $\qquad$ $\boldsymbol{\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}}$

Table 9.1 The Hermite polynomials $H_v(y)$

V	$H_1(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

Table 9-1
Atkins Physical Chemistry, Eighth Edition

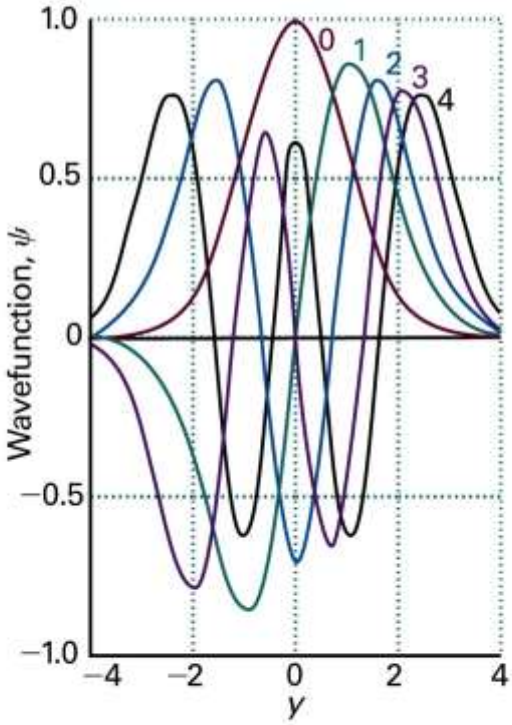

Figure 9-25
Atkins Physical Chemistry, Eighth Edition

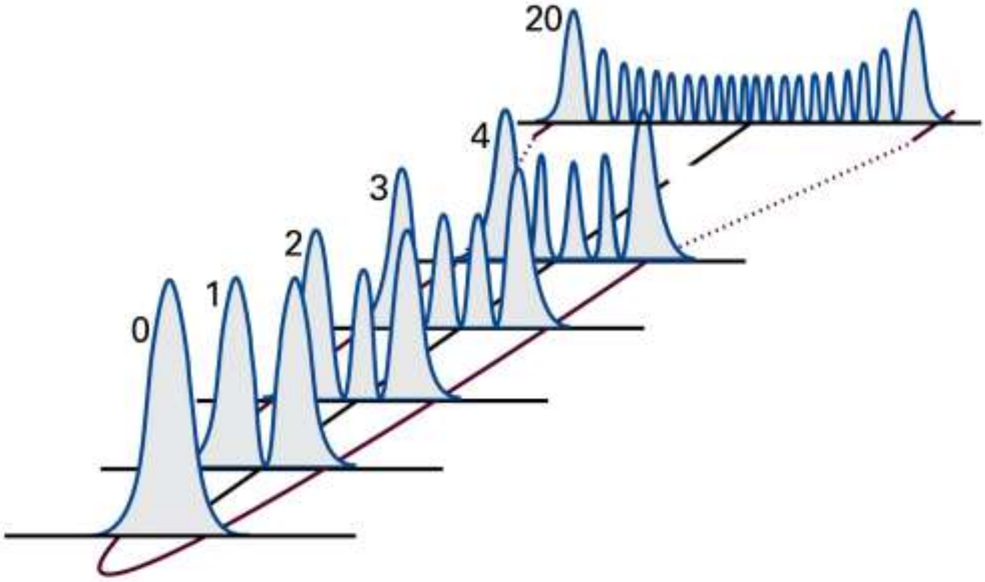

Figure 9-26
Atkins Physical Chemistry, Eighth Edition

1. The Gaussian goes very strongly to zero as the displacement increases.
2. The exponent y^2 is proportional to $x^2 \times (mk)^{1/2}$. So larger masses, stiffer springs decay faster
3. As v increases, the Hermite polynomials become large at large displacements (x^v), so wavefunctions grow till larger displacements before the exponent damps them