Vibrational Motion

Chapter 5

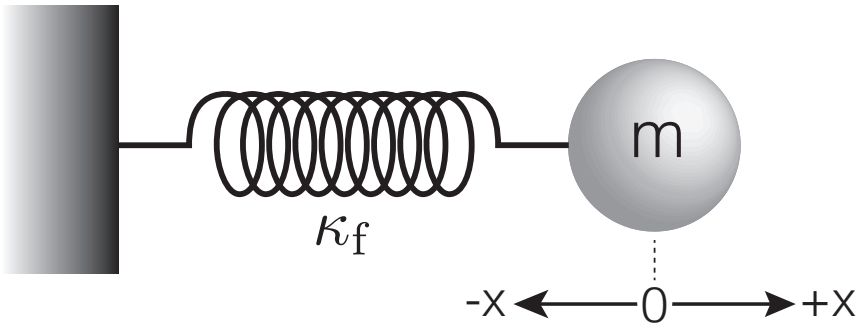
P. J. Grandinetti

Chem. 4300

Sep. 13, 2017

Simple Harmonic Oscillator

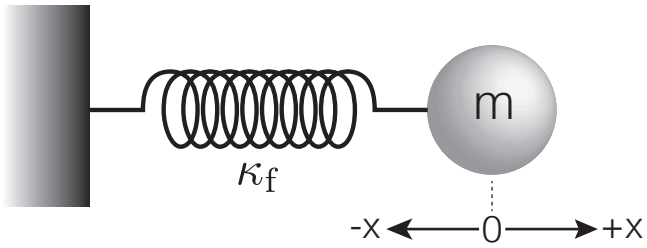
Simplest model for harmonic oscillator—mass attached to one end of spring while other end is held fixed



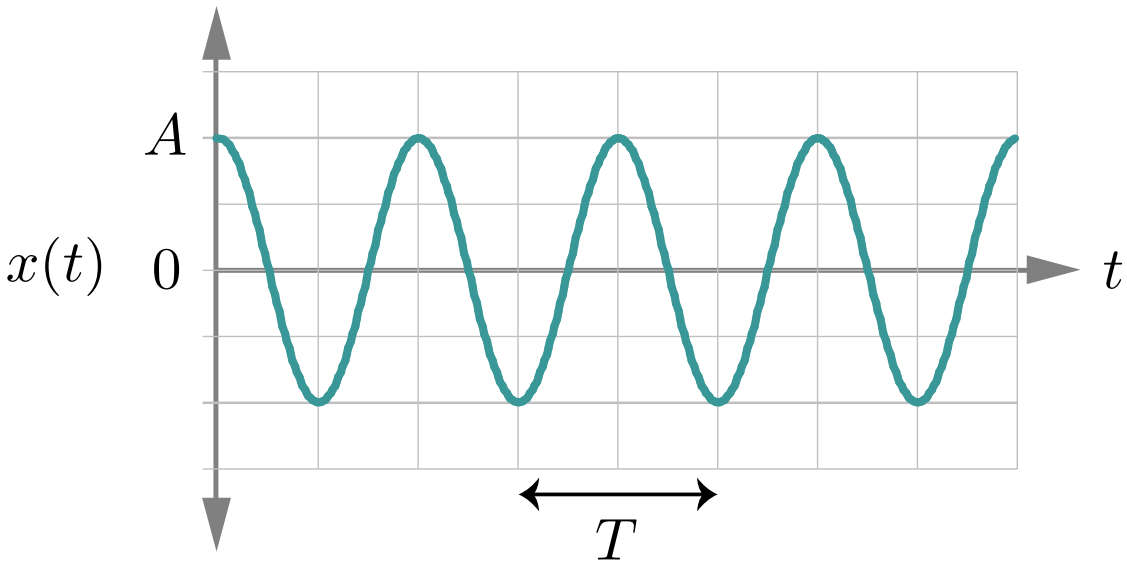
- Mass at $x = 0$ corresponds to equilibrium position
- x is displacement from equilibrium.
- Assume no friction and that spring itself has no mass.

Simple Harmonic Oscillator

Pull the mass and let go.



What happens? An oscillation.



The time for one complete cycle is T.

How do we get and solve the equation of motion for this system?

Simple Harmonic Oscillator

Hooke's law

For small displacements from equilibrium restoring force is

$$F = -\kappa_f x$$

κ_f is the force constant for the spring.
Using Newton's 2nd law

$$F = ma = -\kappa_f x$$

we obtain differential equation of motion

$$m\ddot{x}(t) + \kappa_f x(t) = 0$$

Propose the solution

$$x(t) = A\cos(\omega t + \phi)$$

Substituting into the differential equation gives

$$\left(\kappa_f - m\omega^2\right) A\cos(\omega t + \phi) = 0$$

Simple Harmonic Oscillator

$$\left(\kappa_f - m\omega^2\right) A\cos(\omega t + \phi) = 0$$

To make true for all values of t we set $\omega = \omega_0 = \sqrt{\kappa_f/m}$.
ω_0 is called the natural oscillation frequency

Velocity of the mass is

$$v(t) = \dot{x}(t) = -\omega A \sin(\omega_0 t + \phi)$$

Make equation satisfy initial conditions of

$$x(t=0) = A \quad \text{and} \quad \dot{x}(t=0) = 0$$

by setting $\phi = 0$ and $A = x(0)$ to get final solution to equation of motion

$$x(t) = x(0)\cos\omega_0 t$$

Energy of simple harmonic oscillator

Energy of simple harmonic oscillator

Total energy of simple harmonic oscillator is sum of the kinetic and potential energy of mass and spring.

Kinetic energy is given by

$$K = \frac{1}{2}mv^2, \quad \text{or} \quad K = \frac{p^2}{2m}$$

where p is mass momentum, $p = mv$.

Potential energy is the energy stored in spring and is equal to work done in extending and compressing spring,

$$V(x) = -\int_0^x F(x')dx' = \int_0^x \kappa_f x' dx' = \frac{1}{2}\kappa_f x^2$$

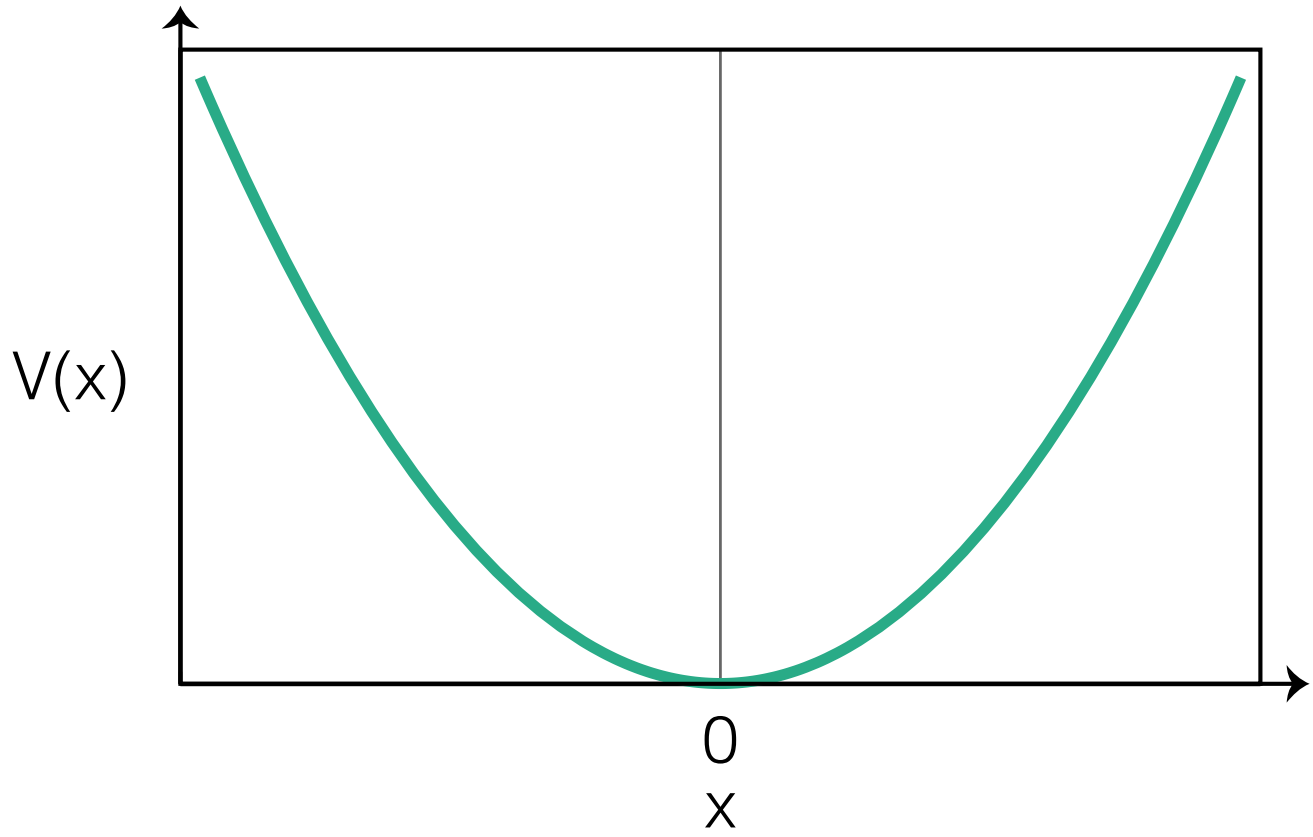
Expression above is work associated with extending spring.

For work in compressing the spring just change integral limits to $-x$ to 0 (you get same result).

Energy of simple harmonic oscillator

Potential energy is given by

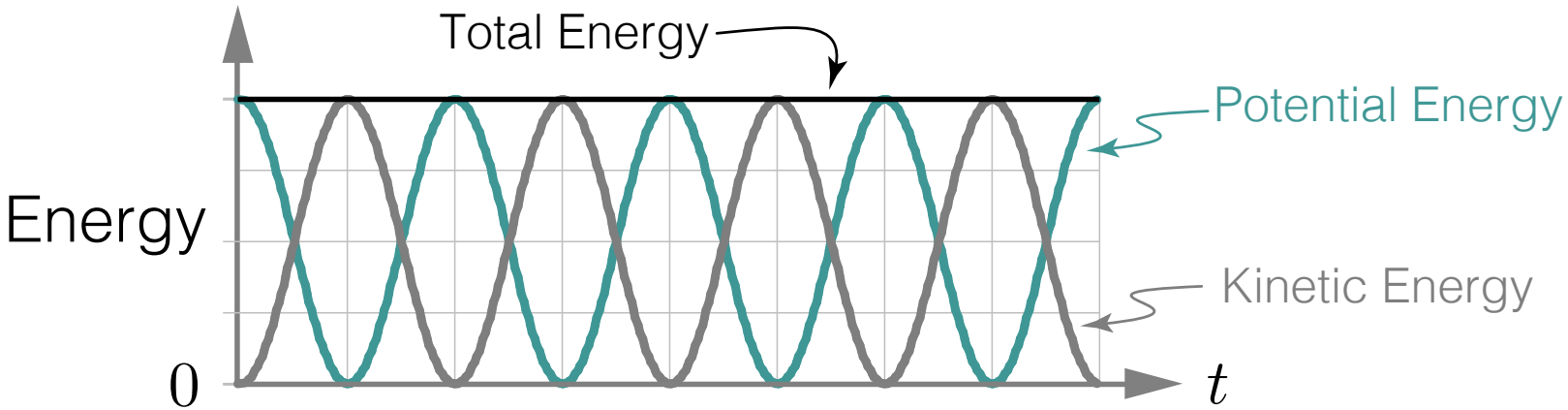
$$V(x) = \frac{1}{2}\kappa_f x^2$$



Energy of simple harmonic oscillator

Although both K and V are time dependent during harmonic motion the total energy, $E = K + V$, for a simple harmonic oscillator remains time independent.

$$E = \frac{1}{2}mv^2(t) + \frac{1}{2}\kappa_f x^2(t) \quad \text{or} \quad E = \frac{p^2(t)}{2m} + \frac{1}{2}\kappa_f x^2(t)$$



Energy of simple harmonic oscillator

Substitute equation of motion into energy expression

$$E = \frac{1}{2}\kappa_f x^2(0) = \frac{1}{2}m\omega_0^2 x^2(0)$$

Solve for $x(0)$ in terms of energy

$$x(0) = \frac{1}{\omega_0}\sqrt{\frac{2E}{m}}$$

and rewrite oscillation as

$$x(t) = x(0)\cos\omega_0 t = \sqrt{\frac{2E}{\omega_0^2 m}}\cos\omega_0 t$$

Position probability distribution for harmonic oscillator

Position probability distribution for harmonic oscillator

Scale $x(t)$ by initial amplitude $x(0)$, to obtain a function, $y(t)$, that oscillates between $y = -1$ and $y = +1$

$$y(t) = x(t)/x(0) = \cos \omega_0 t$$

Calculate normalized probability density, $p(y)$, for finding the mass at any scaled position between $y = \pm 1$.

Probability of finding mass in interval dy at given y is proportional to the time spent in dy interval,

$$p(y)\,dy = b\,dt = b\,dt\frac{dy}{dy} = b\,dy\frac{dt}{dy} = b\,\frac{dy}{\dot{y}}$$

$\dot{y}$ is the speed at a given y and b is proportionality constant.

Derivative of $y(t)$ is

$$\dot{y}(t) = -\omega_0 \sin \omega_0 t$$

so

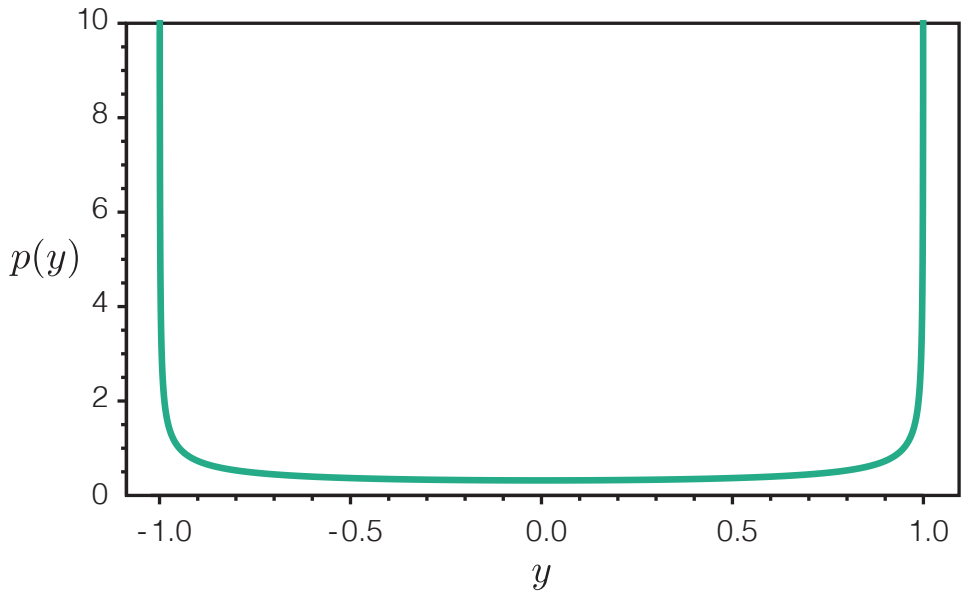
$$p(y) = \frac{b}{\dot{y}(t)} = \frac{b}{-\omega_0 \sin \omega_0 t} = \frac{b}{-\omega_0 (1 - \cos^2 \omega_0 t)^{1/2}} = \frac{b}{-\omega_0 (1 - y^2)^{1/2}}$$

Position probability distribution for harmonic oscillator

$$p(y) = \frac{b}{-\omega_0(1-y^2)^{1/2}}$$

After normalizing probability distribution becomes

$$p(y) = \frac{1}{\pi(1-y^2)^{1/2}}$$



Mass spends majority of time at maximum excursions, that is, turning points where velocity is slowest and changes sign.

Diatomic molecule vibration as Harmonic oscillator

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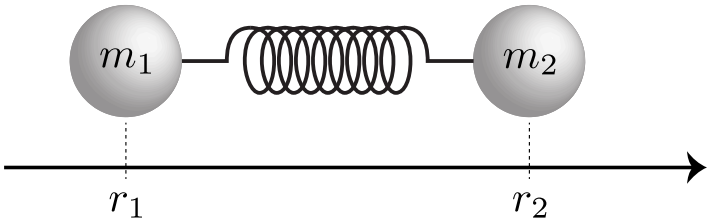
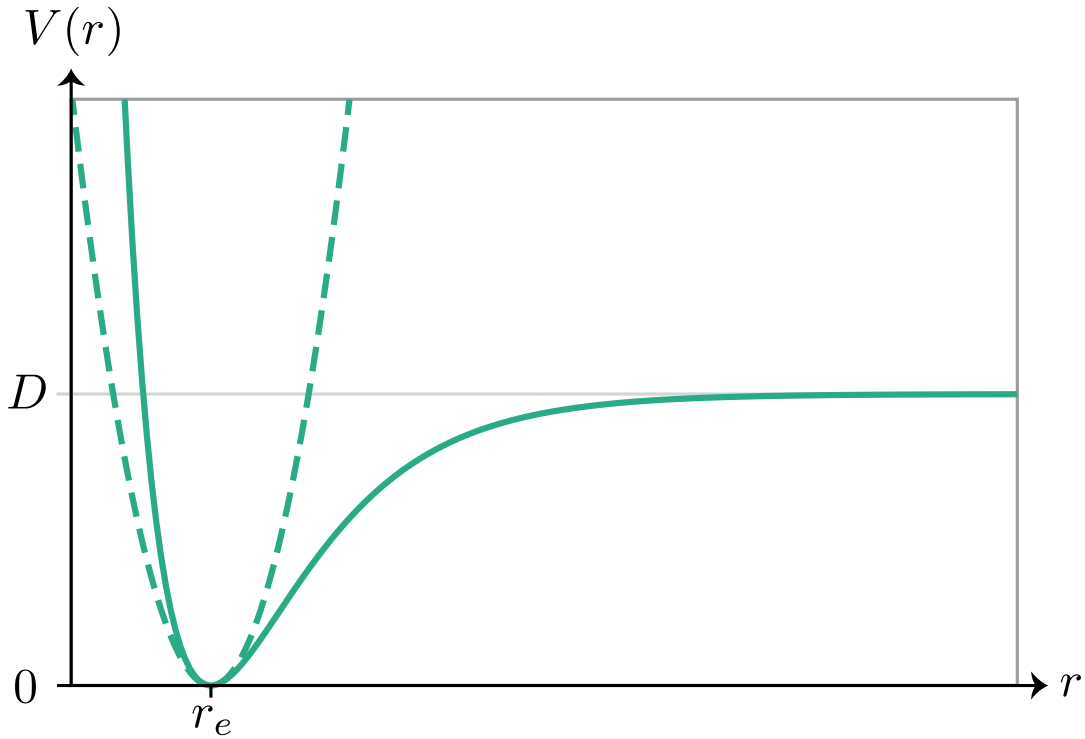




Dashed line is harmonic oscillator potential. Solid line is Morse potential.

- $V(r)$ reaches minimum at r_e—where restoring force is zero.
- $V(r)$ causes repulsive force at $r < r_e$ and attractive force at $r > r_e$.
- $V(r)$ increases steeply at $r < r_e$ but levels out to constant at $r > r_e$.
- At $r \to \infty$ there is no attractive force as $V(r)$ has a slope of zero.

Diatomic molecule vibration as Harmonic oscillator

For small displacements from equilibrium bond length the interatomic potential can be approximated as a harmonic oscillator potential.
Taylor series expansion of $V(r)$ about equilibrium bond length, $r = r_e$, gives

$$V(r) \approx V(r_e) + \cancelto{0}{\frac{dV(r_e)}{dr}}(r-r_e) + \frac{1}{2!}\frac{d^2V(r_e)}{dr^2}(r-r_e)^2 + \frac{1}{3!}\frac{d^3V(r_e)}{dr^3}(r-r_e)^3 + \cdots$$

$V(r_e)$ is the potential energy at equilibrium bond length.
1st-order term is zero since no restoring force, $F = -dV(r_e)/dr$, at $r = r_e$
Truncate expansion at the 3rd-order term and define 2 constants

$$\kappa_f = \frac{d^2V(r_e)}{dr^2} \quad \text{and} \quad \gamma_f = \frac{d^3V(r_e)}{dr^3}$$

and get potential expansion

$$V(r) - V(r_e) \approx \frac{1}{2}\kappa_f(r-r_e)^2 + \frac{1}{6}\gamma_f(r-r_e)^3 + \cdots$$

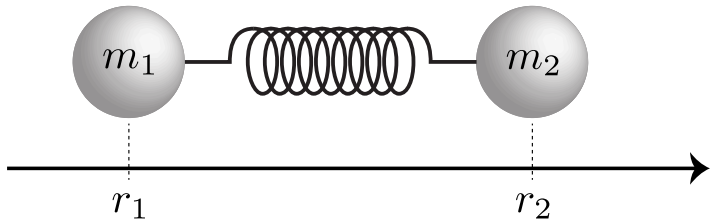
Diatomic molecule vibration as Harmonic oscillator

$$V(r) - V(r_e) \approx \frac{1}{2}\kappa_{\mathrm{f}}(r - r_e)^2 + \frac{1}{6}\gamma_{\mathrm{f}}(r - r_e)^3 + \cdots$$

- For small displacements we drop 3rd-order term and see that potential energy has form of simple harmonic oscillator.

- For slightly larger displacements we could re-add 3rd-order term to potential energy to account for anharmonicity in bond vibration.

Diatomic molecule vibration equations of motion



Make harmonic oscillator approximation taking force on m_1 and m_2 as

$$F_1 = -\kappa_f(r_1 - r_2 + r_e) \quad \text{and} \quad F_2 = -\kappa_f(r_2 - r_1 - r_e)$$

Equations of motion are 2 coupled differential equations:

$$m_1\frac{d^2r_1}{dt^2} = \kappa_f(r_2 - r_1 - r_e) \quad \text{and} \quad m_2\frac{d^2r_2}{dt^2} = -\kappa_f(r_2 - r_1 - r_e)$$

Move into center of mass frame: $M = m_1 + m_2$ and $R = \frac{1}{M}(m_1r_1 + m_1r_2)$
Obtain 2 uncoupled differential equations,

$$M\frac{d^2R}{dt^2} = 0, \quad \text{and} \quad \mu\frac{d^2\Delta r}{dt^2} = -\kappa_f\Delta r$$

$\Delta r = r_2 - r_1 - r_e$ and μ is the reduced mass given by $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

Diatomic molecule vibration equations of motion

Differential equation of motion describing the vibration

$$\mu \frac{d\Delta r^2(t)}{dt^2} + \kappa_f \Delta r(t) = 0$$

Same differential equation of motion as simple harmonic oscillator.

Solutions takes the same form,

$$\Delta r(t) = \Delta r(0) \cos \omega_0 t \quad \text{where} \quad \omega_0 = \sqrt{\kappa_f / \mu}$$

Vibration of Polyatomic Molecules

Link: Normal modes of vibration