# Lecture #7: Classical Mechanical Harmonic Oscillator

Last time

What was surprising about Quantum Mechanics?

Free particle (almost exact reprise of 1D Wave Equation)

Can't be normalized to 1 over all space! Instead: Normalization to one particle between $x_1$ and $x_2$. What do we mean by "square integrable?"

$\langle p \rangle = \frac{|a|^2 - |b|^2}{|a|^2 + |b|^2}$. What does this mean in a click-click experiment?

Motion not present, but $\psi$ is encoded for it.
Node spacing: $\lambda/2$ (generalize this to get "semiclassical")
Semiclassical: $\lambda(x) = \frac{h}{p(x)}$, $p_{\text{classical}}(x) = \left[2m\left(E - V(x)\right)\right]^{1/2}$

Particle in Infinite Box

$$E_n = \frac{h^2}{8ma^2} n^2 \qquad \psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi}{a} x\right)$$

nodes, zero-point energy
change: $a$, $V_0$, location of left edge
importance of pictures

3D box

$$\hat{H} = \hat{h}_x + \hat{h}_y + \hat{h}_z \qquad \text{(commuting operators)}$$

$$E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z}$$

$$\psi_{n_x n_y n_z} = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$$

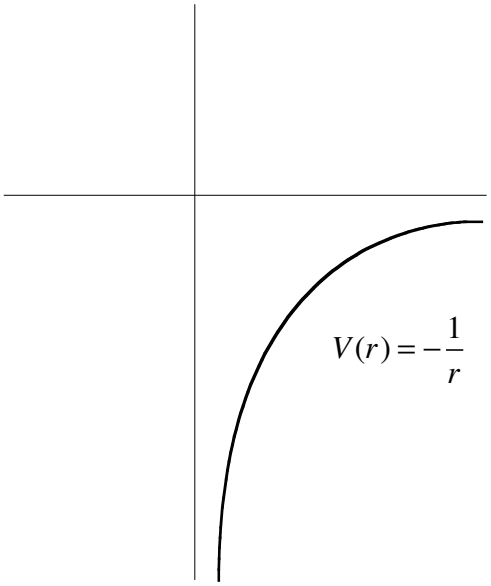
Today (and next 3+ lectures) Harmonic Oscillator

1) Classical Mechanics ("normal modes" of vibration in polyatomic molecules arise from classical mechanics). Preparation for Quantum Mechanics treatment.
2) Quantum mechanical brute force treatment — Hermite Polynomials

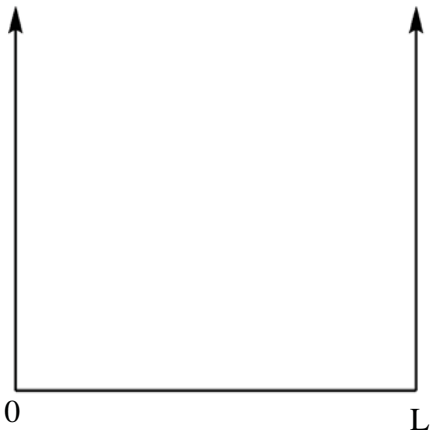
3) Elegant treatment with memorable selection rules: creation/annihilation operators.
4) Non-stationary states (i.e. moving) of Quantum Mechanical Harmonic Oscillator: wavepackets, dephasing and recurrence, and tunneling through a barrier.
5) Perturbation Theory.

Harmonic Oscillator

We have several kinds of potential energy functions in atoms and molecules.



$V(r) = -\frac{1}{r}$ H atom $E_n \propto -\frac{1}{n^2}$




$E_n \propto n^2$

particle in infinite-wall finite-length box
(also particle on a ring)

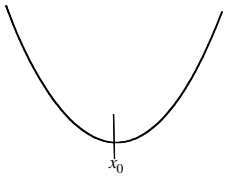
Level pattern tells us *qualitatively* what kind of system we have.

Level splittings tell us *quantitatively* what are the properties of the class of system we have.

Rigid rotor

$$E_n \propto n(n+1)$$

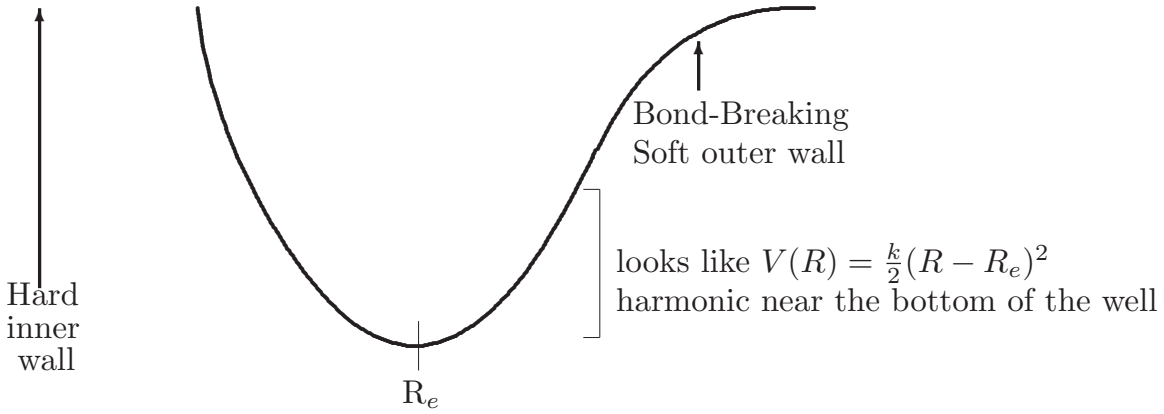
Harmonic Oscillator




$$V(x) = \frac{1}{2}kx^2 \qquad E_n \propto (n+1/2)$$

The pattern of energy levels tells us which underlying microscopic structure we are dealing with.

Typical interatomic potential energy:




We will use *x* rather than *R* here.

Expand any potential energy function as a power series:

$$X - X_0 \equiv x$$

$$V(x) = V(0) + \left.\frac{dV}{dx}\right|_{x=0} x + \left.\frac{d^2V}{dx^2}\right|_{x=0} \frac{x^2}{2} + \frac{d^3V}{dx^2}\frac{x^3}{6}$$

For small *x*, OK to ignore terms of higher order than $x^2$. [What do we know about $\frac{dV}{dx}$ at the *minimum* of any *V(x)*?]
For example, Morse Potential

$\left(1-2ax+\frac{4a^2x^2}{2}+\ldots\right)$

$\left(1-ax+\frac{a^2x^2}{2}+\ldots\right)$

$$V(x)=D_e\left[1-e^{-ax}\right]^2=D_e\left[1-2e^{-ax}+e^{-2ax}\right]$$

some algebra

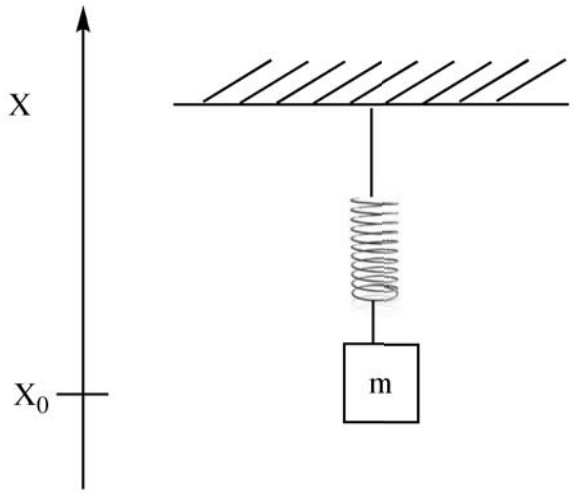
$$=V(0)+0+a^2D_ex^2-a^3D_ex^3+\frac{7}{12}a^4D_ex^4+\ldots$$

why physically is there no linear in $x$ term?

$V(\infty) = D_e$ (dissociation energy), $V(0) = 0$.
If $ax \ll 1$, $V(x) \approx V(0)+(D_ea^2)x^2$. A very good starting point for the molecular vibrational potential energy curve.

Call $D_ea^2 = k/2$. Ignore the $x^3$ and $x^4$ terms.

Let's first focus on a simple harmonic oscillator in classical mechanics.




Hooke's Law

$$F=\underbrace{-k\left(X-X_0\right)}_{\text{force is } - \text{ gradient of potential}}$$

When $X > X_0$
Force pushes mass back down toward $X_0$

$$F=-\frac{dV}{dX}$$

When $X < X_0$
Force pulls mass back up toward $X_0$

$$\therefore V(x)=\frac{1}{2}k\left(X-X_0\right)^2$$

Newton's equation:

$$F = ma = m\frac{d^2\left(X - X_0\right)}{dt^2} = -k\left(X - X_0\right)$$

$$x \equiv X - X_0$$

substitute and rearrange

$$\frac{\mathrm{d}^2 x}{dt^2} = -\frac{k}{m}x$$

2nd order ordinary linear differential equation: solution contains two linearly independent terms, each multiplied by one of 2 constants to be determined

$$x(t) = A\sin\left(\frac{k}{m}\right)^{1/2} t + B\cos\left(\frac{k}{m}\right)^{1/2} t$$

It is customary to write

$$\left(\frac{k}{m}\right)^{1/2} = \omega\,.$$ (ω is conventionally used to specify an angular frequency: radians/second)

Why?

What is frequency of oscillation? τ is period of oscillation.

$$x\left(t+\tau\right) = x(t) = A\sin\left[\left(\frac{k}{m}\right)^{1/2} t\right] + B\cos\left[\left(\frac{k}{m}\right)^{1/2} t\right] = A\sin\left[\left(\frac{k}{m}\right)^{1/2}\left(t+\tau\right)\right] + B\cos\left[\left(\frac{k}{m}\right)^{1/2}\left(t+\tau\right)\right]$$

requires

$$\left(\frac{k}{m}\right)^{1/2}\tau = 2\pi \qquad \tau = \frac{2\pi}{\omega} = \frac{2\pi}{2\pi\nu} = \frac{1}{\nu}$$ as required.

$$\nu = \frac{1}{\underbrace{\tau}_{\text{period}}}$$

How long does one full oscillation take?

we have sin, cos functions of $\left(\frac{k}{m}\right)^{1/2} t = \omega t$

when the argument of sin or cos goes from 0 to 2π, we have one period of oscillation.

$$2\pi = \left(\frac{k}{m}\right)^{1/2}\tau = \omega\tau$$

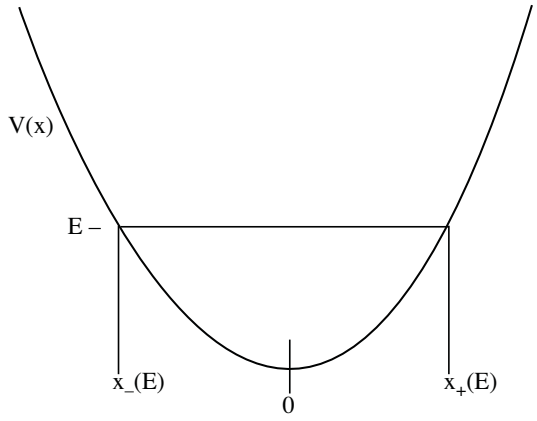
$$\tau = \frac{2\pi}{\omega} = \frac{1}{\nu}.$$

So everything makes sense.

| | |
|---|---|
| ω is "angular frequency" | radians/sec. |
| *v* is ordinary frequency | cycles/sec. |
| τ is period | sec |

$x(t) = A \sin \omega t + B \cos \omega t$

Need to get A,B from *initial conditions*:




[e.g. starting at a $\overbrace{\text{turning point}}^{\text{ASK!}}$ where $E = V(x_\pm) = (1/2)kx_\pm^2$]

$$\Downarrow$$

$$\boxed{\pm\left(\frac{2E}{k}\right)^{1/2} = x_\pm}$$

Initial amplitude of oscillation depends on the strength of the pluck!

If we start at $x_+$ at $t = 0$ (the sine term is zero at $t = 0$, the cosine term is B at $t = 0$)

$$x(0) = \left(\frac{2E}{k}\right)^{1/2} \Rightarrow B = \left(\frac{2E}{k}\right)^{1/2}$$

Note that *the frequency of oscillation does not depend on initial amplitude*. To get *A* for initial condition $x(0) = x_+$, look at $t = \tau/4$, where $x(\tau/4) = 0$. Find $A = 0$.

Alternatively, we can use frequency, phase form. For $x(0) = x_+$ initial condition:

$$x(t) = C \sin\left(\left(\frac{k}{m}\right)^{1/2} t + \phi\right)$$

$$\text{if } x(0) = x_+ = \left(\frac{2E}{k}\right)^{1/2}$$

$$C = \left(\frac{2E}{k}\right)^{1/2}, \phi = -\pi/2$$

We are done.Now explore Quantum Mechanics - relevant stuff.

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What is: Oscillation Frequency
Kinetic Energy $T(t)$, $\bar{T}$
Potential Energy, V($t$), $\bar{V}$
Period $\tau$?

Oscillation Frequency: $\nu = \dfrac{\omega}{2\pi}$ independent of E

Kinetic Energy: $T(t) = \dfrac{1}{2} m \mathrm{v}(t)^2$

$$x(t) = \left[\frac{2E}{k}\right]^{1/2} \sin[\omega t + \phi]$$

take derivative of $x(t)$ with respect to $t$

$$\mathrm{v}(t) = \omega \left[\frac{2E}{k}\right]^{1/2} \cos[\omega t + \phi]$$

$$T(t) = \frac{1}{2} m \underbrace{\omega^2}_{k/m} \left[\frac{2E}{k}\right] \cos^2[\omega t + \phi]$$

$$= E \cos^2(\omega t + \phi)$$

Now some time averaged quantities:

$$\langle T \rangle = \bar{T} = E \frac{\int_0^\tau dt \cos^2(\omega t + \phi)}{\tau} \qquad \text{recall } \tau = \frac{2\pi}{\omega}$$

$$= E/2$$

$$V(t) = \frac{1}{2} k x^2 = \frac{k}{2}\left(\frac{2E}{k}\right) \sin^2(\omega t + \phi)$$

$$= E \sin^2(\omega t + \phi)$$

Calculate $\langle V \rangle$ by $\int_0^\tau dt$ or by simple algebra, below

$$E = T(t) + V(t) = \bar{T} + \bar{V}$$

$$\bar{V} = E/2$$

Really neat that $\bar{T} = \bar{V} = E/2$.

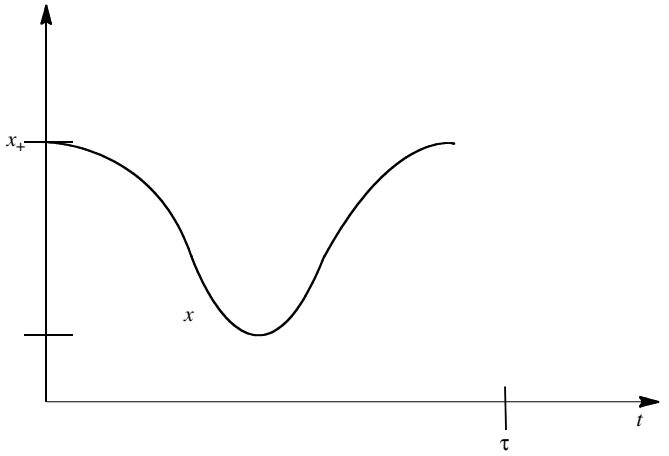
Energy is being exchanged between *T* and *V*. They oscillate π/2 out of phase: $V(t) = T\left(t - \dfrac{\tau}{4}\right)$

V lags T.

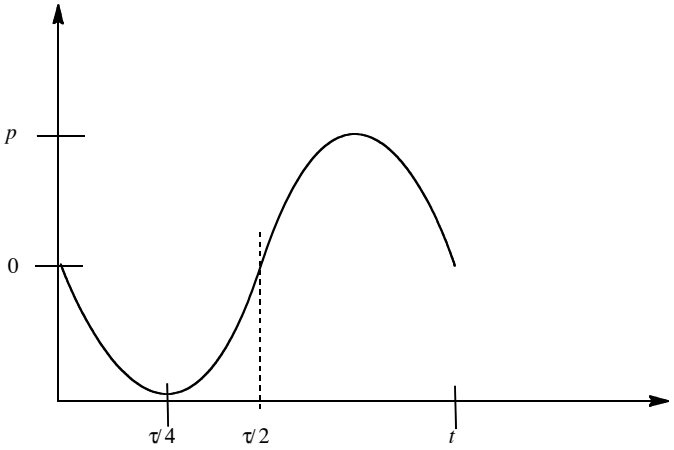
What about x(t) and p(t) when x is near the turning point?

$$x(t) = \left[\frac{2E}{k}\right]^{1/2} \cos \omega t$$

$$x(t = 0) = x_+$$




*x* changing slowly near *x* turning point




*p* changing fastest near *x* turning point

Insights for wavepacket dynamics. We will see that "survival probability" $\left|\Psi^*(x,t)\Psi(x,0)\right|^2$ decays near t.p. mostly because of $\hat{p}$ rather than $\hat{x}$.

What about *time-averages* of $x, x^2, p, p^2$?

$\left.\begin{aligned}\langle x\rangle = 0\\ \langle p\rangle = 0\end{aligned}\right\}$ is the HOpotential moving in space?

$x^2 = V(x)/(k/2)$

take *t*-average

$$\langle x^2\rangle = \frac{2}{k}\langle V(x)\rangle = \frac{2}{k}\frac{E}{2} = E/k$$

$p^2 = 2\mathrm{mT}$

$$\langle p^2\rangle = 2m\frac{E}{2} = mE$$

$$\Delta x = \left\langle x^2 - \langle x \rangle^2 \right\rangle^{1/2} = (E/k)^{1/2}$$

$$\Delta p = \left\langle p^2 - \langle p \rangle^2 \right\rangle^{1/2} = (mE)^{1/2}$$

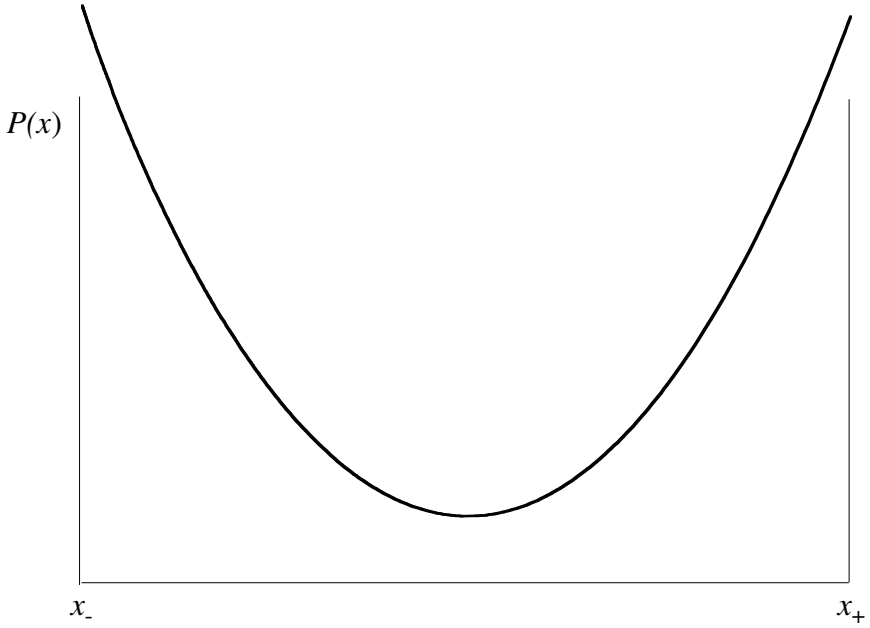
$$\Delta x \Delta p = E\left(\frac{m}{k}\right)^{1/2} = E/\omega \text{ . small at low E}$$

We will see an uncertainty relationship between $x$ and $p$ in Quantum Mechanics.

Probability of finding oscillator between $x$ and $x + dx$: consider one half period, oscillator going from left to right turning point.

$$P(x)dx = \frac{\text{time}(x, x+dx)}{\tau/2} = \frac{\dfrac{\text{distance}}{\text{velocity}}}{\dfrac{1}{2}\left(\dfrac{2\pi}{\omega}\right)}$$

$$= \frac{\dfrac{dx}{v(x)}}{\dfrac{2\pi}{2\omega}} = \frac{2\omega}{v(x)2\pi}dx$$



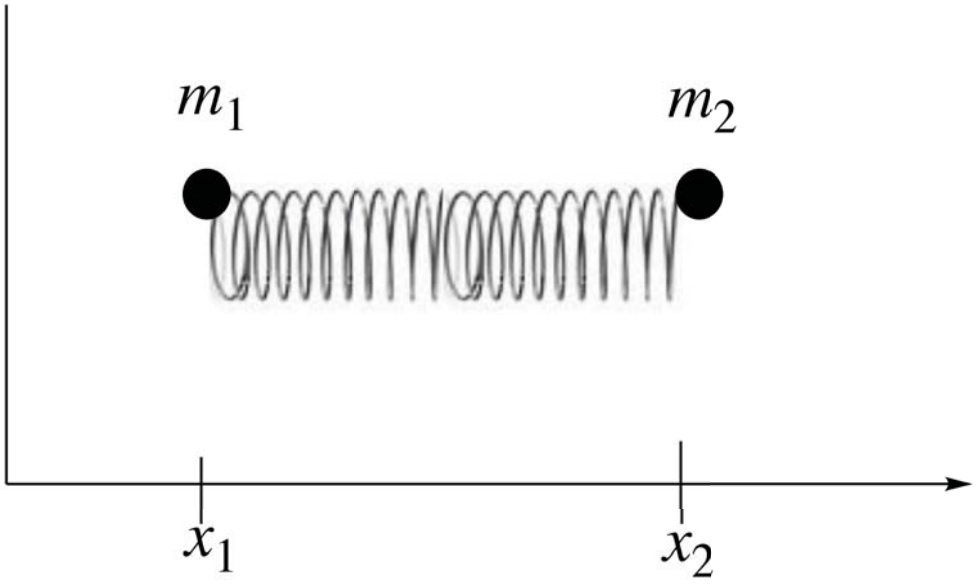

large probability at turning points. Goes to ∞ at $x_{\pm}$.

minimum probability at $x = 0$

In Quantum Mechanics, we will see that P($x_{\pm}$) does not blow up and there is some probability outside the classically allowed region. Tunneling.

Non-Lecture

Next we want to go from one mass *on an anchored spring* to two masses *connected* by a spring.




F = m*a* for each mass

$$m_1 \frac{d^2 x_1}{dt^2} = k\left(x_2 - x_1 - \ell_0\right)$$

length of spring at rest, i.e. when $x_2 - x_1 = \ell_0$

$$m_2 \frac{d^2 x_2}{dt^2} = -k\left(x_2 - x_1 - \ell_0\right)$$

2 coupled differential equations.

Uncouple them easily, as follows:

Add the 2 equations

$$m_1 \frac{d^2 x_1}{dt^2} + m_2 \frac{d^2 x_2}{dt^2} = \frac{d^2}{dt^2} \underbrace{\left(m_1 x_1 + m_2 x_2\right)}_{\substack{\text{we will see that} \\ \text{this is at worst} \\ \text{proportional to } t}} = 0$$

Define a *center of mass* coordinate.

$$\frac{m_1x_1 + m_2x_2}{M} = X \qquad M = m_1 + m_2$$

replace $m_1x_1 + m_2x_2$ by $MX$

$$M\frac{d^2X}{dt^2} = 0$$

integrate once with respect to $t$

$$\frac{dX}{dt}(t) = const.$$

The center of mass is moving at constant velocity — no force acting.

Next find a new differential equation expressed in terms of the relative coordinate

$$x = x_2 - x_1 - \ell_0.$$

Divide the first differential equation (located at the top of page 10) by $m_1$, the second by $m_2$, and subtract the first from the second:

$$\frac{d^2x_2}{dt^2} - \frac{d^2x_1}{dt^2} = -\frac{k}{m_2}\left(x_2 - x_1 - \ell_0\right) - \frac{k}{m_1}\left(x_2 - x_1 - \ell_0\right)$$

$$\frac{d^2}{dt^2}\left(x_2 - x_1\right) = -k\left(\frac{1}{m_2} + \frac{1}{m_1}\right)\left(x_2 - x_1 - \ell_0\right)$$

$$= -k\left(\frac{m_1 + m_2}{m_1m_2}\right)\left(x_2 - x_1 - \ell_0\right)$$

$$\mu \equiv \frac{m_1m_2}{m_1 + m_2}$$

$$\frac{d^2}{dt^2}\underbrace{\left(x_2 - x_1\right)}_{x+\ell_0} = -\frac{k}{\mu}\underbrace{\left(x_2 - x_1 - \ell_0\right)}_{x \text{ is displacement from equilibrium}} = -\frac{k}{\mu}x$$

killed by derivative

We get a familiar looking equation for the intramolecular displacement from equilibrium.

$$\mu\frac{d^2x}{dt^2} + kx = 0$$

Everything is the same as the one-mass-on-a-spring problem except $m \to \mu$.

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Next time: Quantum Mechanical Harmonic Oscillator

$$H = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k\hat{x}^2$$

note that this differential operator does not have time in it!

We will see particle-like motion for harmonic oscillator when we consider the Time Dependent Schrödinger equation (Lecture #10) and $\Psi(x,t)$ is a particle-like state.

$$\Psi(x,t) \qquad \text{where } \Psi(x,0) = \sum_{v=0}^{\infty} c_v \psi_v$$

in the 4th lecture on Harmonic Oscillators (Lecture #11).

# 5.61 Physical Chemistry

Fall 2013