Lecture #7: Classical Mechanical Harmonic Oscillator

Last time

What was surprising about Quantum Mechanics?

Free particle (almost an 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?"

$$\langle \hat{p} \rangle = \frac{|a|^2 - |b|^2}{|a|^2 + |b|^2}$$

What free particle $\psi(x)$ has this expectation value?
What does this mean in a click-click experiment?

Motion not present, but ψ 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

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

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

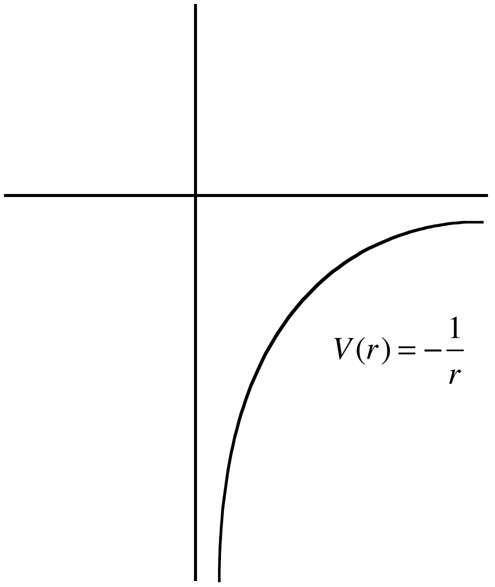
$$\psi_{n_x n_y n_z} = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$$

Today (and next 3+ lectures) Harmonic Oscillator

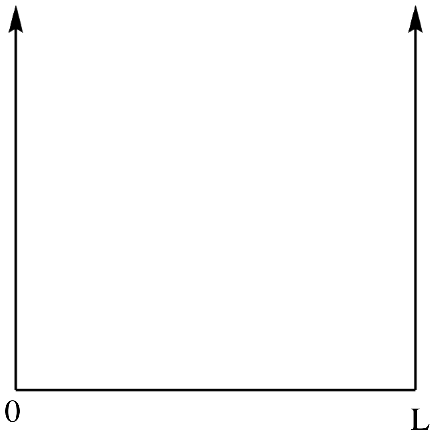
1) Classical Mechanics ("normal modes" of vibration in polyatomic molecules arise from classical mechanics). Preparation for Quantum Mechanical treatment.
2) Quantum mechanical brute force treatment — Hermite Polynomials
3) Elegant treatment with memorable selection rules: "creation/annihilation" operators.
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.



H atom $\quad E_n \propto -\frac{1}{n^2}$



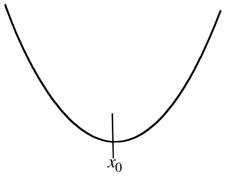
$E_n \propto n^2$

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  $E_n \propto n(n+1)$

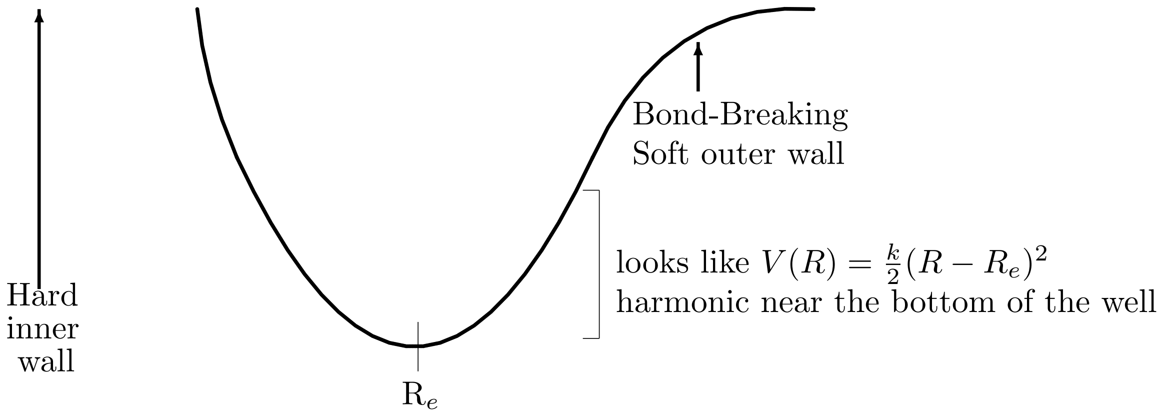
Harmonic Oscillator



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

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

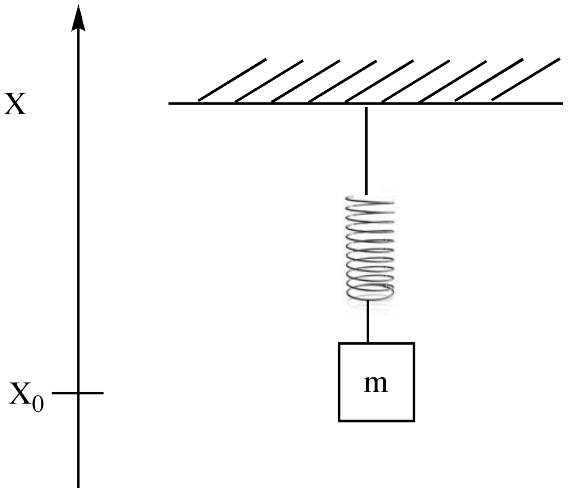
$$=V(0)+0+a^2D_ex^2-a^3D_ex^3+\frac{7}{12}a^4D_ex^4+\ldots$$

why physically is there no linear in x term?

$V(\infty)=D_e$ (dissociation energy), $V(0)=0$.
If ax ● 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

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

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

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

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

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.

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

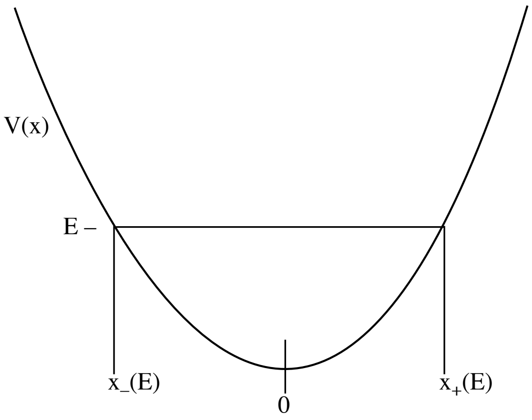
$$\tau = \frac{2\pi}{\omega} = \frac{1}{\nu}.$$

So everything makes sense.

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

x(t) = A sin ωt + B cos ωt

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



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

$$\Downarrow$$

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

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 the 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.

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

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:

$$\langle T \rangle = \overline{T} = E \frac{\int_0^\tau dt \cos^2(\omega t + \phi)}{\tau}$$

recall $\tau = \dfrac{2\pi}{\omega}$

$$= E/2$$

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

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

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

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

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

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

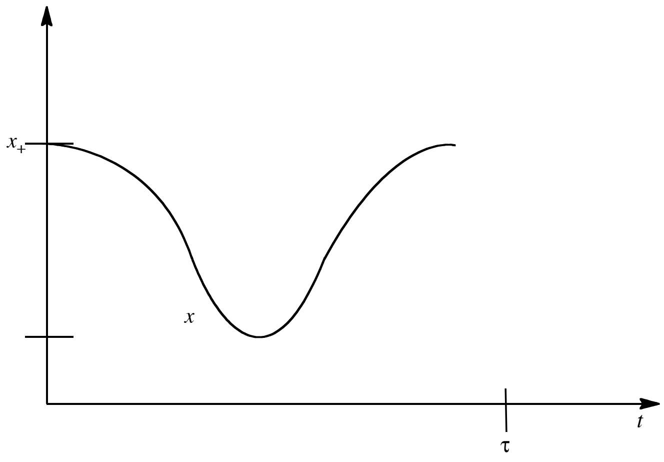
Energy is being exchanged between T and V. They oscillate π/2 out of phase: $V(t) = T\left(t - \dfrac{\tau}{4}\right)$

V lags T.

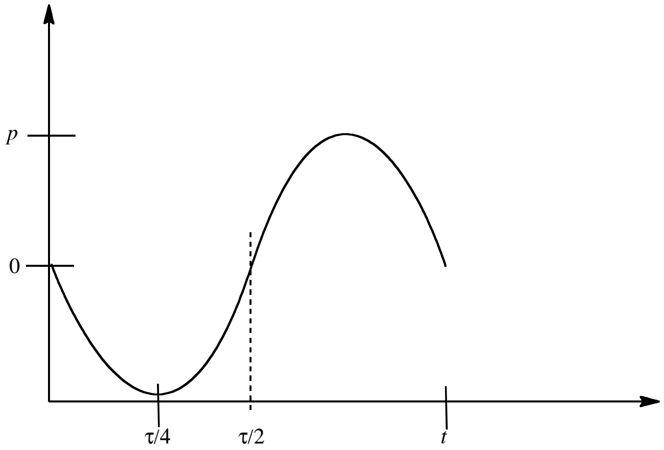
What about x(t) and p(t) when x is near the turning point?

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

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



x changing slowly near x turning point



p changing fastest near x turning point

Insights for wavepacket dynamics. We will see (in Lecture #11) 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?

$$\left.\begin{array}{l}\langle x\rangle = 0\\ \langle p\rangle = 0\end{array}\right\}\text{ is the HO potential moving in space?}$$

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

take t-average

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

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

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

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

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

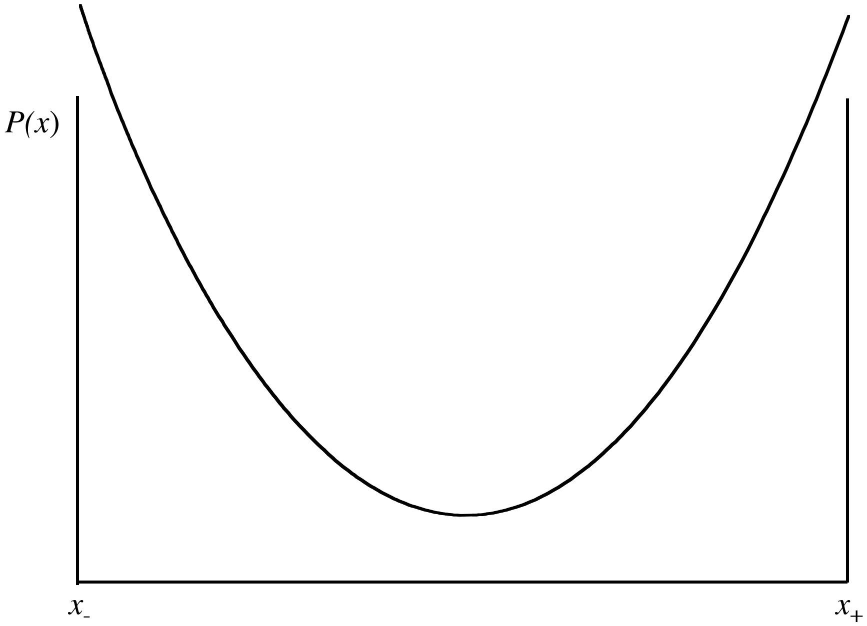
$$\Delta x \Delta p = E\left(\frac{m}{k}\right)^{1/2} = E/\omega\,. \text{ small at low E}$$

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.

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

$$= \frac{\frac{dx}{v(x)}}{\frac{2\pi}{2\omega}} = \frac{2\omega}{v(x)2\pi}dx \quad \left(v(x) \text{ small at } x = x_{\pm}\right)$$



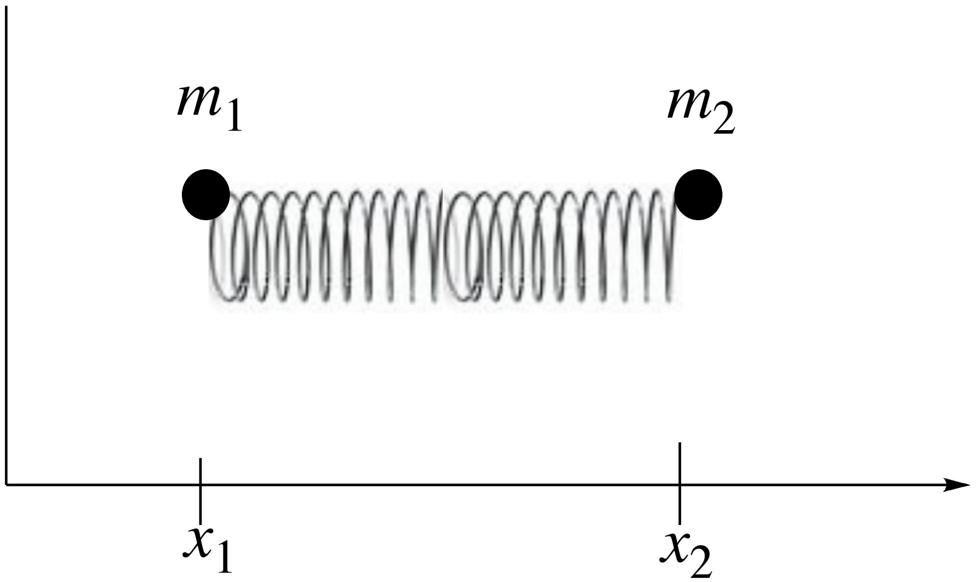
large probability at turning points. Goes to ∞ at $x_{\pm}$.

minimum probability at $x = 0$

In Quantum Mechanics, we will see that P($x_{\pm}$) does not blow up and also that 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

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

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

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

2 coupled differential equations.

Uncouple them easily, as follows:

Add the 2 equations

$$m_1 \frac{d^2x_1}{dt^2} + m_2 \frac{d^2x_2}{dt^2} = \frac{d^2}{dt^2}\underbrace{\left(m_1x_1 + m_2x_2\right)}_{\substack{\text{we will see that}\\ \text{this is at worst}\\ \text{proportional to } t}} = 0$$

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 <u>relative</u> 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:

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

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

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

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

killed by derivative

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

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-an-anchored-spring problem except $m \rightarrow \mu$.

Next time: Quantum Mechanical Harmonic Oscillator

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

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 constructed to be a particle-like state.

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

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

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