Chapter 11 Part 1

Dr. Turner

The classical harmonic oscillator

- The classical harmonic oscillator is a repetitive motion that follow's Hooke's law.

$$\boldsymbol{F} = -k\boldsymbol{x}$$

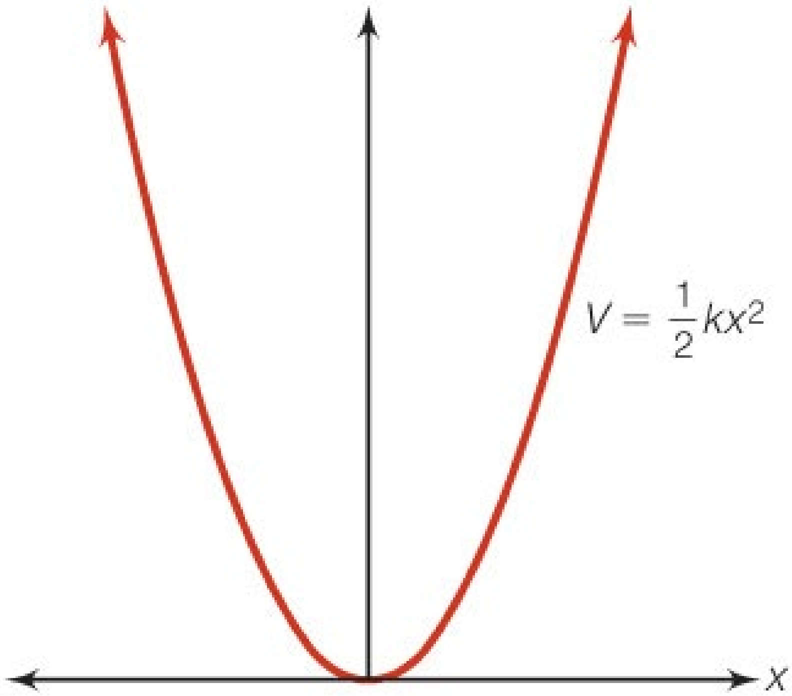
  - $\boldsymbol{x}$ is some one-dimensional displacement from some equilibrium position (in m)
  - $\boldsymbol{F}$ is the force acting to return the mass to the equilibrium point (in N)
  - k is the force constant of the system (in N/m)
- The equation for the potential energy of the harmonic oscillator is

$$V = \frac{1}{2}kx^2$$

  - Note that the potential energy does not depend on the mass of the oscillator

The classical harmonic oscillator

- A plot of the potential energy diagram $V(x) = \frac{1}{2}kx^2$ for an ideal harmonic oscillator



The classical harmonic oscillator

- The behavior of the harmonic oscillator can be modeled by the equation below

$$x(t) = x_0 \sin\left(\sqrt{\frac{k}{m}}t + \phi\right)$$

  - x_0 is the maximum amplitude of the oscillation (in m)
  - m is the mass (in kg)
  - t is the time (in s)
  - ϕ is the phase factor that indicates the absolute position of the mass at the starting time, when $t = 0$ (in m)

The classical harmonic oscillator

- The frequency oscillations of the harmonic oscillator can be modeled by the equation below

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

  - ν is the frequency in number of oscillations per second
  - τ is the amount of time that it takes to complete one cycle

The classical harmonic oscillator

A. For small displacements, a clock's pendulum can be treated as a harmonic oscillator. A pendulum has a frequency of $1.00\ \mathrm{s}^{-1}$. If the mass of the pendulum is 5.00 kg, what is the force constant acting on the pendulum in units of N/m.

B. Calculate the similar force constant for a hydrogen atom having a mass 1.673×10^{-27} kg attached to an atomically flat metal surface and vibrating with a frequency of $6.000 \times 10^{13}\ \mathrm{s}^{-1}$.

The classical harmonic oscillator Part A

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$1.00\ s^{-1} = \frac{1}{2\pi}\sqrt{\frac{k}{5.00\ kg}}$$

$$2\pi\ s^{-1} = \sqrt{\frac{k}{5.00\ kg}}$$

$$4\pi^2\ s^{-2} = \frac{k}{5.00\ kg}$$

$$k = 20\pi^2 \frac{kg}{s^2} = 20\pi^2 \frac{N}{m}$$

The classical harmonic oscillator Part B

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$6.00 \times 10^{13}\ s^{-1} = \frac{1}{2\pi}\sqrt{\frac{k}{1.673 \times 10^{-27} kg}}$$

Following the same steps as before we get

$$\mathrm{k} = 237.8\,\frac{\mathrm{N}}{\mathrm{m}}$$

The quantum-mechanical harmonic oscillator

- The Schrödinger equation for the quantum-mechanical harmonic oscillator is

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}kx^2\right]\Psi = E\Psi$$

- The force constant, k, is equal to

$$k = 4\pi^2\nu^2 m$$

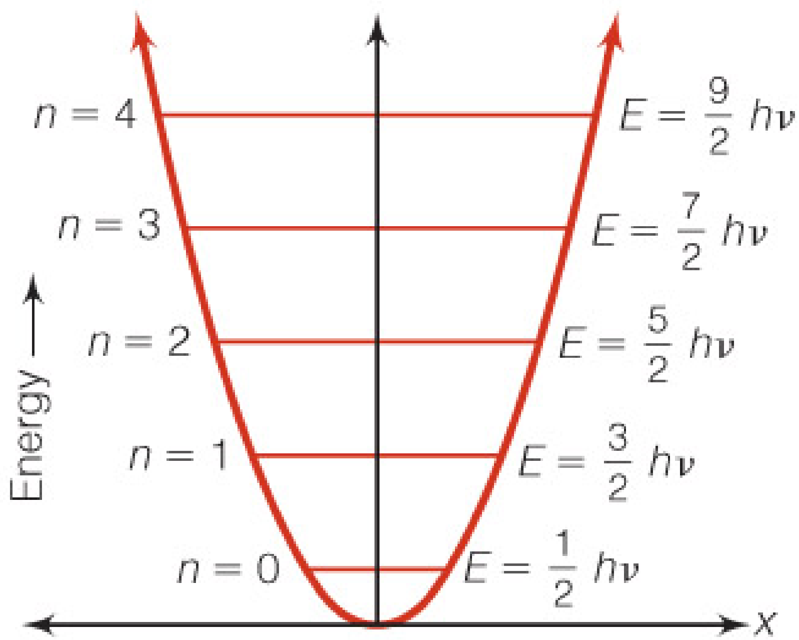
- The energy of the harmonic oscillator is shown below

$$E = \left(n+\frac{1}{2}\right)h\nu$$

  - E is the energy
  - n is a quantum number which can be integers from 0 to $+\infty$
  - H is Planck's constant
  - m is mass

The quantum-mechanical harmonic oscillator

- A diagram of the energy levels of an ideal harmonic oscillator, as predicted by the solutions to the Schrodinger equation.
- Note that the lowest quantized energy level, $E(n = 0)$, does not have zero energy.
- This introduces the concept of zero-point energy
- Energy levels are spaced by $\Delta h\nu$



The quantum-mechanical harmonic oscillator

A. A single oxygen atom attached to a smooth metal surface vibrates at a frequency of $1.800 \times 10^{13} s^{-1}$. Calculate its total energy for the $n = 0, 1,$ and 2 quantum numbers.
B. Calculate the wavelength of light necessary to excite a harmonic oscillator from one energy state to the adjacent higher state in A. Express the wavelength in units of m.

The quantum-mechanical harmonic oscillator

$$E_0 = \left(0 + \frac{1}{2}\right)(6.626 \times 10^{-34}\, Js)(1.800 \times 10^{13}\, s^{-1}) = 5.963 \times 10^{-21}\, J$$

$$E_1 = \left(1 + \frac{1}{2}\right)(6.626 \times 10^{-34}\, Js)(1.800 \times 10^{13}\, s^{-1}) = 1.789 \times 10^{-20}\, J$$

$$E_2 = \left(2 + \frac{1}{2}\right)(6.626 \times 10^{-34}\, Js)(1.800 \times 10^{13}\, s^{-1}) = 2.982 \times 10^{-20}\, J$$

$$\Delta E = (6.626 \times 10^{-34}\, Js)(1.800 \times 10^{13}\, s^{-1}) = 1.193 \times 10^{20}\, J$$

$$c = \lambda \nu$$

$$2.998 \times 10^{8}\, \frac{m}{s} = \lambda(1.800 \times 10^{13}\, s^{-1})$$

$$\lambda = 1.66 \times 10^{-5}\, m$$

Harmonic oscillator wavefunctions

- The wavefunction for the quantum-mechanical harmonic oscillator is given below

$$\Psi_n = \boxed{\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \cdot \left(\frac{1}{2^n\, n!}\right)^{\frac{1}{2}}} \cdot \boxed{H_n\left(\alpha^{\frac{1}{2}}\, x\right)} \cdot \boxed{e^{-\frac{\alpha x^2}{2}}}$$

  - The part in yellow is the normalization constant
  - The part in red is a Hermite polynomial
  - The part in blue is a gaussian function
  - Also, α is defined as

$$\alpha = \frac{2\pi\nu m}{\hbar}$$

Hermite polynomials

- The first six Hermite polynomials are given in the table below

$$\Psi_n = \boxed{\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \cdot \left(\frac{1}{2^n\, n!}\right)^{\frac{1}{2}}} \cdot \boxed{H_n\left(\alpha^{\frac{1}{2}}\, x\right)} \cdot \boxed{e^{-\frac{\alpha x^2}{2}}}$$

  - Note that $\xi = \alpha^{\frac{1}{2}} x$ and $\xi^2 = \alpha x^2$
- Further, the table below applies for integrals of Hermite polynomials

$$\int_{-\infty}^{+\infty} H_a(\xi)^* H_b(\xi) e^{-\xi^2} d\xi = \begin{cases} 0 \text{ if } a \neq b \\ 2^a a! \pi^{1/2} \text{ if } a = b \end{cases}$$

n	$H_n(\xi)$
0	1
1	2ξ
2	$4\xi^2 - 2$
3	$8\xi^3 - 12\xi$
4	$16\xi^4 - 48\xi^2 + 12$
5	$32\xi^5 - 160\xi^3 + 120\xi$
6	$64\xi^6 - 480\xi^4 + 720\xi^2 - 120$

Harmonic oscillator wavefunctions

- Normalize Ψ_1 for a quantum mechanical harmonic oscillator

$$\Psi_n = \boxed{\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \cdot \left(\frac{1}{2^n\, n!}\right)^{\frac{1}{2}}} \cdot \boxed{H_n\left(\alpha^{\frac{1}{2}}\, x\right)} \cdot \boxed{e^{-\frac{\alpha x^2}{2}}}$$

$$\int_{-\infty}^{+\infty} H_a(\xi)^* H_b(\xi) e^{-\xi^2}\, d\xi = \begin{cases} 0 \text{ if } a \neq b \\ 2^a a! \pi^{1/2} \text{ if } a = b \end{cases}$$

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Harmonic oscillator wavefunctions

$$\int_{-\infty}^{\infty} \Psi^* \Psi \, dx = 1$$

$$N^2 \int_{-\infty}^{\infty} \left[H_1\left(\alpha^{\frac{1}{2}} x\right) \cdot e^{-\frac{\alpha x^2}{2}}\right]^* \left[H_1\left(\alpha^{\frac{1}{2}} x\right) \cdot e^{-\frac{\alpha x^2}{2}}\right] dx = 1$$

$$N^2 \int_{-\infty}^{\infty} \left[H_1(\xi) \cdot e^{-\frac{\alpha x^2}{2}}\right]^* \left[H_1(\xi) \cdot e^{-\frac{\alpha x^2}{2}}\right] \frac{d\xi}{\alpha^{\frac{1}{2}}} = 1$$

$$\frac{N^2}{\alpha^{\frac{1}{2}}} \int_{-\infty}^{\infty} H_1(\xi) \cdot H_1(\xi) \cdot e^{-\alpha x^2} \, d\xi = 1$$

$$\frac{N^2}{\alpha^{\frac{1}{2}}} \int_{-\infty}^{\infty} H_1(\xi) \cdot H_1(\xi) \cdot e^{-\xi^2} \, d\xi = 1$$

$$\frac{N^2}{\alpha^{\frac{1}{2}}} \left(2^1 1! \, \pi^{\frac{1}{2}}\right) = 1$$

Harmonic oscillator wavefunctions

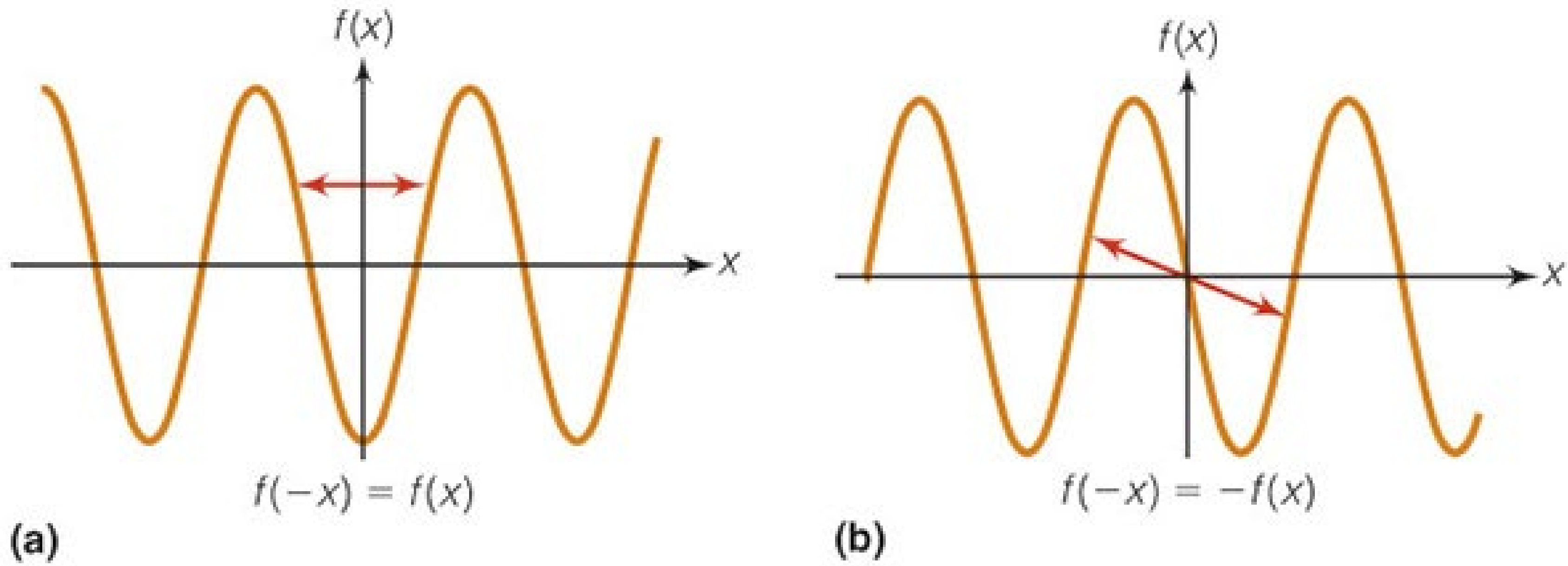
$$\frac{N^2}{\alpha^{\frac{1}{2}}}\left(2^1 1!\,\pi^{\frac{1}{2}}\right) = 1$$

$$N^2 = \frac{\alpha^{\frac{1}{2}}}{2\pi^{\frac{1}{2}}}$$

$$N = \frac{\alpha^{\frac{1}{4}}}{\sqrt{2}\pi^{\frac{1}{4}}} = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}}$$

$$\Psi_1 = \left(\frac{\alpha}{4\pi}\right)^{\frac{1}{4}} \cdot H_1\left(\alpha^{\frac{1}{2}}x\right) \cdot e^{-\frac{\alpha x^2}{2}}$$

Odd and Even functions



In even functions, changing the value of x from x to $-x$ yields the same value for $f(x)$

In odd functions, changing the value of x from x to $-x$ yields $-f(x)$

Odd and Even Functions

- For an odd function ranging from $+\infty$ to $-\infty$, the integral is exactly zero
- For multiplying odd and even functions
  - $(\text{odd}) \times (\text{odd}) = (\text{even})$
  - $(\text{even}) \times (\text{even}) = (\text{even})$
  - $(\text{even}) \times (\text{odd}) = (\text{odd})$
  - This mimics the rules for multiplication of positive and negative numbers.
- The parity (whether a number is odd or even) of Hermite polynomials corresponds with it's n value.
  - For example, $\mathrm{H}_0, \mathrm{H}_2, \mathrm{H}_4,$ and H_6 are even, and $\mathrm{H}_1, \mathrm{H}_3,$ and H_5 are odd

Harmonic oscillator average values

Evaluate $\langle x \rangle$ for Ψ_3 of a harmonic oscillator by inspection. That is, evaluate by considering the properties of the functions instead of calculating the average value mathematically.

Harmonic oscillator average values

$$N^2 \int_{-\infty}^{-\infty} \left[H_3(\xi) \cdot e^{-\frac{\alpha x^2}{2}}\right]^* \hat{x} \left[H_3(\xi) \cdot e^{-\frac{\alpha x^2}{2}}\right] dx$$

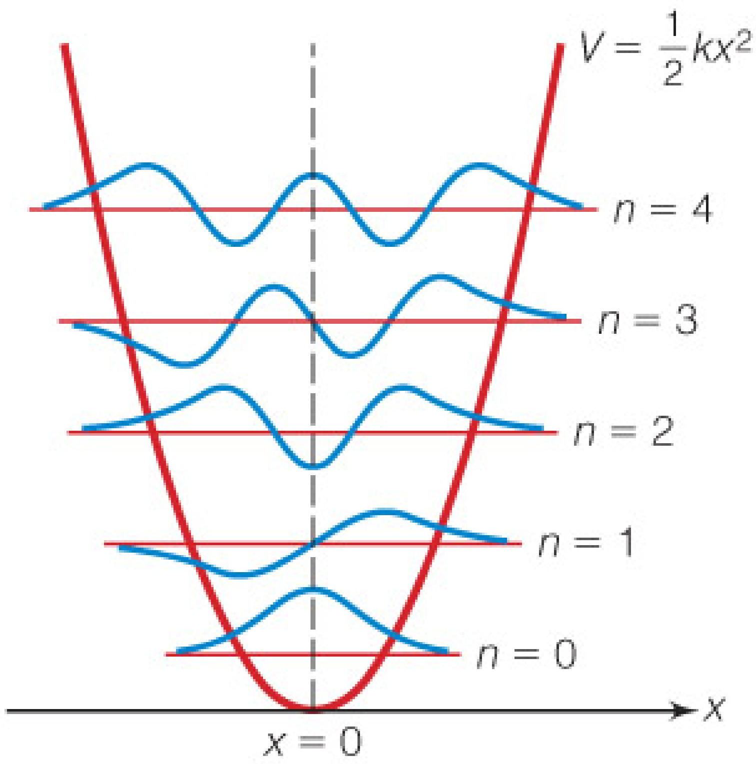
$$N^2 \int_{-\infty}^{-\infty} x \cdot [H_3(\xi)]^2 \cdot e^{-\alpha x^2} dx$$

$$N^2 \int_{-\infty}^{-\infty} \text{odd} \times \text{even} \times \text{even}\ dx$$

$$N^2 \int_{-\infty}^{-\infty} \text{odd}\ dx = 0$$

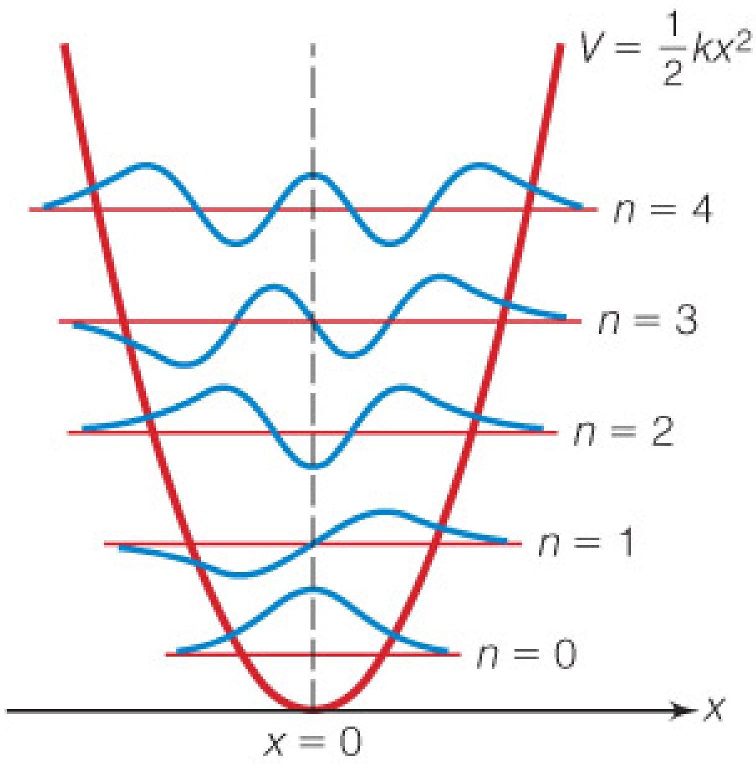
Classical Turning Point

- In classical mechanics, as the oscillating mass moves back and forth about a center is bound by the potential energy.
- As the mass extends father away from the center, the potential energy grows until all of the energy is potential, and none is kinetic.



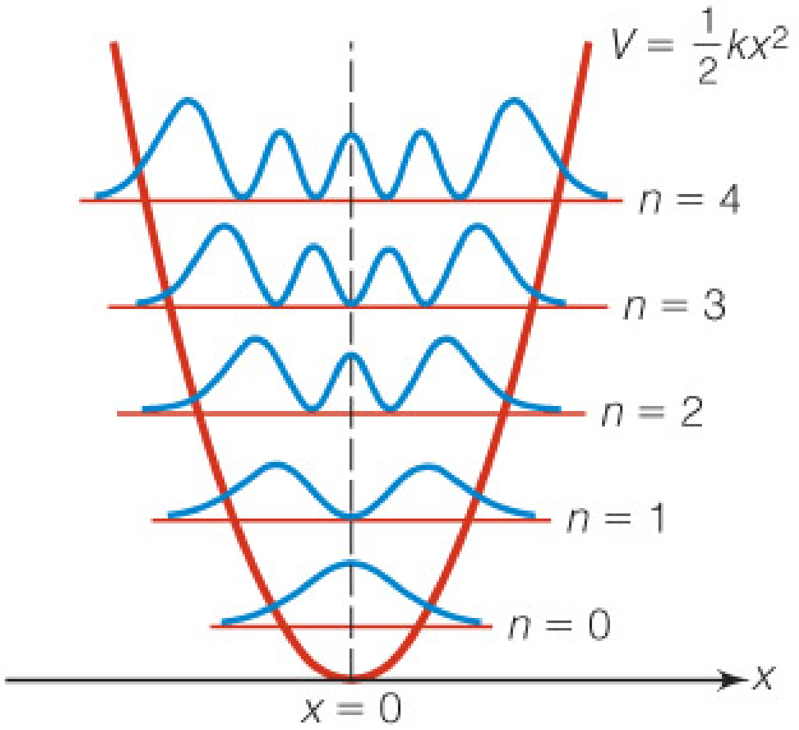
Classical Turning Point

- The point at which the mass turns around is the classical turning point.
- As one can see, wavefunctions for quantum mechanical harmonic oscillators exist beyond the point where all classical energy would be potential energy.
- This necessitates that the oscillator must have negative kinetic energy past the classical turning point potential energy "wall"



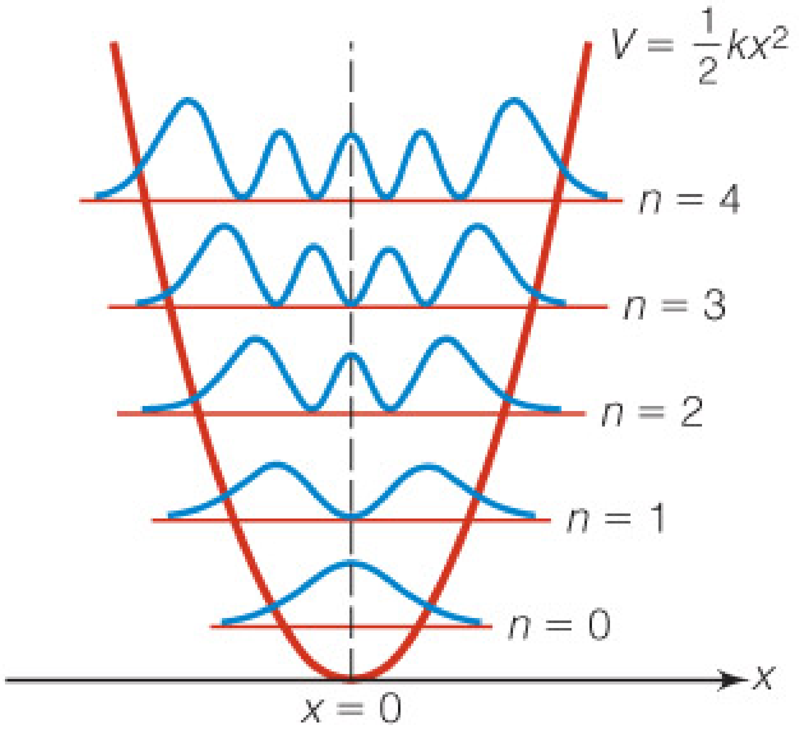
Harmonic oscillator probability

- Several $|\Psi|^2$ plots are shown.
- The top plot has a high quantum number and is beginning to mimic the behavior of the classical harmonic oscillator.
- It moves very quickly at $x = 0$, has a low probability of being found there, and has a high probability of being found when it slows near the turning point.



Harmonic oscillator probability

- This is an example of the correspondence principle that says that at high quantum numbers, quantum mechanics approaches the expectation of classical mechanics.



Harmonic oscillator average values

Evaluate $\langle \rho_x \rangle$ for Ψ_1 of a harmonic oscillator.

Harmonic oscillator average values

$$\langle \rho_x \rangle = N^2 \int_{-\infty}^{-\infty} \left[H_1(\xi) \cdot e^{-\frac{\alpha x^2}{2}} \right]^* \hat{\rho}_x \left[H_1(\xi) \cdot e^{-\frac{\alpha x^2}{2}} \right] dx$$

$$\langle \rho_x \rangle = N^2 \int_{-\infty}^{-\infty} \left[2\alpha^{\frac{1}{2}} x \cdot e^{-\frac{\alpha x^2}{2}} \right]^* - i\hbar \frac{d}{dx} \left[2\alpha^{\frac{1}{2}} x \cdot e^{-\frac{\alpha x^2}{2}} \right] dx$$

$$\langle \rho_x \rangle = -4\alpha i\hbar N^2 \int_{-\infty}^{-\infty} x \cdot e^{-\frac{\alpha x^2}{2}} \cdot (e^{-\frac{\alpha x^2}{2}} - \alpha x^2 e^{-\frac{\alpha x^2}{2}}) dx$$

$$\langle \rho_x \rangle = -4\alpha i\hbar N^2 \int_{-\infty}^{-\infty} x e^{-\alpha x^2} - \alpha x^3 e^{-\alpha x^2} dx$$

$$\langle \rho_x \rangle = -4\alpha i\hbar N^2 \int_{-\infty}^{-\infty} (\mathrm{odd} - \mathrm{odd})\, dx$$

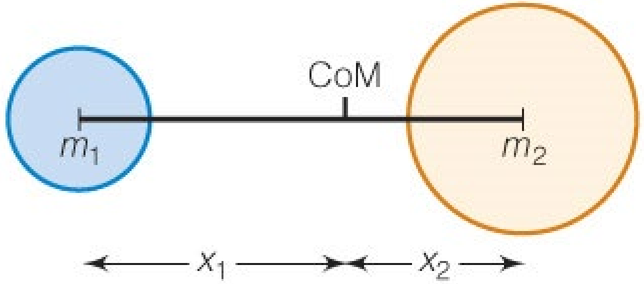
$$\langle \rho_x \rangle = 0$$

Reduced Mass

- Many harmonic oscillators aren't just a single mass moving back and forth like a pendulum and instead are like diatomic molecules with two atoms each moving back and forth.
- A reduced mass can be used to express two masses moving back and forth as a single mass and is defined as

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

  - m_1 and m_2 are masses
  - x_1 and x_2 are the distances between the center of mass



Reduced Mass

- All the previous quantum mechanical harmonic oscillator equations apply with the reduced mass of the system.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\left[-\frac{\hbar}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]\Psi = E\Psi$$

$$k = 4\pi^2\nu^2\mu$$

Reduced Mass

The hydrogen gas molecule vibrates at a frequency of about 1.32×10^{14} Hz. Calculate the following.

A. The force constant of the H–H bond.

B. The change in energy that accompanies a transition from the $n = 1$ to $n = 2$ vibrational level, assuming that the hydrogen molecule is acting as an ideal harmonic oscillator.

Reduced Mass

$$1 \text{ atom H} \left(\frac{1 \text{ mol H}}{6.022 \times 10^{23} \text{ atoms H}} \right) \left(\frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right)$$
$$= 1.674 \times 10^{-27} \text{ kg H}$$

$$\mu = \frac{(1.674 \times 10^{-27} \text{ kg})(1.674 \times 10^{-27} \text{ kg})}{1.674 \times 10^{-27} \text{ kg} + 1.674 \times 10^{-27} \text{kg}} = 8.370 \times 10^{-28} \text{ kg}$$

$$k = 4\pi^2 \nu^2 \mu$$
$$k = 4\pi^2 (1.32 \times 10^{14} \text{ s}^{-1})^2 (8.370 \times 10^{-28} \text{ kg}) = 575 \frac{\text{kg}}{\text{s}^2}$$

$$\Delta E = h\nu = (6.626 \times 10^{-34} \text{ Js})(1.32 \times 10^{14} \text{ s}^{-1}) = 8.75 \times 10^{-20} \text{ J}$$

Reduced Mass

The HF molecule has a harmonic vibrational frequency of 1.241×10^{14} Hz.

A. Determine its force constant using the reduced mass of HF.

B. Assume that the F atom doesn't move and that the vibration is due solely to the motion of the H atom. Using the mass of the H atom and the force constant just calculated, what is the expected frequency of the atom? Comment on the difference.

Reduced Mass

$$1 \text{ atom H}\left(\frac{1 \text{ mol H}}{6.022 \times 10^{23} \text{ atoms } H}\right)\left(\frac{1.008 \text{ g H}}{1 \text{ mol H}}\right)\left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 1.674 \times 10^{-27} \text{ kg H}$$

$$1 \text{ atom F}\left(\frac{1 \text{ mol F}}{6.022 \times 10^{23} \text{ atoms F}}\right)\left(\frac{19.00 \text{ g F}}{1 \text{ mol F}}\right)\left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 3.154 \times 10^{-26} \text{ kg F}$$

$$\mu = \frac{(1.674 \times 10^{-27} \text{ kg})(3.154 \times 10^{-26} \text{ kg})}{1.674 \times 10^{-27} \text{ kg} + 3.154 \times 10^{-26} \text{kg}} = 1.590 \times 10^{-28} \text{ kg}$$

$$k = 4\pi^2 \nu^2 \mu$$

$$k = 4\pi^2 (1.241 \times 10^{14} \text{ s}^{-1})^2 (1.590 \times 10^{-27} \text{ kg}) = 966.7 \frac{\text{kg}}{\text{s}^2}$$

Reduced Mass

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{966.7\,\frac{\mathrm{kg}}{\mathrm{s}^2}}{1.674\times 10^{-27}\ \mathrm{kg}}} = 1.209\times 10^{14}\ \mathrm{Hz}$$

$$\frac{|1.209\times 10^{14}\ \mathrm{Hz} - 1.241\times 10^{14}\ \mathrm{Hz}|}{1.241\times 10^{14}\ \mathrm{Hz.}} \times 100 = 3.97\%$$

Reduced Mass

- In cases where multiple particles are moving relative to one another in our system, the reduced mass must be considered in place of the actual mass.
- In the harmonic oscillator, two particles are moving relative to each other, and so the reduced mass is used.
- In a purely, translational motion, two masses are moving through space but remain in the same positions relative to each other. Therefore, the sum of the masses, the total mass, is the correct mass needed to describe the translational motion.