

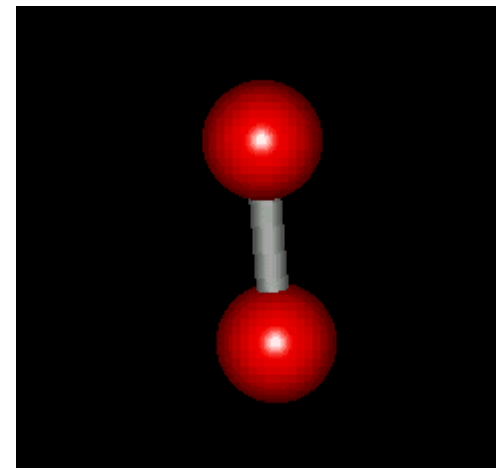
# The Quantum Mechanical Harmonic Oscillator

## Motivation:

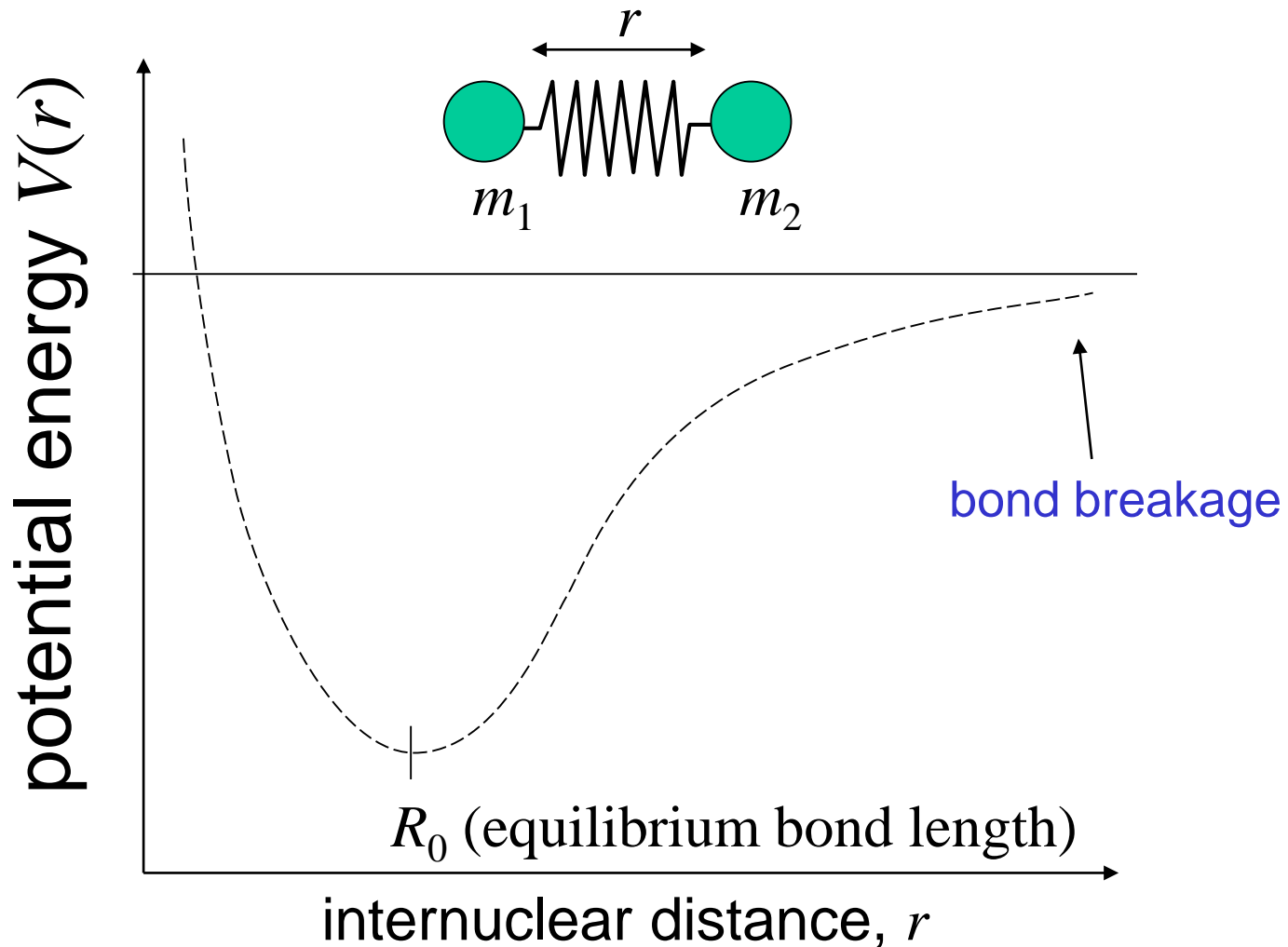
The quantum mechanical treatment of the harmonic oscillator serves as a good model for vibrations in diatomic molecules.

The harmonic oscillator model accounts for the infrared spectrum a diatomic molecule.

Using “normal mode analysis”, it also serves as the basis for vibrational analysis in larger molecules which are commonly used in chemistry today to interpret infrared spectra.



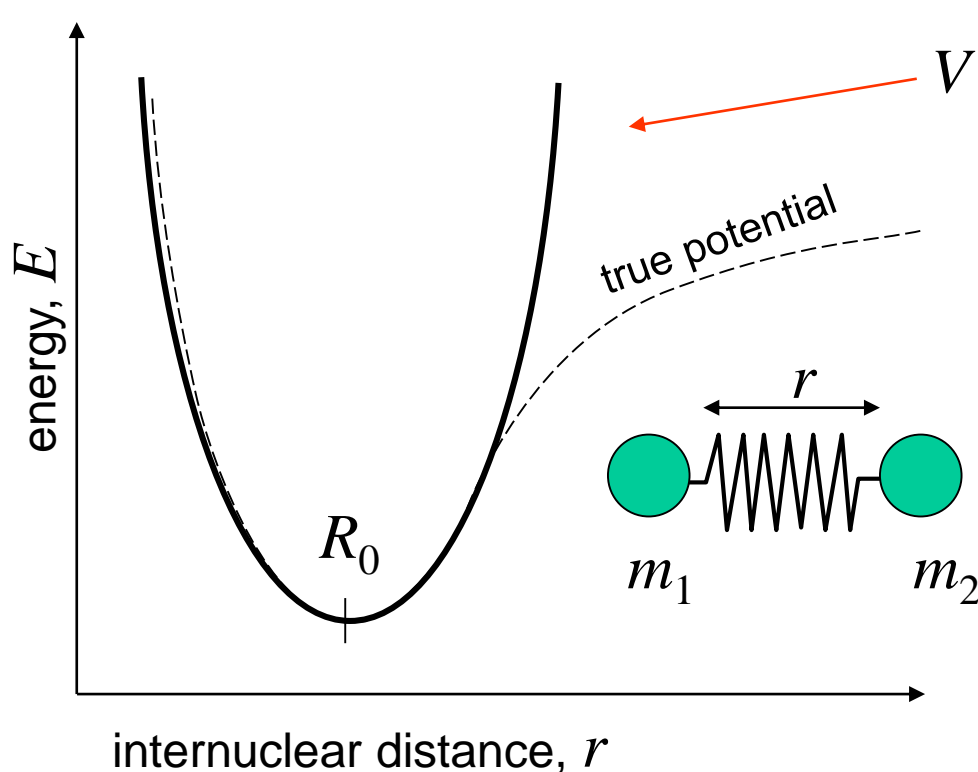
# Potential Energy Surface of a Typical Diatomic Molecule



The potential energy surface relates the geometry of a molecule (given by its nuclear coordinates) to the molecule's potential energy.

# The Harmonic Oscillator

With the harmonic oscillator, we approximate the true internuclear potential with a **harmonic (parabolic) potential** given by:



$$V(r) = \frac{1}{2} k(r - R_0)^2$$

$R_0$  is the equilibrium bond length

$k$  is the force constant.

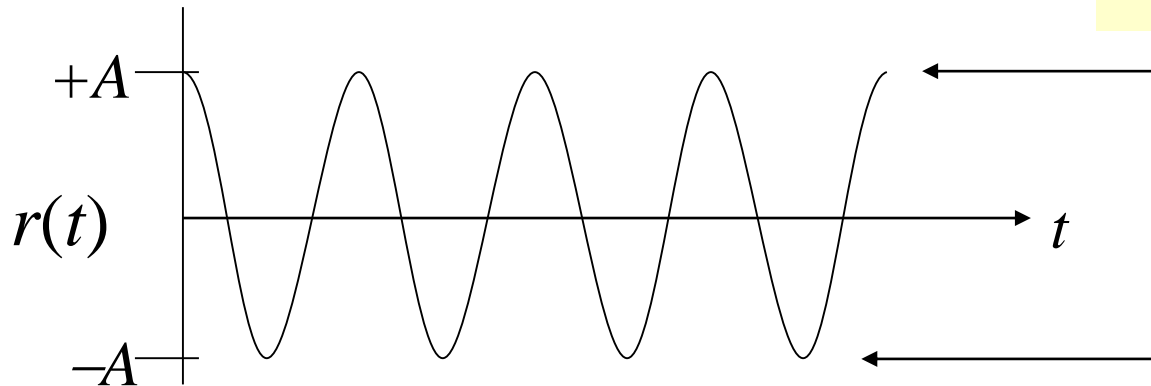
$R_0$  and  $k$  are different for various diatomic molecule, *i.e.* HCl, N<sub>2</sub>, O<sub>2</sub>, ...

The harmonic oscillator is usually a good approximation for  $r$  values close to  $R_0$  (for example, "low" temperatures such as room temperature).

# The Classical Picture of the Harmonic Oscillator

If we took our classical harmonic oscillator and stretched it to a length  $A$  at time zero, and let it go with zero velocity at time  $t = 0$ , then the harmonic oscillator would vibrate according to:

$$r(t) = A \cos \omega t$$



**classical turning points  
at  $r = A$  and  $r = -A$**

The displacements of the masses never go beyond amplitude  $|A|$ .

The total energy of the system can assume any value depending on how far we initially displace the spring:

$$E = \frac{1}{2} k A^2$$

**continuous energy**

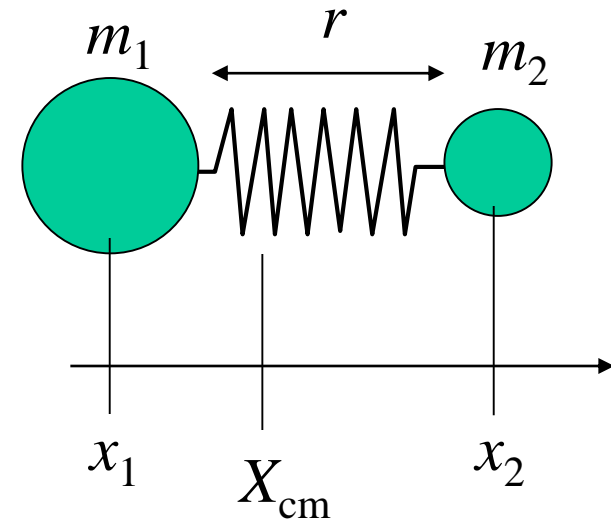
The system can have zero energy if the oscillator is not moving ( $A = 0$ ).

## Reduction of the two-body problem to two one-body problems

Consider the motion of the diatomic molecule in one dimension. The **classical Hamiltonian** function is given by:

$$H = \frac{1}{2} m_1 |\dot{x}_1|^2 + \frac{1}{2} m_2 |\dot{x}_2|^2 + \frac{1}{2} k (x_2 - x_1 - R_o)^2$$

$$r = x_2 - x_1$$



**But wait!!!** We can reduce this two-body problem to a one-body problem for the translational motion of the center of mass,  $X_{\text{cm}}$ , of the diatomic and the vibrational motion in terms of  $r$ , the distance between the nuclei.

$$X_{\text{CM}} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

**center of mass coordinate**

$$r = x_2 - x_1$$

**internuclear distance coordinate**

$$X_{\text{CM}} = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \qquad r = x_2 - x_1$$

Using these two equations, we can also express  $x_1$  and  $x_2$  in terms of  $X_{\text{cm}}$  and  $r$ . (i.e., two equations and two unknowns)

$$x_1 = X_{\text{CM}} - \frac{m_2}{m_1 + m_2} r \qquad x_2 = X_{\text{CM}} + \frac{m_1}{m_1 + m_2} r$$

Use these relationships to derive the kinetic energy in terms of the center of mass coordinate and the bond distance coordinate (**next tutorial!**).



*The ultimate goal is to separate the translational motion from the vibrational motion.*

After some straightforward algebra, we end up with:

$$T = \underbrace{\frac{1}{2}(m_1 + m_2) \dot{X}_{CM}^2}_{\text{translational motion}} + \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} \dot{r}^2$$

The first term can be interpreted as the kinetic energy of **translational motion** of the whole molecule ( $m_1 + m_2$ ) through space.

The second term is the **internal kinetic energy of the relative motion** of the two nuclei, or the vibrational motion. To simplify things, we define

the **reduced mass**: 
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The vibrational kinetic energy therefore **reduces from a two body problem** with masses  $m_1$  and  $m_2$  **to a one-body problem** with an 'effective' mass equal to  $\mu$ .

$$T_{\text{vib}} = \frac{1}{2} \mu \dot{r}^2$$

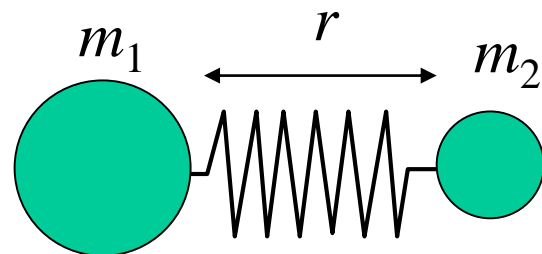
## Separation of Translational and Vibrational Motion

It is reasonable to assume that the vibrational motion is independent of the motion of the center of mass as long as the molecule is isolated and does not interact with anything. The vibration of the molecule will then be unaffected by how fast or slow the center of mass is moving.

We have already examined the quantum mechanical treatment of the translational motion in one dimension. This was the 'free particle'.

We now consider the vibrational motion of the molecule. The classical Hamiltonian function for **vibrational motion only** is:

$$H = \frac{1}{2} \mu \dot{r}^2 + \frac{1}{2} k (r - R_o)^2$$



where  $r$  is the internuclear distance and  $\mu$  is the reduced mass.



$$H = \frac{1}{2} \mu \dot{r}^2 + \frac{1}{2} k (r - R_0)^2$$

Let's make a further simplification by defining a new coordinate,  $x$ :

$$x = r - R_0 = x_2 - x_1$$

**Note:** *this new coordinate  $x$  (the displacement from the equilibrium internuclear separation) is not the same as the  $x_1$  and  $x_2$  coordinates used previously.*

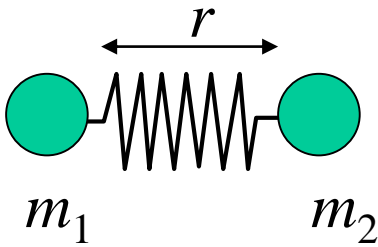
In this way our **classical Hamiltonian** becomes:

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

recall that

$$\dot{x} = \frac{d}{dt} (r(t) - R_0) = \frac{dr(t)}{dt} = \dot{r}$$

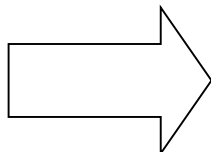
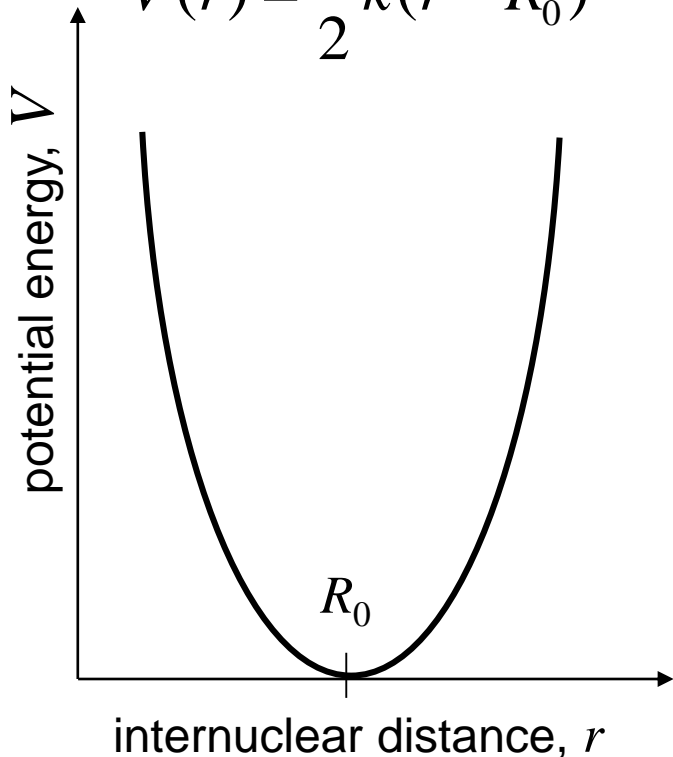
so  $\dot{x}^2 = \dot{r}^2$



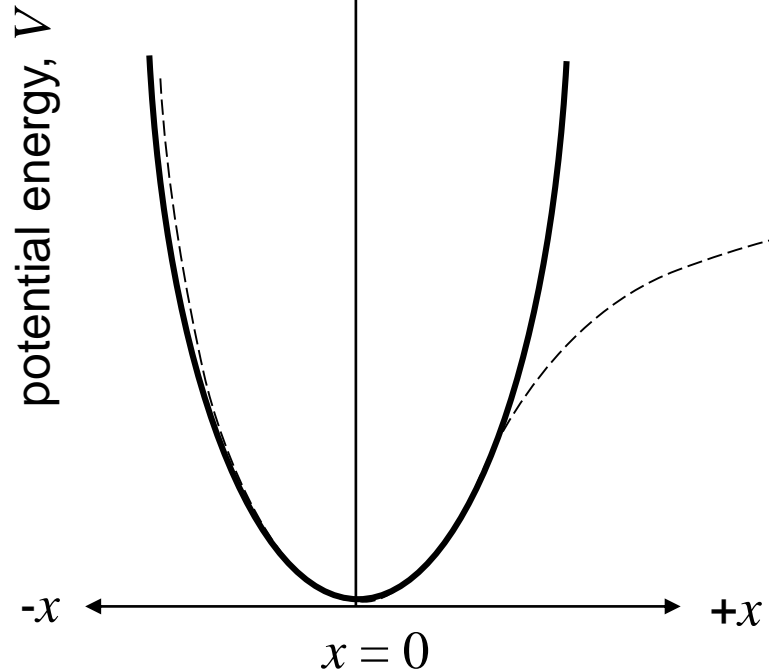
displacement:

$$x = r - R_0$$

$$V(r) = \frac{1}{2} k (r - R_0)^2$$



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

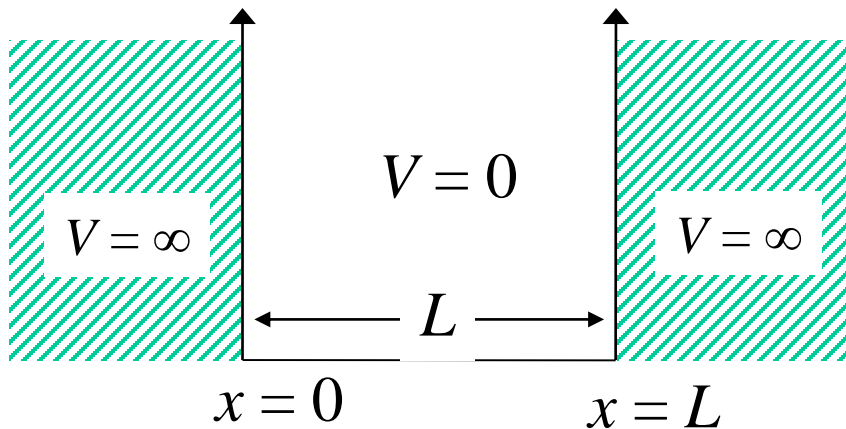


When  $x$  is negative, the bond is compressed, and when  $x$  is positive, the bond is stretched.

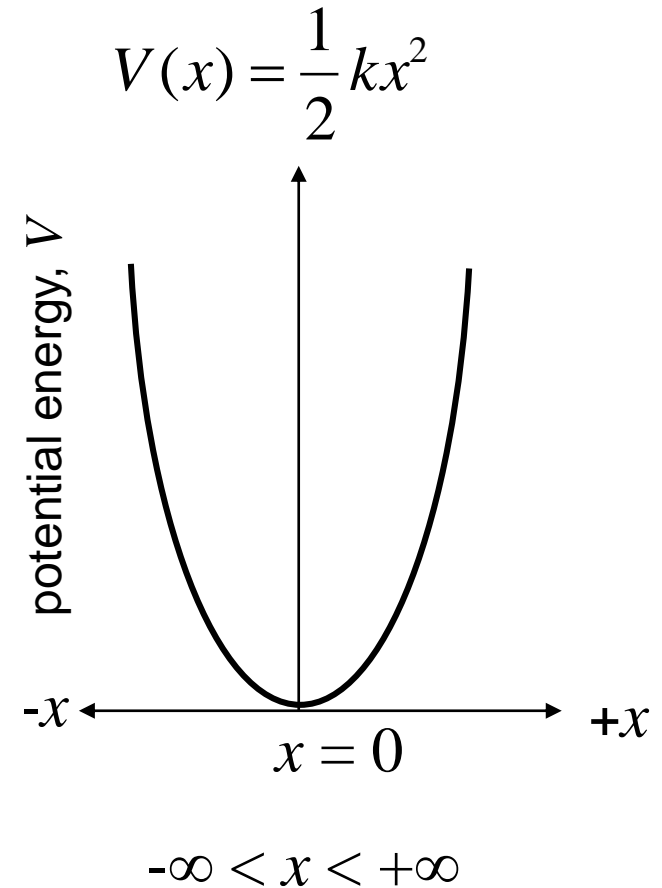
We have now reduced our vibrational motion of two bodies into the effective motion of a single particle. Before we look at solving for the quantum mechanical behavior, let's relate what we've just done to the particle-in-a-box problem.

$$V(x) = 0 \quad 0 < x < L$$

$$V(x) = \infty \quad 0 \leq x \text{ and } x \geq L$$



$$0 < x < L$$



$$-\infty < x < +\infty$$

# The Quantum Mechanical Harmonic Oscillator

Now solve for the wave function of the Harmonic Oscillator. We first need the Hamiltonian operator. We know the classical Hamiltonian is

$$H = \frac{1}{2} \mu \dot{x}^2 + \frac{1}{2} kx^2$$

So our **quantum mechanical Hamiltonian operator** is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Notice the reduced mass is retained.

The **Schrödinger equation for the harmonic oscillator** is therefore

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

We again have a ordinary differential equation. Rearranging into a more standard form, we get

$$\frac{d^2}{dx^2} \psi(x) + \frac{2\mu}{\hbar^2} \left( E - \frac{1}{2} kx^2 \right) \psi(x) = 0 \quad -\infty < x < +\infty$$

$E - V$  is not constant in this case, but a function of  $x$

When  $E - V$  is variable, there is no general way of solving this type of differential equation. Each case must be studied individually, depending of the function.

It turns out that we can use a power series method. This is a bit tedious and involves math we have not yet covered.

For the moment, the solutions will only be presented and interpreted.

# The Quantum Mechanical Harmonic Oscillator

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

## The Harmonic Oscillator Energies

$$E_n = \hbar \left( \frac{k}{\mu} \right)^{1/2} \left( n + \frac{1}{2} \right) \quad n = 0, 1, 2, 3, \dots$$

The energy levels are **quantized**:  $E_0, E_1, E_2, E_3, \dots$

The states are expressed in terms of the **quantum number  $n$** .

$k$  is the force constant (characteristic of each diatomic bond).

$\mu$  is the **reduced mass** defined by: 
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

This is usually rewritten as

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, 3, \dots \quad \omega = \left(\frac{k}{\mu}\right)^{1/2}$$

where  $\omega$  is classically interpreted as the **vibration frequency in radians per second (the angular vibration frequency)**.

Many textbooks also use:

$$E_n = h\nu\left(\nu + \frac{1}{2}\right) \quad \nu = 0, 1, 2, 3, \dots \quad \nu = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{1/2} = \frac{\omega}{2\pi}$$

where  $\nu$  (“Nu”) is the **frequency in cycles per second (Hz)**.

where  $\nu$  (“Upsilon”) is the harmonic oscillator quantum number.

# The Harmonic Oscillator Energies

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, 3, \dots$$

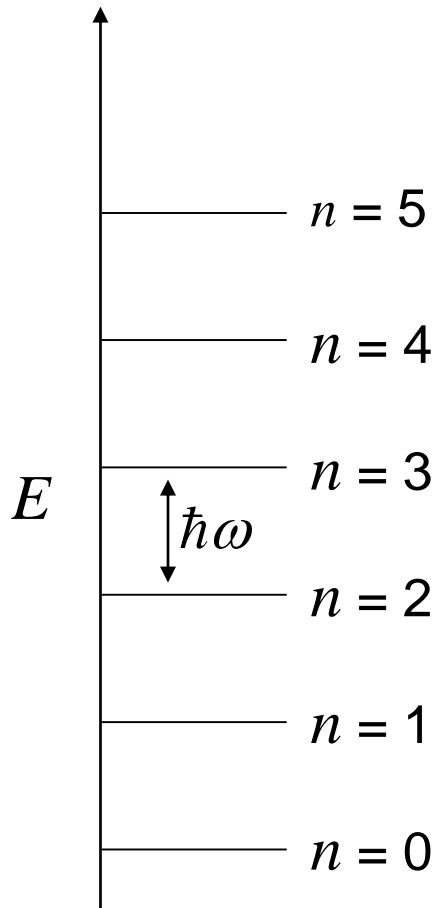
- Energy levels are all **equally spaced**.

$$\text{spacing} = \hbar\omega$$

- Notice that the ground state in this case has an index of  $n = 0$ , not  $n = 1$  as with the particle in a box.

- Again there is a **zero-point energy** with the ground state having a positive non-zero energy:

$$E_0 = \frac{\hbar\omega}{2} \quad \leftarrow \text{vibrational zero-point energy}$$





# The Harmonic Oscillator Wave Functions

Solving the harmonic oscillator time-independent Schrödinger equation gives time-independent wave functions of the following form:

$$\psi_n(x) = N_n \cdot H_n(\xi) \cdot e^{-\alpha x^2 / 2} \quad n = 0, 1, 2, 3, \dots$$

$$x = x_2 - x_1 \quad \alpha = \frac{\sqrt{k\mu}}{\hbar} \quad N_n = \frac{1}{\sqrt{2^n n!}} \left( \frac{\alpha}{\pi} \right)^{1/4} \text{ (normalization constant)}$$

$H_n(\xi)$  are **Hermite polynomials**, functions of “xi” =  $\xi = \alpha^{1/2} x$

$$H_0(\xi) = 1 \quad H_1(\xi) = 2\xi \quad H_3(\xi) = 8\xi^3 - 12\xi$$

$H_n(\xi)$  is an  $n^{\text{th}}$  order polynomial in  $\xi$  and therefore an  $n^{\text{th}}$  order polynomial in  $x$ .

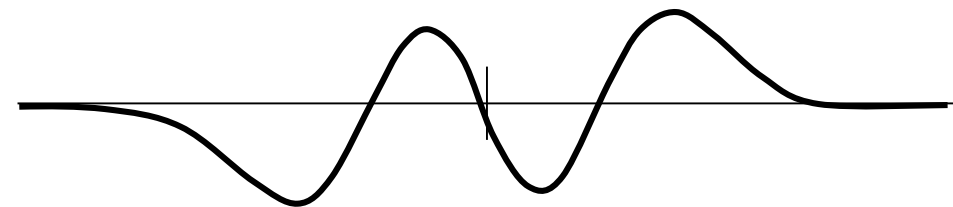
# The First Four Harmonic-Oscillator Wave Functions

$$\psi_0 = \left( \frac{\alpha}{\pi} \right)^{1/4} \exp(-\alpha x^2 / 2) \qquad \alpha = \frac{\sqrt{k\mu}}{\hbar}$$

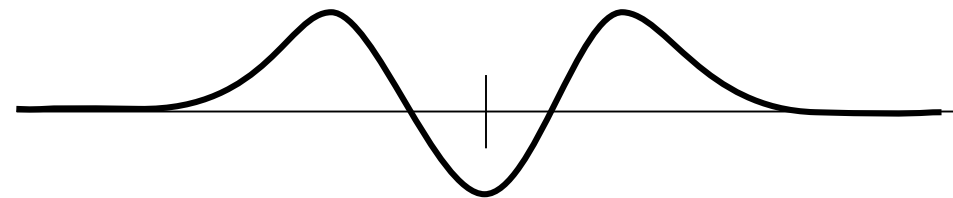
$$\psi_1 = \left( \frac{4\alpha^3}{\pi} \right)^{1/4} x \exp(-\alpha x^2 / 2)$$

$$\psi_2 = \left( \frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) \exp(-\alpha x^2 / 2)$$

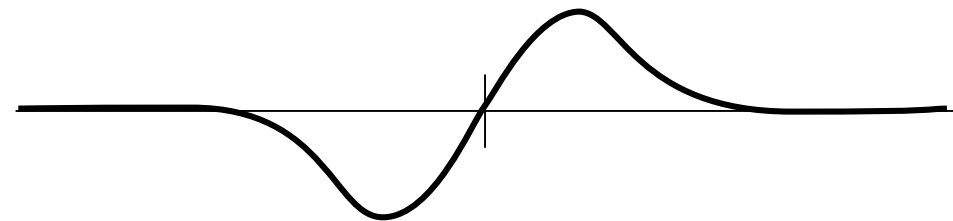
$$\psi_3 = \left( \frac{\alpha^3}{9\pi} \right)^{1/4} (2\alpha x^3 - 3x) \exp(-\alpha x^2 / 2)$$



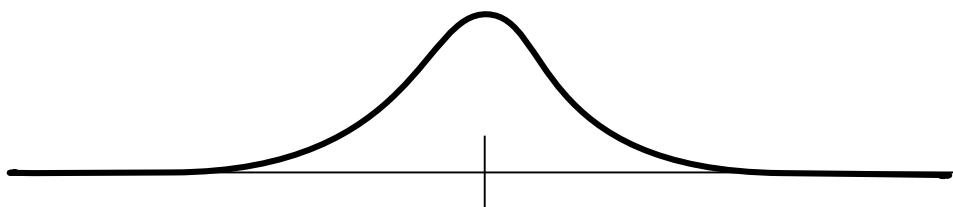
$$\psi_3 = \left( \frac{\alpha^3}{9\pi} \right)^{1/4} (2\alpha x^3 - 3x) e^{-\frac{\alpha x^2}{2}}$$



$$\psi_2 = \left( \frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{\alpha x^2}{2}}$$



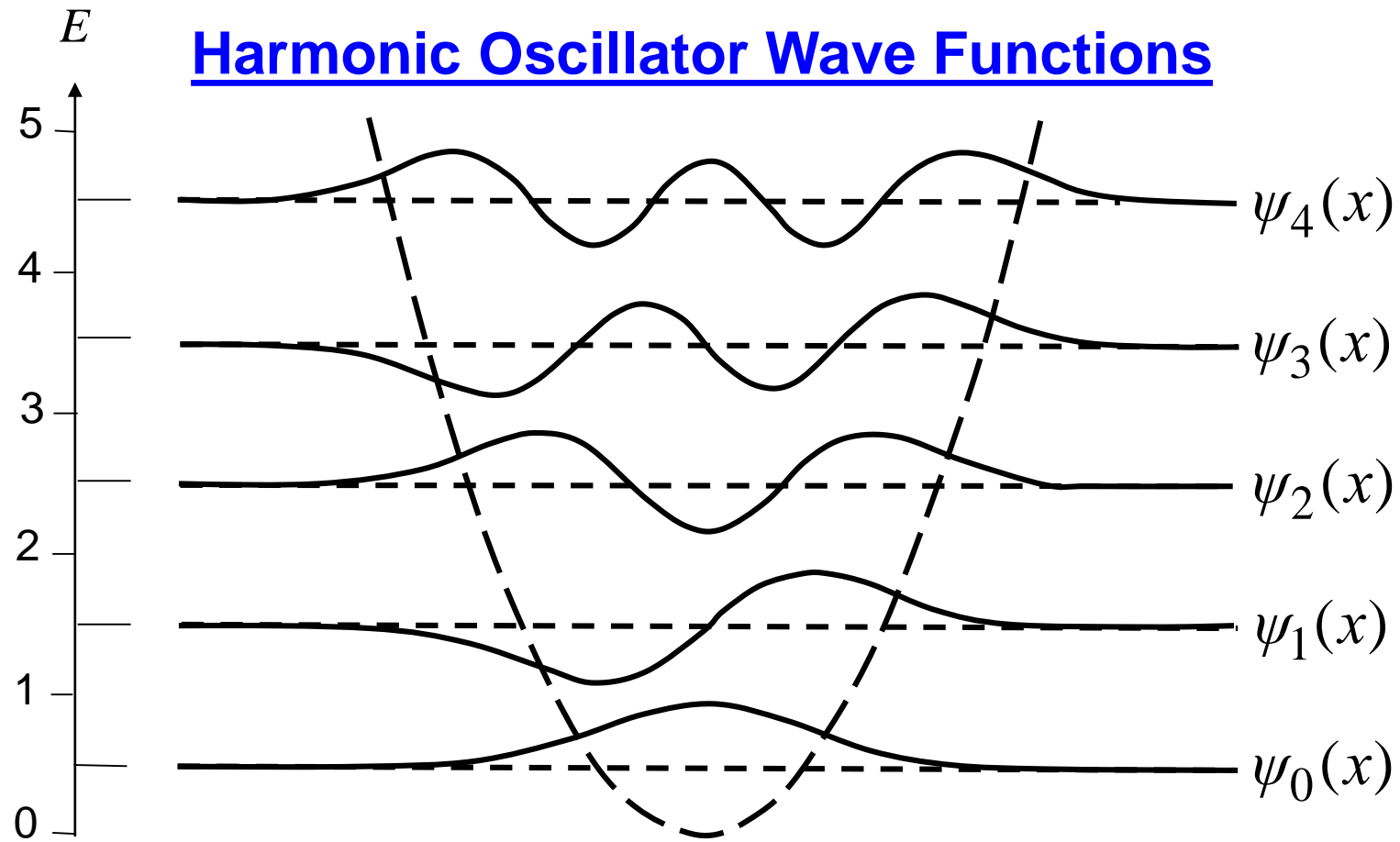
$$\psi_1 = \left( \frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{\alpha x^2}{2}}$$



$$\psi_0 = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha x^2}{2}}$$

$x = 0$

$\longrightarrow x$



The harmonic oscillator wave functions are often superimposed on the potential.

As  $n$  increases, the wave function ‘widens’ (*i.e.*, it has more energy and can “stretch out more” than the classical oscillator).

Verify that  $\psi_0(x)$  is normalized.



$$\psi_0 = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha x^2}{2}}$$

Verify that  $\psi_0(x)$  and  $\psi_1(x)$  are orthogonal.



$$\psi_1 = \left( \frac{4\alpha^3}{\pi} \right)^{1/4} x e^{-\frac{\alpha x^2}{2}}$$

# Integrals involving Even and Odd Functions

An **even function** is a function that satisfies:  $f(x) = f(-x)$

Even functions are 'symmetric' about the origin (e.g.,  $\cos(x)$  or  $x^2$ ).

If a function  $f(x)$  is even, then: 
$$\int_{-A}^A f(x)dx = 2\int_0^A f(x)dx$$

$$\int_{-\infty}^{\infty} f(x)dx = 2\int_0^{\infty} f(x)dx$$

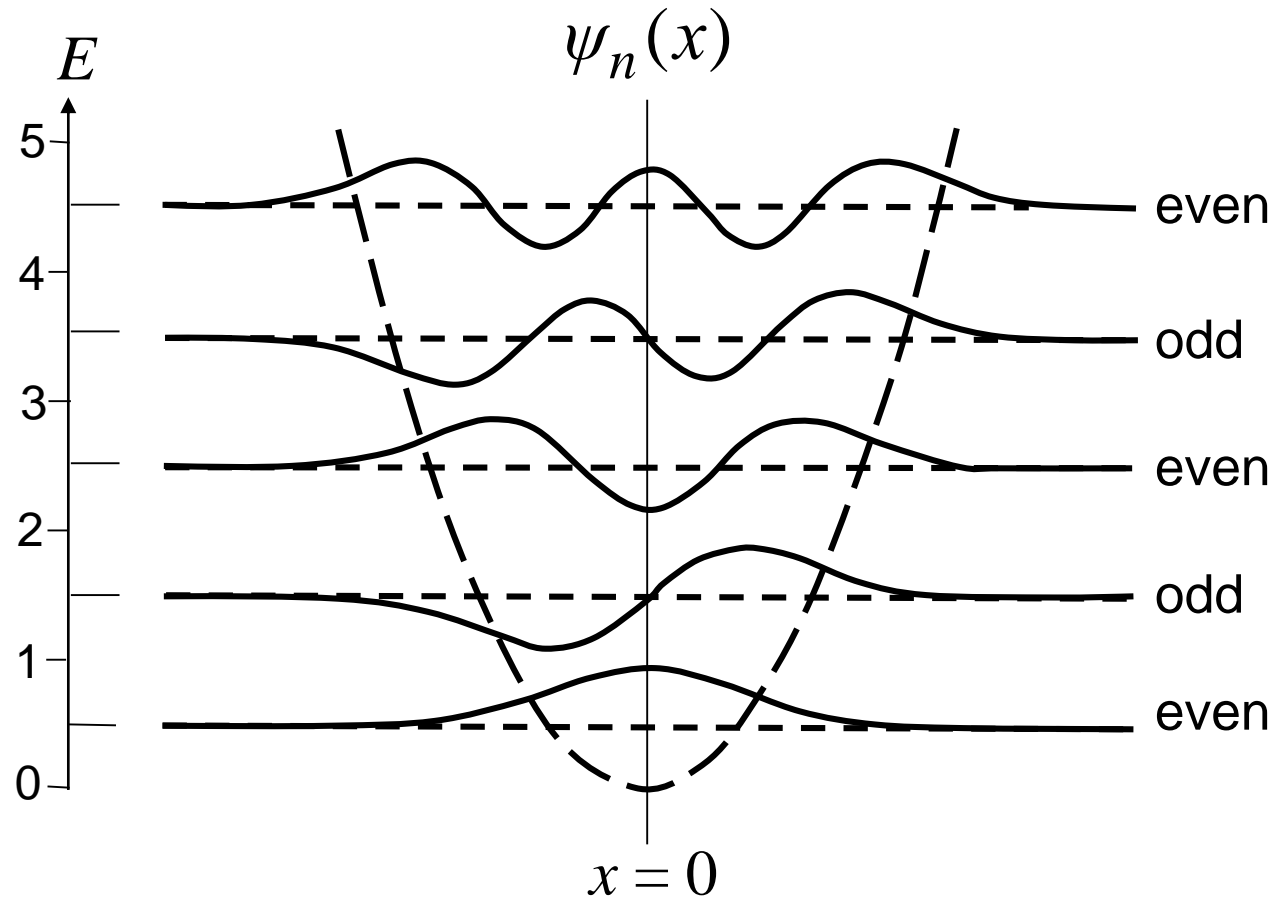
An **odd function** is a function that satisfies:  $-f(x) = f(-x)$

Odd functions are 'antisymmetric' about the origin (e.g.,  $\sin(x)$  or  $x^3$ ).

$$\int_{-A}^A f(x)dx = 0$$

$$\int_{-\infty}^{\infty} f(x)dx = 0$$

Notice that the Harmonic Oscillator wave functions alternate between even and odd functions.



The harmonic oscillator wave functions with  **$n$  odd are odd functions.**

The harmonic oscillator wave functions with  **$n$  even are even functions.**

An odd function multiplied by an odd function is an even function.

**odd times odd = even**

An odd function multiplied by an even function is an odd function.

**odd times even = odd**

An even function multiplied by an even function is an even function.

**even times even = even**

We can use these properties to help us evaluate certain properties.



$\langle x \rangle$



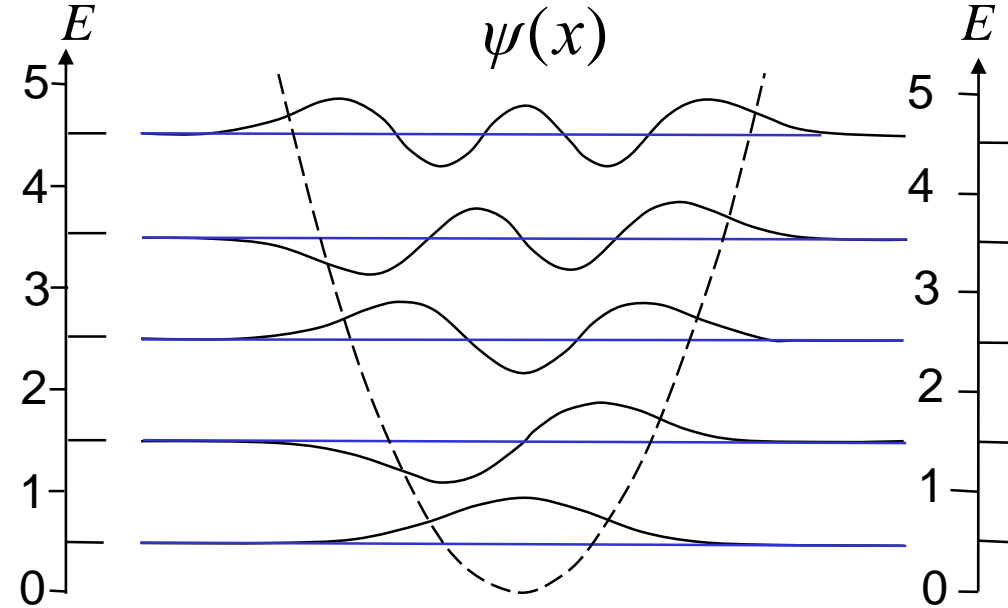
$\langle p_x \rangle$



# Harmonic Oscillator and Barrier Penetration

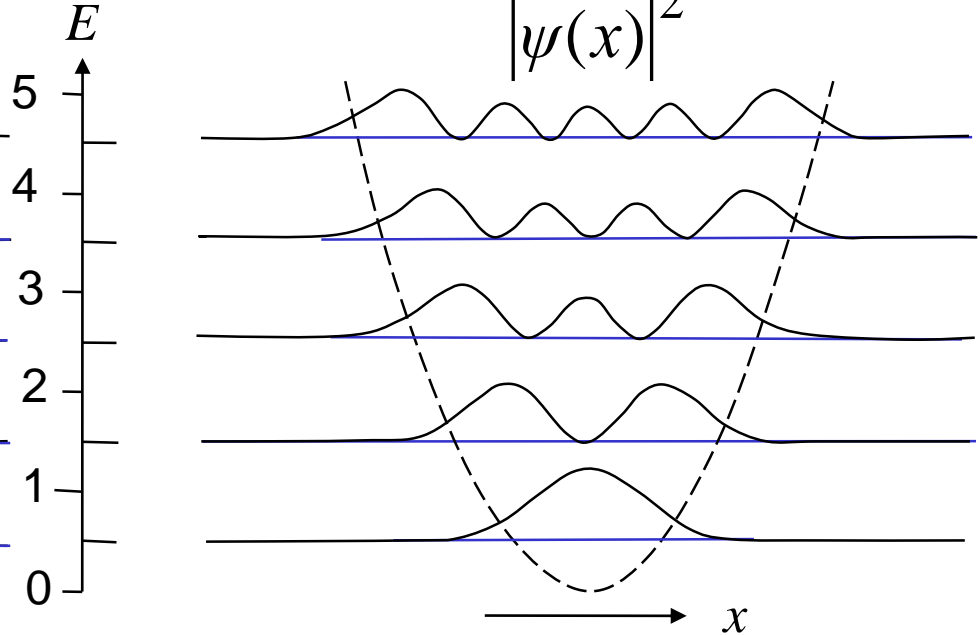
wave functions

$$\psi(x)$$



probability density

$$|\psi(x)|^2$$



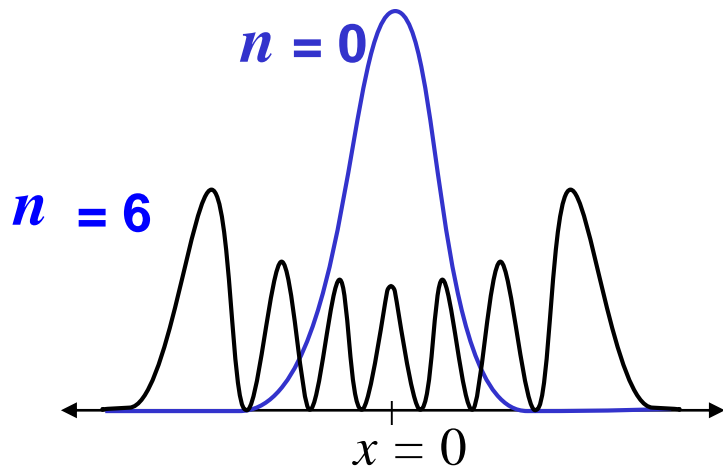
The harmonic function (dotted line) shows the classical turning point for each energy level.

The harmonic oscillator wave functions show that there is penetration into the classically forbidden regions.

Because the system is in a bound state, the particle cannot escape, and therefore this is barrier penetration, not tunneling (“getting through”).

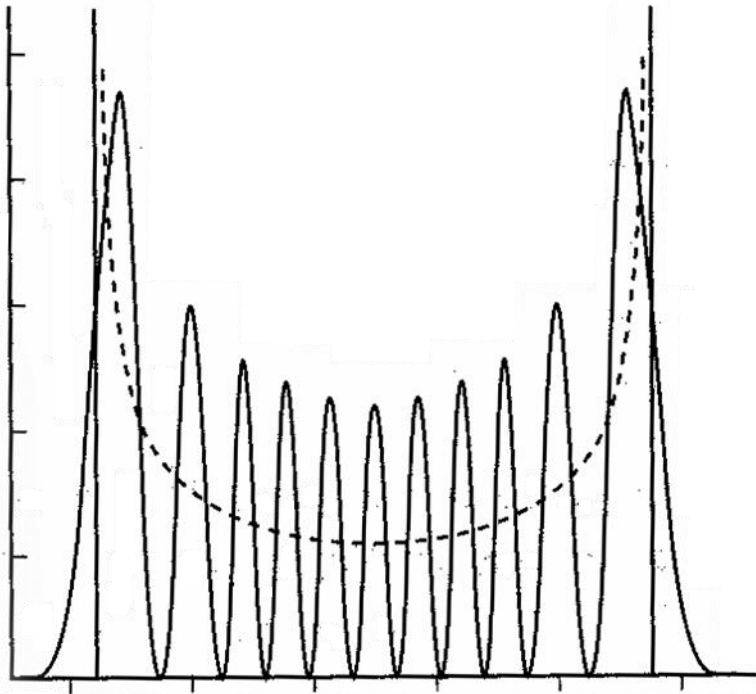
Determine where the classical turning point is for the quantum mechanical Harmonic Oscillator in the ground state.





Also notice that as  $n$  increases, the probability increases at the classical turning point.

Plotted below is the probability density for the  $n = 10$  state.



The dotted line shows the probability density derived from the classical harmonic oscillator of the same energy.

It shows that the probability of finding the system is greatest at the turning point, where the particles slow down and change direction.

# Harmonic Oscillator Model Accounts for the Infrared Spectrum of Diatomic Molecules

What are the spectroscopic predictions of the Harmonic Oscillator model?

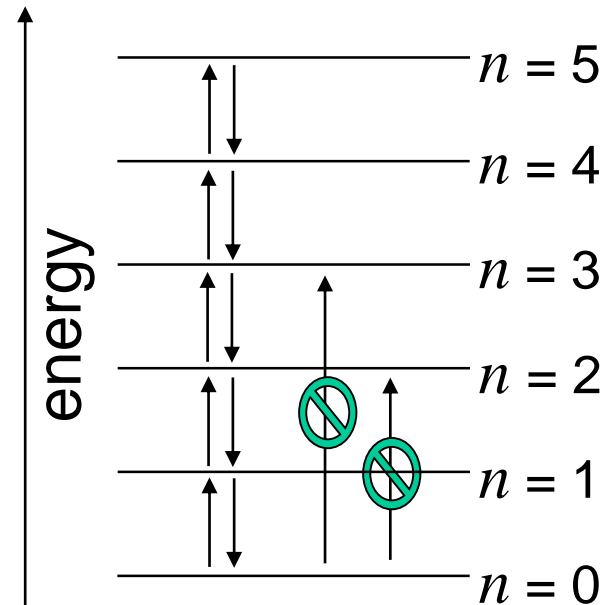
To rigorously examine spectroscopic transitions, we would have to learn more quantum mechanics, namely *time-dependent theory*, which is covered in more detail in advanced courses.

So some of the statements will not be derived rigorously. Be aware that they were derived using the Harmonic Oscillator wave functions (an approximation of real molecules).

A diatomic molecule can make transitions from one vibrational energy state to another by absorbing or emitting photons or light.

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, 3, \dots$$

But **not all transitions are allowed**.



From quantum mechanical time-dependent perturbation theory, a transition probability (or intensity) can be determined as:

$$I \propto \left| \int \psi_f^* \cdot \hat{x} \cdot \psi_i d\tau \right|^2$$

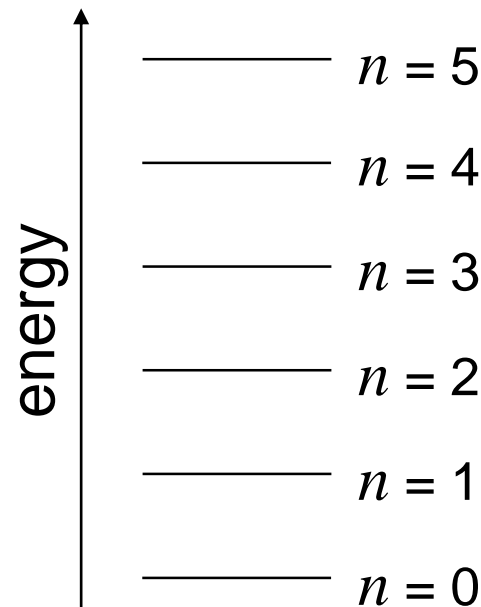
It can be shown (*but not here!*) that the harmonic oscillator model only allows transitions between adjacent energy states with:

$$\Delta n = \pm 1$$

The above condition is an example of a **spectroscopic selection rule**.

$$\Delta n = \pm 1$$

Given that only the above transitions are allowed, how many peaks should we see?



$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

This is known as the **fundamental vibrational frequency**. In units of  $\text{cm}^{-1}$  (“wavenumbers”) it is given by:

$$\tilde{\nu}_{\text{obs}} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2}$$

( $c$  is the speed of light in  $\text{cm/s}$ )

## Example:

The infrared spectrum of HCl has a very intense line at  $2886\text{ cm}^{-1}$ .  
What is the force constant of the H-Cl bond?



From the IR spectra, we can determine some information about the strength of the H-Cl bond (because we know the masses of the nuclei).

Furthermore, for a vibration to be infrared 'active', **the dipole moment of the molecule must change as the molecule vibrates.**

For diatomic molecules, this means that the molecule must have a permanent dipole moment to be infrared active. In other words, for diatomics, **only hetero-diatomic molecules are infrared active.**

e.g. HCl absorbs in the IR but not  $\text{N}_2$ .

**Why?**

molecule	fundamental frequency (cm <sup>-1</sup> )	force constant (N/m)
H <sub>2</sub>	4159	520
H <sup>35</sup> Cl	2886	482
H <sup>79</sup> Br	2559	385
H <sup>127</sup> I	2230	293
<sup>12</sup> C <sup>16</sup> O	2143	1870
<sup>14</sup> N <sup>16</sup> O	1876	1550

Why are we so concerned about the isotopes?

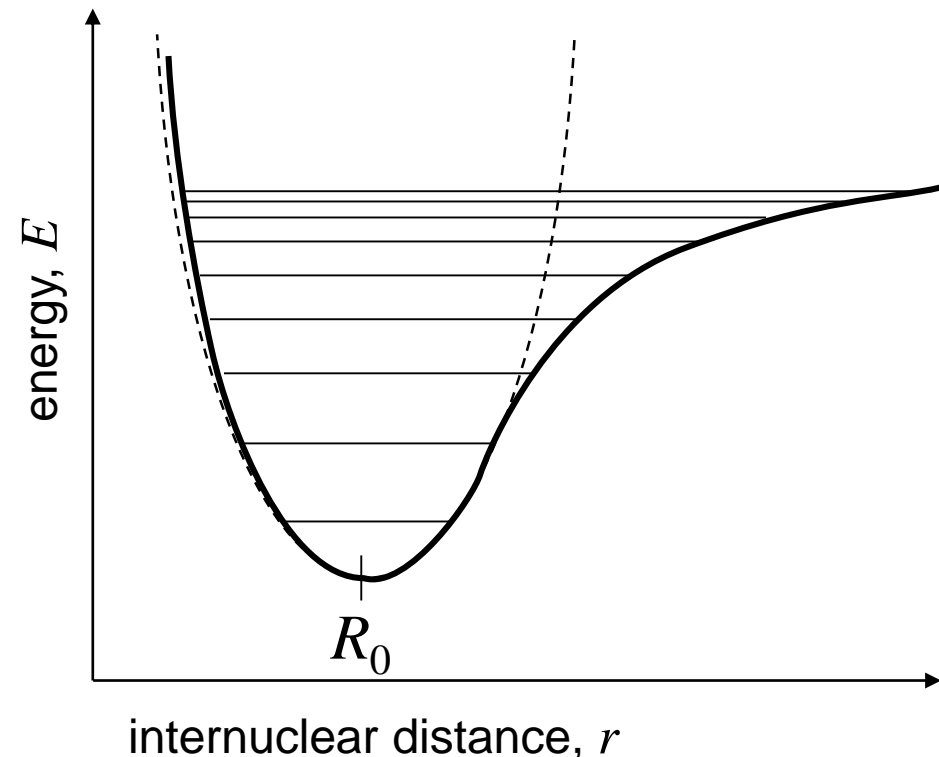
Will the isotope change the force constant?



## The Harmonic Oscillator Model is an *Approximation*

What have approximated the true diatomic potential with a harmonic potential. However, the true potential is **anharmonic**.

The **anharmonicity** has the following consequences:



The energy levels are not all equally spaced. The spacings get smaller and smaller until the bond breaks.

The selection rule  $\Delta n = \pm 1$  is not rigorously obeyed.

IR intensities of non-fundamental transitions are typically small. (Shows that the harmonic oscillator approximation is a good one.)

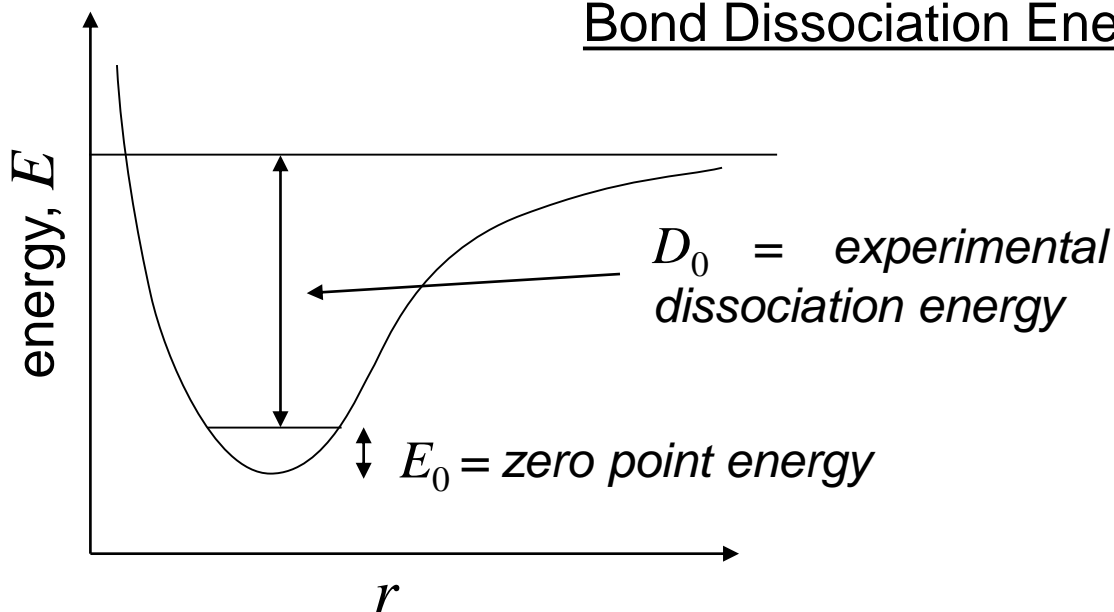
# The Vibrational Zero-Point Energy Is Not Negligible

As with the particle in a box, the harmonic oscillator has a zero-point energy correction. Meaning the lowest energy state of the particle has a positive, non-zero energy.

$$E_0 = \frac{\hbar\omega}{2} = \frac{\hbar}{2} \left( \frac{k}{\mu} \right)^{1/2} \leftarrow \text{vibrational zero-point energy}$$

The **vibrational zero-point energy** has significant implications for dissociation energies and the kinetic isotope effect.

## Bond Dissociation Energies



e.g., for  $\text{H}_2$

$$D_0 = 103.2 \text{ kcal/mol}$$

$$\text{ZPE} = 6.5 \text{ kcal/mol}$$

*What happens with  $D_2$ ?*

# Vibrations in Polyatomic Molecules can be Approximated by Harmonic Oscillator Solutions

A generalization of our simple quantum mechanical treatment of the harmonic oscillator is frequently used to approximate vibrations in polyatomic molecules.

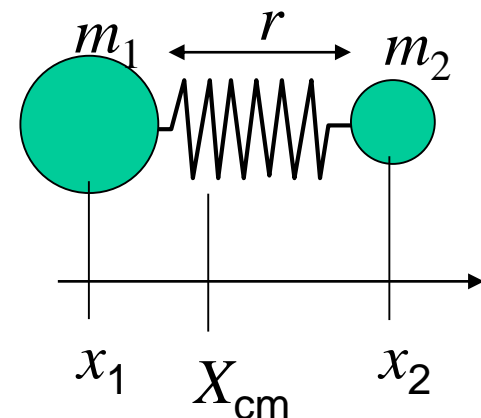
Simulation of molecular vibrations are used today by quantum chemists and experimental chemists to:

- interpret and predict IR and Raman spectra.
- calculate zero-point energies for accurate determination of thermodynamic data.

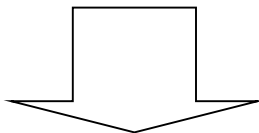
The same approximation is made, in that we are at low temperatures and close to the equilibrium geometry. (The approximation also breaks down with very weak bonds, such as hydrogen bonds).

In our one-dimensional Harmonic Oscillator problem we reduced the two body problem into an effective one body problem.

We made a coordinate transformation from Cartesians to CM (center of mass) and relative coordinates.



$$\hat{H} = -\frac{\hbar^2}{2m_1} \frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m_2} \frac{d^2}{dx_2^2} + \frac{1}{2} k(x_2 - x_1 - R_0)^2$$



$$\hat{H}_{\text{trans}} = -\frac{\hbar^2}{2(m_1 + m_2)} \frac{d^2}{dX_{CM}^2} \quad \hat{H}_{\text{vib}} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

If we assume the translational (and rotational) motion are independent of the vibrational motion we can solve for the vibrational Schrödinger Equation, which gives:

$$\psi_n(x) \quad E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, 3, \dots$$

A 3-dimensional and polyatomic (more than 2 atoms) extension of this procedure can be made. A **coordinate transformation** to what are known as **normal coordinates** gives:

$$\hat{H}_{\text{vib}} = \sum_{i=1}^{N_{\text{VIB}}} \left( -\frac{\hbar^2}{2\mu_i} \frac{d^2}{dQ_i^2} + \frac{1}{2} k_i Q_i^2 \right)$$

where the  **$Q_i$ 's are the normal coordinates**. (They can be determined from straightforward matrix algebra.)

The sum is over all molecular vibrations (vibrational degrees of freedom).

Each vibration has its own effective mass and force constant.

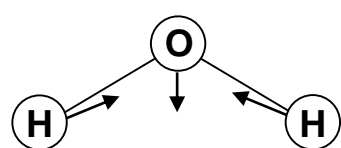
The vibrational energy of the whole molecule becomes:

$$E_{\text{vib}} = \sum_{i=1}^{N_{\text{vib}}} \left( h\omega_i \left( n_i + \frac{1}{2} \right) \right)$$

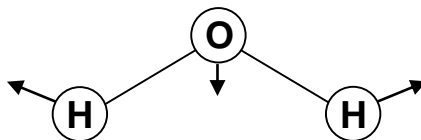
There is a quantum number  $n_i$  for each vibration.

The vibrations along the normal coordinates are called **normal modes**.

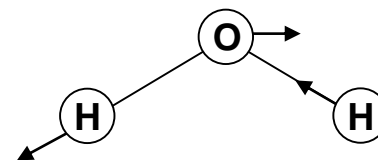
## Normal Modes of Water



3657  $\text{cm}^{-1}$



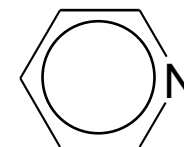
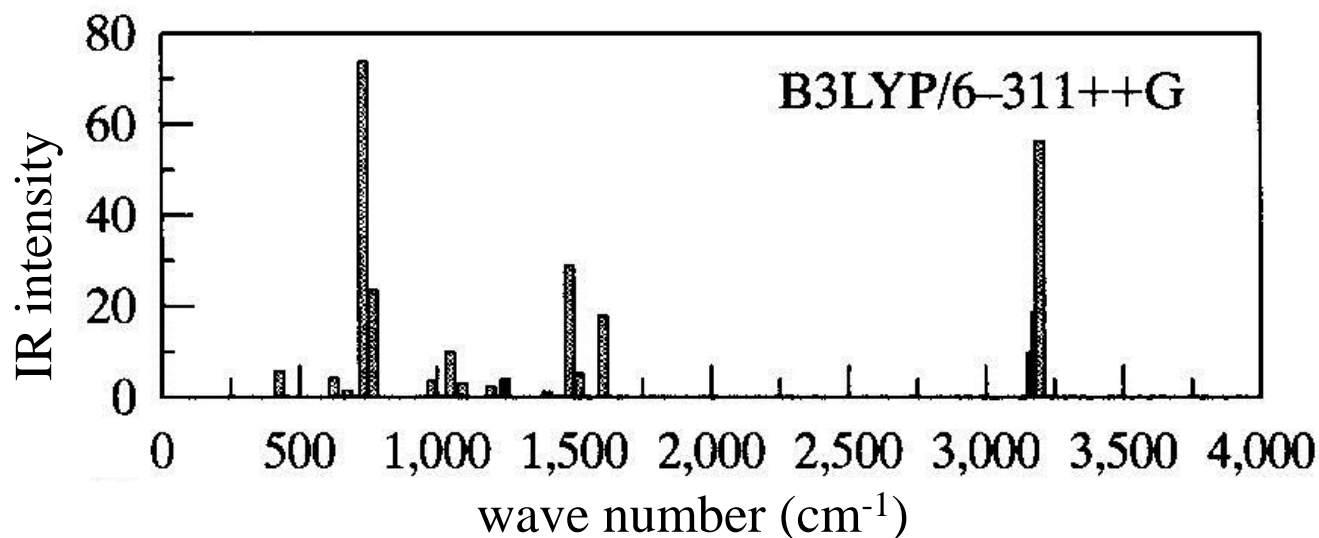
1595  $\text{cm}^{-1}$



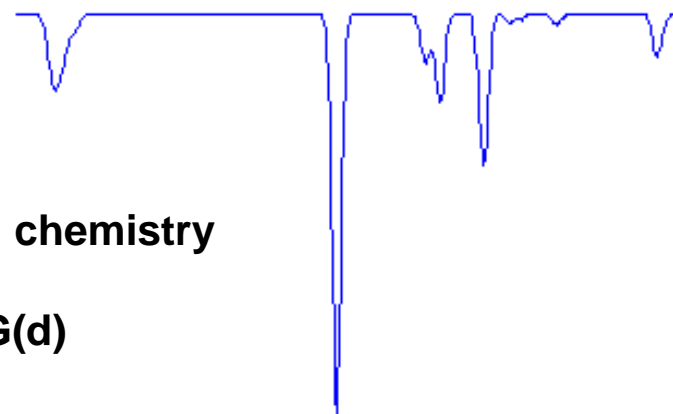
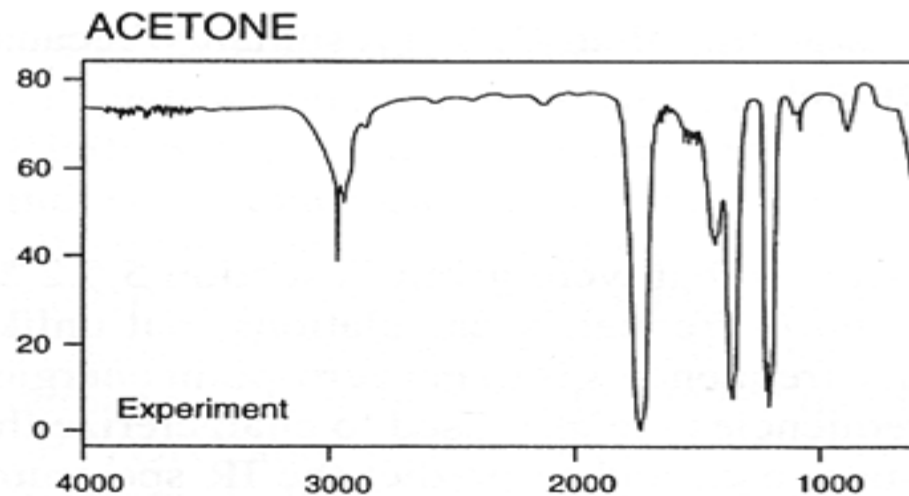
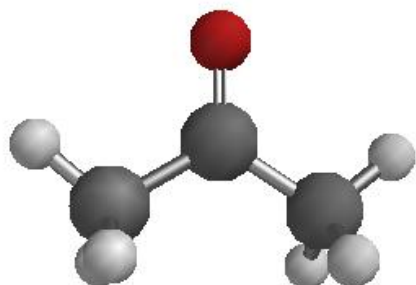
3756  $\text{cm}^{-1}$

## Predicted Infrared spectra of Pyridine

Below is a spectra for pyridine determined from a quantum mechanical calculation using the generalized 'harmonic oscillator' approximation.



rms deviation from experimental is about 30  $\text{cm}^{-1}$



**simulated spectra from quantum chemistry**

**HF/6-31G(d)**