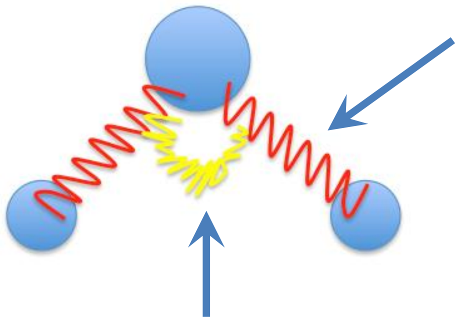
HARMONIC OSCILLATOR

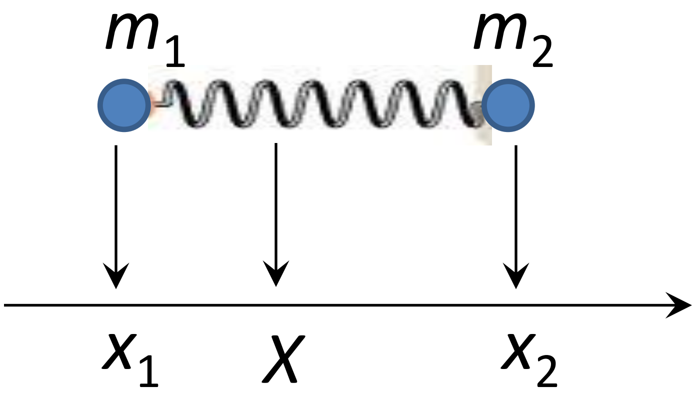
The harmonic oscillator is the simplest
model to describe the vibrational motions of a molecule

Normal modes in a molecule are basically harmonic vibrations



Stretching mode

Bending mode



Center of mass

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

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A molecule can translate, rotate and vibrate.
How to compute the quantum dynamical states of a molecule?
(not electronic states)

We have to solve the Schrödinger equation for all the atoms of the molecule

Coordinates of the atoms

$$\left[\hat{T}_{atoms}(x_1, y_1, \ldots) + V(x_1, y_1, z_1, x_2, y_2, z_2, \ldots)\right] \psi = E\, \psi$$

Imagine that the center of mass of the molecule is fixed and that the molecule cannot rotate. With such restrictions, the molecule can only vibrate.
For simplicity, let consider a biatomic molecule. In this case, the potential energy depends only on the distance r between the atoms

$$\left[\hat{T}_{atoms}(r) + V(r)\right] \psi(r) = E\, \psi(r)$$

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How to compute the potential energy $V(r)$ of two atoms? (biatomic molecule)

1. We fix the nuclei at a distance $r = r_1$ and then we solve the «complete» Schrödinger equation of the system. This gives the energy of the 2 atoms at that distance, say $V(r_1)$.

2. We put the nuclei at a slightly different distance r_2. The Schrödinger equation of the system is solved again. This gives the energy of the 2 atoms at the new distance, $V(r_2)$.
   And so on …

3. Performing the calculation for many values of r, we build a function $V(r)$. In $V(r)$ there are all energies of the system, apart from the kinetic energies of the nuclei (they are zero in each calculation). $V(r)$ is to be considered the potential energy of the atoms

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So, the state of the two atoms can be described by a wave-function depending on their distance r. This wave-function can be obtained by solving the Schrödinger equation

$$\left[\hat{T}_{atoms}(r) + V(r)\right] \psi(r) = E\, \psi(r)$$

The kinetic energy operator, $\hat{T}_{atoms}$, depends on the r coordinate. We will see this better when discussing the Born-Oppenheimer approximation

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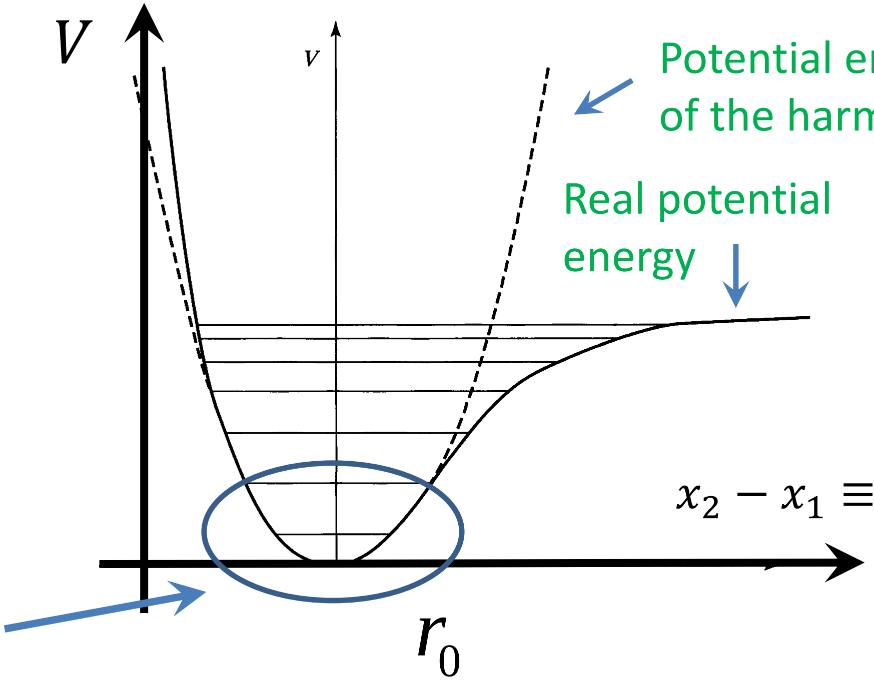
The **potential energy** of a harmonic oscillattor depends on the distance between the two atoms as

$$V(x_1, x_2) = \frac{1}{2}k(x_2 - x_1 - r_0)^2 \qquad V(r) = \frac{1}{2}k(r - r_0)^2$$

k is called **force constant**, while r_0 is the **equilibrium distance**

Potential energy for vibration of a diatomic molecule (solid line) and for a harmonic oscillator (dashed line). Also shown are the bound-state vibrational energy levels for the diatomic molecule



Potential energy of the harm. osc.

Real potential energy

Region of interest

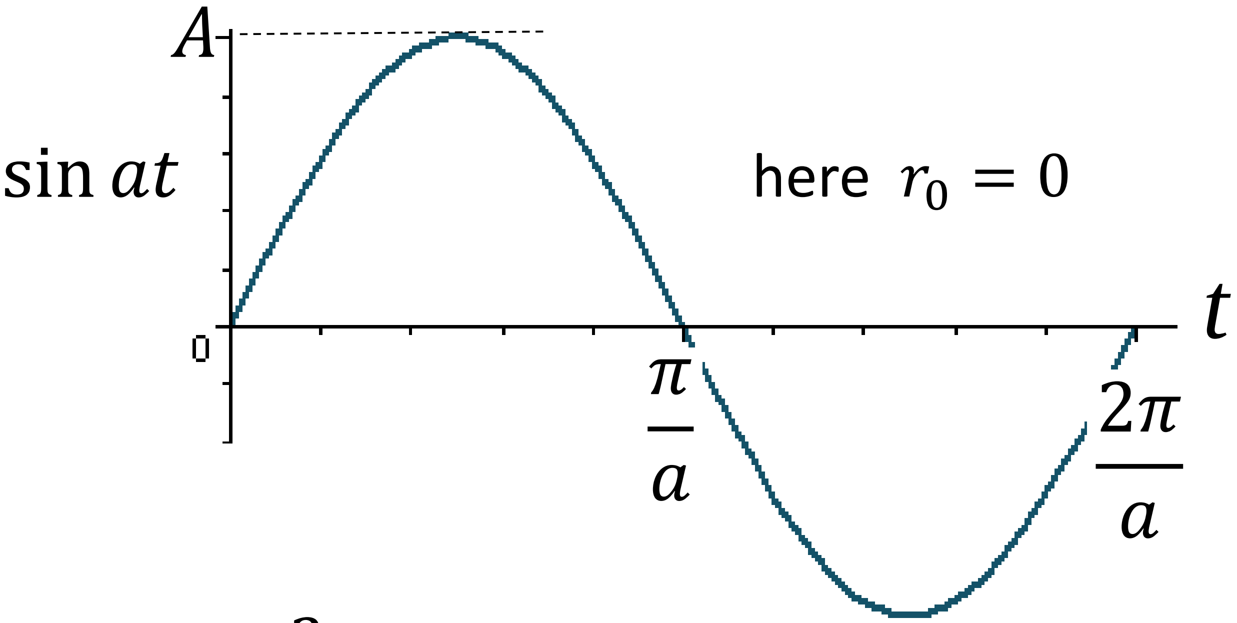
CLASSICAL HARMONIC OSCILLATOR

Suppose that $r(0) = r_0$

$$r(t) = r_0 + A \sin \sqrt{k/\mu}\, t$$

where μ is the **reduced mass**

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



Note: $a = \sqrt{k/\mu}$

Period of the oscillator: $T = \frac{2\pi}{a} = 2\pi\sqrt{\mu/k}$

Frequency of the oscillator: $\nu = \frac{1}{T} = \frac{1}{2\pi}\sqrt{k/\mu}$

QUANTUM HARMONIC OSCILLATOR

To make the treatment a bit more exciting, let consider a **biatomic molecule moving along only one direction**, say x. The molecule cannot rotate, but only translate and vibrate

To write down the Hamiltonian, we must find the classical energy E, namely the sum of kinetic and potential energies

$$E = \frac{p_{x_1}^2}{2m_1} + \frac{p_{x_2}^2}{2m_2} + \frac{1}{2}k(x_2 - x_1 - r_0)^2$$

Transforming the classical quantities into QM operators, we get the Hamiltonian in the variables x_1 and x_2

$$\hat{H} = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} + \frac{1}{2}k(x_2 - x_1 - r_0)^2$$

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The Hamiltonian cannot be written as sum of independent «pseudo-Hamiltonians» because the variables are mixed in the potential energy term. To solve the problem, it is easier to change the variables from x_1 and x_2 to X and r, where

$$X = \frac{m_1 x_1 + m_2 x_2}{M} \qquad\qquad r = x_2 - x_1$$

Center of mass coordinate

Interatomic distance

with $M = m_1 + m_2$

The potential energy is trivial. It changes as follows

$$V(x_1, x_2) = \frac{1}{2}k(x_2 - x_1 - r_0)^2 \quad \Rightarrow \quad V(r) = \frac{1}{2}k(r - r_0)^2$$

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The problem is now to convert the partial derivatives

$\frac{\partial}{\partial x_1}$ and $\frac{\partial}{\partial x_2}$ into $\frac{\partial}{\partial X}$ and $\frac{\partial}{\partial r}$

We use the **chain rule** for derivatives

$$\frac{\partial}{\partial x_1} = \left(\frac{\partial X}{\partial x_1}\right)_{x_2} \frac{\partial}{\partial X} + \left(\frac{\partial r}{\partial x_1}\right)_{x_2} \frac{\partial}{\partial r}$$

$$\frac{\partial}{\partial x_2} = \left(\frac{\partial X}{\partial x_2}\right)_{x_1} \frac{\partial}{\partial X} + \left(\frac{\partial r}{\partial x_2}\right)_{x_1} \frac{\partial}{\partial r}$$

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$$\frac{\partial}{\partial x_1} = \left(\frac{\partial X}{\partial x_1}\right)_{x_2}\frac{\partial}{\partial X} + \left(\frac{\partial r}{\partial x_1}\right)_{x_2}\frac{\partial}{\partial r}$$

Memo

$$X = \frac{m_1 x_1 + m_2 x_2}{M}$$

$$r = x_2 - x_1$$

$$\frac{\partial}{\partial x_2} = \left(\frac{\partial X}{\partial x_2}\right)_{x_1}\frac{\partial}{\partial X} + \left(\frac{\partial r}{\partial x_2}\right)_{x_1}\frac{\partial}{\partial r}$$

$$\left(\frac{\partial X}{\partial x_1}\right)_{x_2} = \frac{m_1}{M}$$

$$\left(\frac{\partial r}{\partial x_1}\right)_{x_2} = -1$$

$$\left(\frac{\partial X}{\partial x_2}\right)_{x_1} = \frac{m_2}{M}$$

$$\left(\frac{\partial r}{\partial x_2}\right)_{x_1} = 1$$

Applying the chain rule we get

$$\frac{\partial}{\partial x_1} = \frac{m_1}{M}\frac{\partial}{\partial X} - \frac{\partial}{\partial r}$$

$$\frac{\partial}{\partial x_2} = \frac{m_2}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial r}$$

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Memo $X = \dfrac{m_1 x_1 + m_2 x_2}{M}$ $\quad r = x_2 - x_1$

Actually, the square partial derivatives, reported below, appear in the Hamiltonian:

$$\frac{\partial^2}{\partial x_1^2} = \left(\frac{m_1}{M}\frac{\partial}{\partial X} - \frac{\partial}{\partial r}\right)^2 = \frac{m_1^2}{M^2}\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial r^2} - \frac{2m_1}{M}\frac{\partial^2}{\partial X \partial r}$$

$$\frac{\partial^2}{\partial x_2^2} = \left(\frac{m_2}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial r}\right)^2 = \frac{m_2^2}{M^2}\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial r^2} + \frac{2m_2}{M}\frac{\partial^2}{\partial X \partial r}$$

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Using the previous derivatives in the Hamiltonian, we get

$$\widehat{H} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{1}{2}k(r - r_0)^2$$

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QUANTUM HARMONIC OSCILLATOR

The potential energy is independent on time. We look for stationary state solutions (time-independent Schr. eq.)

$$-\frac{\hbar^2}{2M}\frac{\partial^2\psi}{\partial X^2}-\frac{\hbar^2}{2\mu}\frac{\partial^2\psi}{\partial r^2}+\frac{1}{2}k(r-r_0)^2\psi=E_\psi\,\psi$$

We can adopt the method of "separation of variables".

Wave-function

$$\psi(X,r)=F(X)\,g(r)$$

Energy

$$E_\Psi=E+E_X$$

$$-\frac{\hbar^2}{2M}\frac{\partial^2 F(X)}{\partial X^2}=E_X F(X)$$

Schr. Eq. for a free particle

As we are interested only in the intermolecular distance, we must solve the following equation

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{\partial^2 g(r)}{\partial r^2}+\frac{1}{2}k(r-r_0)^2 g(r)=Eg(r)}$$

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QUANTUM HARMONIC OSCILLATOR

Vibrational wave-functions

$$\boxed{g(r) = e^{-\alpha(r-r_0)^2/2} \sum_{n=0,2,4,\ldots}^{u} c_n (r-r_0)^n}$$

For u even

$$\boxed{g(r) = e^{-\alpha(r-r_0)^2/2} \sum_{n=1,3,5,\ldots}^{u} c_n (r-r_0)^n}$$

For u odd

where $$c_{n+2} = \frac{2\alpha(n-u)}{(n+2)(n+1)} c_n \qquad \alpha = \frac{2\pi\,\nu\,\mu}{\hbar}$$

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

Vibrational quantum number

$u = 0,1,2,3,\ldots$

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Are all coefficients c_n known? Let consider, for example, a wave function corresponding to a even value, say $u = 4$. For the sake of simplicity, we use the variable x rather than r. At the end we can substitute back x with r

$$\psi(x) = e^{-\alpha x^2/2} \sum_{n=0,2,\dots}^{4} c_n x^n = e^{-\frac{\alpha x^2}{2}}\left(c_0 + c_2 x^2 + c_4 x^4\right)$$

$$c_2 = -4\alpha\, c_0 \qquad c_4 = -\frac{\alpha}{3} c_2 \quad \Rightarrow \quad c_4 = \frac{4\alpha^2}{3} c_0$$

$$\psi(x) = e^{-\alpha x^2/2}\left(c_0 - 4\alpha c_0 x^2 + \frac{4\alpha^2}{3} c_0 x^4\right)$$

$$\psi(x) = c_0\, e^{-\alpha x^2/2}\left(1 - 4\alpha x^2 + \frac{4\alpha^2}{3} x^4\right)$$

c_0 is found by normalization

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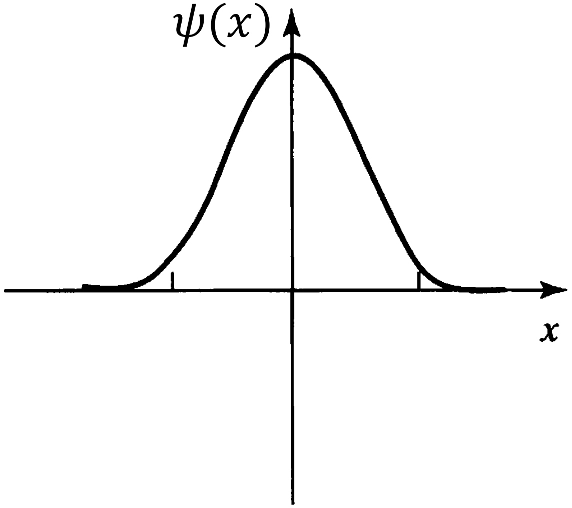
The harmonic-oscillator ground-state energy is nonzero; this energy, $h\nu/2$, is called the **zero-point energy**. This would be the vibrational energy of a harmonic oscillator at a **temperature of absolute zero**. The zero-point energy can be **understood from the uncertainty principle**

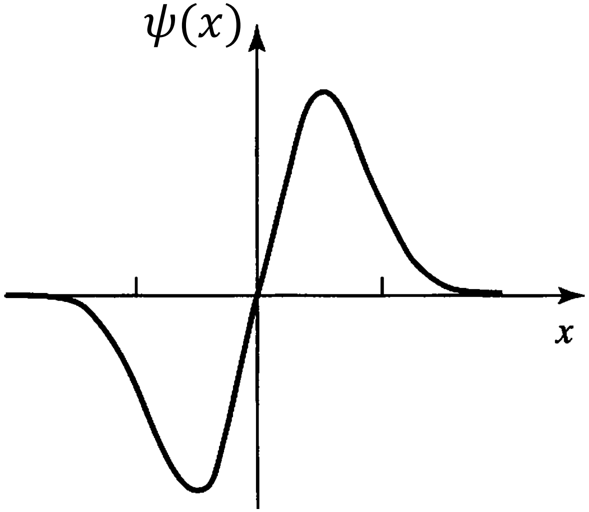
If the lowest state had an energy of zero, both its potential and kinetic energies, which are nonnegative, would have to be zero. Zero kinetic energy would mean that the momentum was exactly zero (no uncertainty on it). Zero potential energy would mean that the bond is fixed (no uncertainty on the position of the atoms). But we cannot know both momentum and position at the same time

QUANTUM HARMONIC OSCILLATOR (even and odd functions)

even function



odd function



$$\psi(-x) = \psi(x)$$

$$\psi(-x) = -\psi(x)$$

$$\int_{-a}^{a} \psi(x)\,\mathrm{d}x = 2\int_{0}^{a} \psi(x)\,\mathrm{d}x$$

$$\int_{-a}^{a} \psi(x)\,\mathrm{d}x = 0$$

even × even = even even × odd = odd odd × odd = even

QUANTUM HARMONIC OSCILLATOR

Find the explicit form of of the wave functions of the lowest three levels

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

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

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

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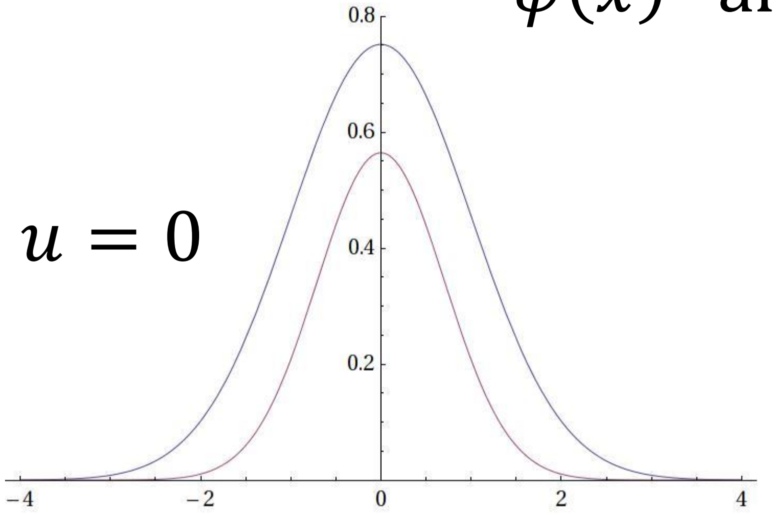
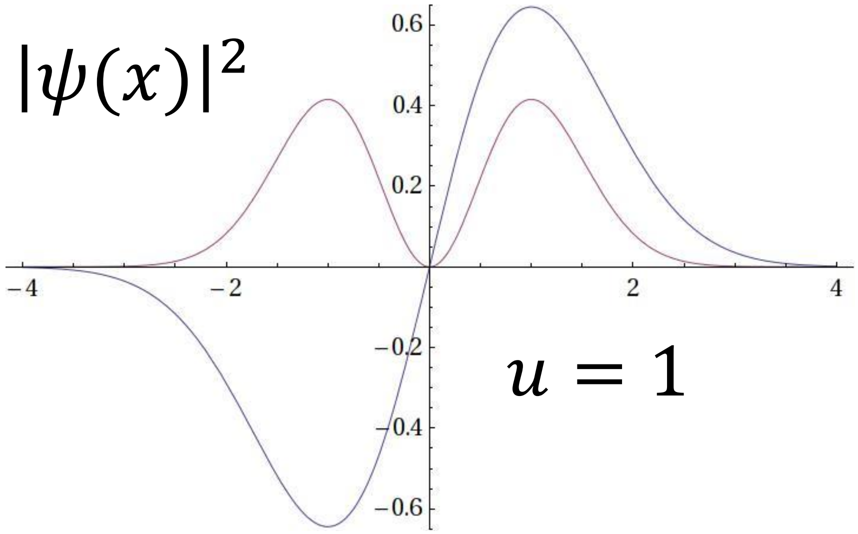
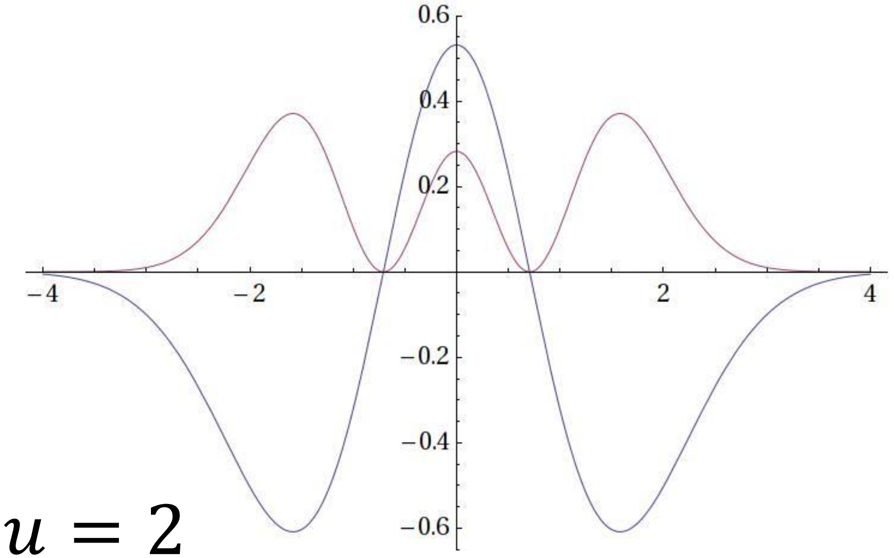
$\psi(x)$ and $|\psi(x)|^2$



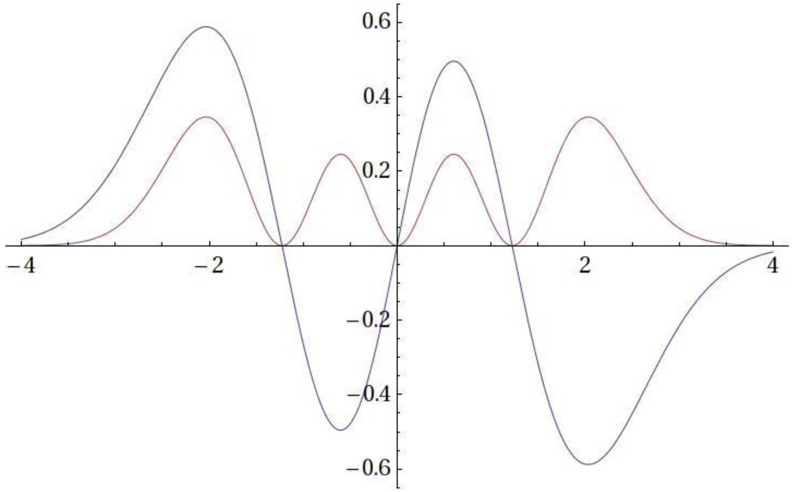
$u = 0$



$u = 1$



$u = 2$



$u = 3$

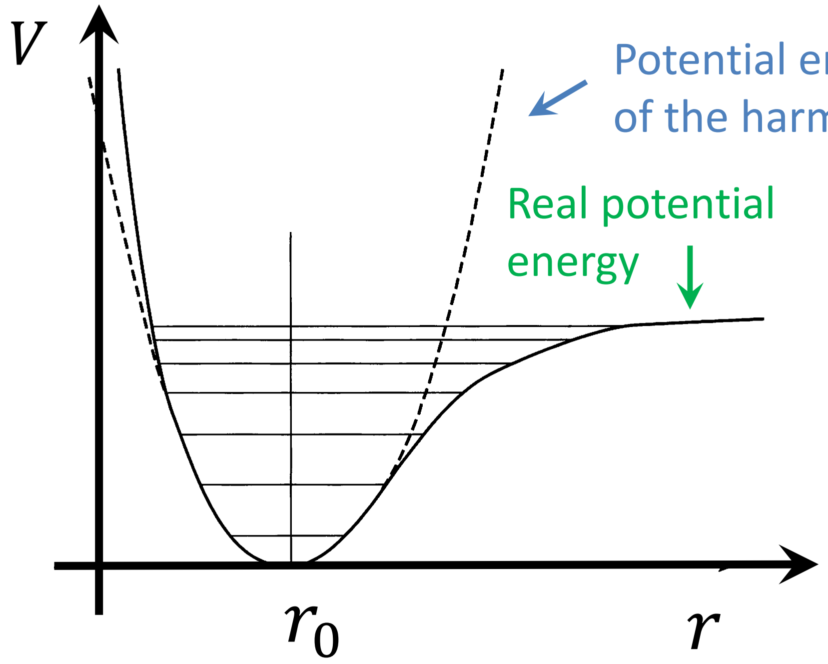
QUANTUM HARMONIC OSCILLATOR (paradox)

According to the QM solution, we can find the particle at any point on the x axis (except at the nodes). Classically, $E = T + V$ and the kinetic energy T cannot be negative. Hence, $E - V = T \geq 0$ and $V \leq E$. A classical particle is confined to the region of space where $V \leq E$ (classically forbidden region)

In QM we have that $E = \langle T \rangle + \langle V \rangle$ and $\langle T \rangle > 0$, so $\langle V \rangle \leq E$, but we cannot write $V \leq E$, and a particle has some probability to be found in classically forbidden regions

QUANTUM HARMONIC OSCILLATOR

In the figure, we report the potential energy for the vibration of a diatomic molecule (solid curve) and of a harmonic oscillator (dashed curve). Also shown are the bound-state vibrational energy levels for the diatomic molecule. In contrast to the harmonic oscillator, a diatomic molecule has only a finite number of bound vibrational levels



Potential energy of the harm. osc.

Real potential energy

The energy levels of a harmonic oscillator are separed by a fixed quantity: $h\nu$. In a molecule, instead, the energy levels become closer each other with increasing the quantum number. A molecule is an **anharmonic oscillator**. However for the lowest energy levels the harmonic oscillator model is a good approximation