

# DOING PHYSICS WITH PYTHON

## QUANTUM MECHANICS

### VIBRATIONS AND THE HARMONIC OSCILLATOR

### TRUNCATED PARABOLIC POTENTIAL WELL

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### **DOWNLOAD DIRECTORY FOR PYTHON SCRIPTS**

**qm045.py      Truncated parabolic potential well**

Solution of the [1D] Schrodinger equation by finding the eigenvalues and eigenvectors for a truncated parabolic well.

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## VIBRATIONS OF A HARMONIC OSCILLATOR: TRUNCATED PARABOLIC POTENTIAL WELL

In most Quantum Mechanics textbooks, the treatment of the harmonic oscillator only discusses analytical methods. In this approach, there is not much physics but lots of mathematics. A better approach which gives more insight into the physics is to use a numerical method which involves solving the time independent Schrodinger equation to find the eigenstates using a [matrix method](#) for finding the eigenvalues and eigenvectors of the Hamiltonian operator. Nearly all the important concepts of the harmonic oscillator can be investigated by this numerical approach.

Much of what we know about the structure of molecules has been obtained from the vibrational spectra in the infrared due to the interactions of electromagnetic radiation or its emission from molecules. A very useful model in quantum mechanics is the harmonic oscillator as this model provides the basis for exploring the vibration of chemical bonds. Hence, one of the most important examples of applying the Schrodinger equation is to consider the **harmonic oscillator** represented by a **truncated parabolic potential well**.

The potential energy function  $U(x)$  is given by the parabolic function

$$U = \frac{1}{2}kx^2 + U_0$$

where  $k$  is the effective spring constant,  $x$  is the displacement from the equilibrium position and  $U_0$  is the well depth. The potential energy function for the well is defined in terms of the well depth  $U_0$  and its width  $w$  (figure 1).

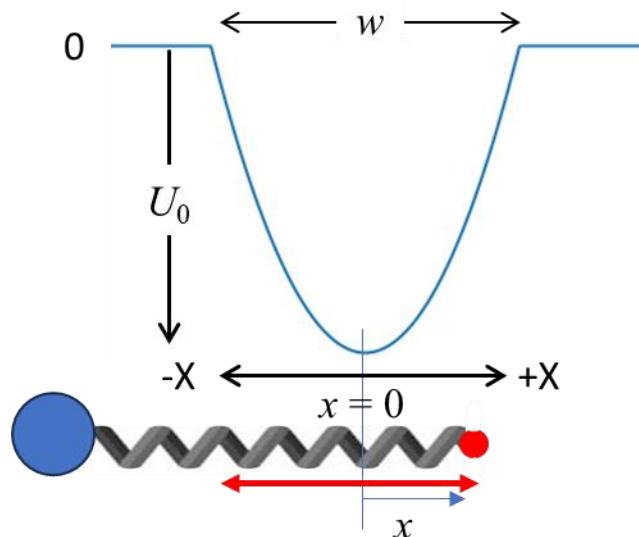


Fig. 1. Truncated parabolic potential well: depth  $U_0$  ( $U_0 < 0$ ) and width  $w$ .

In figure 1, the blue dot represents a stationary particle while the red dot represents an electron. The binding force acting on the electron can be modelled by using a spring to connect the two particles. Classically, the electron would vibrate about the equilibrium position

executing simple harmonic motion and the total energy of the system can vary continuously and when the electron is at rest, its total energy is zero. But the bound electron does not obey the laws of classical physics. The time evolution of the system is governed by the laws of quantum mechanics. The predictions of quantum mechanics include: the total energy of the system is always greater than zeros and the total energy has discrete values and does not vary continuously, but in jumps. The notation of a particle vibrating back and forth has no meaning in the quantum world. We can only predict the probability of finding the location of the electron after a measurement is made. Due to the wave nature of the electron, there maybe locations where the probability of finding the particle is zero. So, how can our electron be vibrating back and forth?

A potential well as shown in figure 1 has a minimum at  $x = 0$  and tends to zero away from the origin. A classical particle would be trapped by this potential well and oscillate to-and-fro about  $x = 0$  because the force on the particle is always directed towards origin for position since  $F = -dU/dx$ .

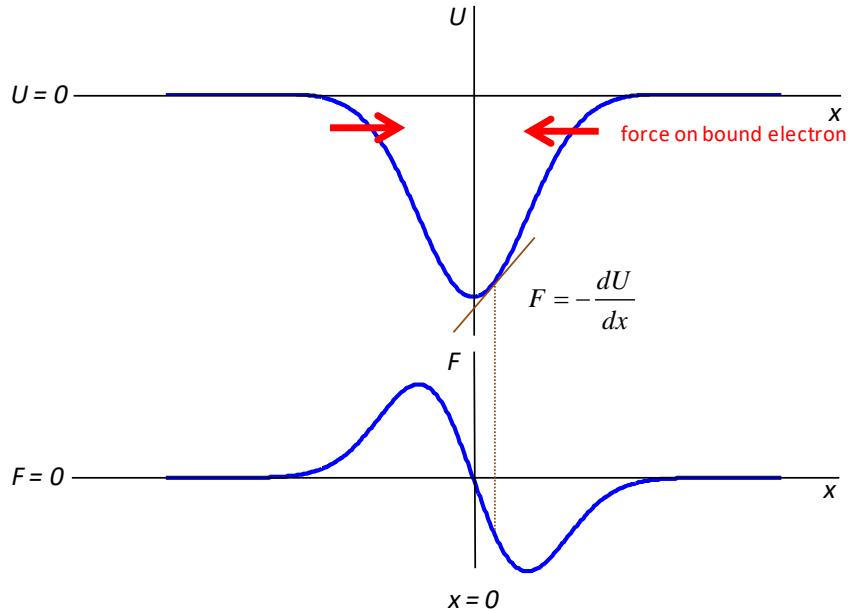


Fig. 2. Potential energy function and the force experienced by the bound electron. The predicted behaviour of the electron described by quantum mechanics and classical physics are very different.

The truncated parabolic potential well used for the simulation in the Python Code **qm045.py** sis defined by

$$U(x) = \frac{1}{2}k x^2 + U_0$$

$$U(0) = U_0 \quad U(-w/2) = 0 \quad U(w/2) = 0 \quad k = -8U_0 w^2$$

$$U(x) = U_0 \left( 1 - \frac{4x^2}{w^2} \right)$$

The Schrodinger equation that is solved by the matrix method is

$$\hat{H}\psi(x) = E\psi(x)$$

where the Hamiltonian operator is expressed as a matrix

$$\hat{H} = C_{se} \frac{d^2}{dx^2} + U(x) \quad C_{se} = \frac{-\hbar^2}{2m_e}$$

In solving this Schrodinger equation, all distances are measured in metres and energies in joules, but for display purposes, distances are in nanometres and energies in electron-volts.

For the harmonic oscillator simulation, given the values for  $U_0$  and  $w$ , the spring constant  $k$  and angular frequency  $\omega$  are calculated from the equations

$$k = \frac{-8U_0}{x_1^2} \quad \omega = \sqrt{\frac{k}{m_e}}$$

mass of electron  $m_e$

The total energy spectrum for the harmonic oscillator with a parabolic well is given by

$$E_M = \left(M - \frac{1}{2}\right)\hbar\omega + U_0 \quad M = 1, 2, 3, \dots$$

Since the total energy is measured from the bottom of the well and not from the zero level. The ground state energy is

$$E_1 = \frac{1}{2}\hbar\omega + U_0$$

The **ground state** is the **zero-point energy**. The total energy of the system is always greater than the bottom of the potential well.

## SIMULATIONS

### qm045.py

The default simulation parameters are:

```
N = 599          # grid size
xMin = -0.5*sx    # default = -0.2 nm
xMax = 0.5*sx     # default = +0.2 nm
U0 = -400*se      # Depth of well: default = -1200 eV
w = 0.5*sx        # Width of well: default 0.2 nm
M = 50            # number of eigenvalues returned
# >>> Enter 1,2,3,4,5,6 eigenstate number for expectation
#      calculations and plots
n = 2
```

## Energy spectrum: Energy eigenvalues [eV]

E1 = -384.386	EM = -384.385
E2 = -353.160	EM = -353.154
E3 = -321.938	EM = -321.923
E4 = -290.721	EM = -290.693
E5 = -259.508	EM = -259.462
E6 = -228.300	EM = -228.231
E7 = -197.096	EM = -197.001
E8 = -165.898	EM = -165.770
E9 = -134.713	EM = -134.539
E10 = -103.565	EM = -103.309
E11 = -72.547	EM = -72.078
E12 = -41.992	EM = -40.847
E13 = -13.239	EM = -9.616

There is an excellent agreement between the numerical energy eigenvalues and theoretical predictions. The agreement becomes worse towards the top of the well (higher eigenstates) because the truncated well deviates more from being a parabola. The negative of the total energy is the **binding energy**  $E_B$  where  $E_B = -E$ . The binding energy is the smallest amount of energy required to remove a particle from its bound state. The released particle is now free and its energy can vary continuously. The binding energy for the electron in the ground state ( $n = 1$ ) is 384 eV while it is only 13 eV in the highest energy bound state ( $n = 13$ )

The spacing between adjacent energy levels is constant ( $\Delta E = \pm \hbar \omega$ ) for a parabolic well. For our truncated potential well, the spacing between adjacent energy levels slightly decrease as the quantum number  $n$  increases. A summary of the difference in energy levels is given in the Console Window for transitions  $2 \rightarrow 1, 3 \rightarrow 2, \dots$

Theoretical prediction  $\Delta E = \hbar \omega = 31.23 \text{ eV}$

$2 \rightarrow 1$	31.23
$3 \rightarrow 2$	31.22
$4 \rightarrow 3$	31.22
$5 \rightarrow 4$	31.21
$6 \rightarrow 5$	31.21
$7 \rightarrow 6$	31.20
$8 \rightarrow 7$	31.20
$9 \rightarrow 8$	31.19
$10 \rightarrow 9$	31.15
$11 \rightarrow 10$	31.02
$12 \rightarrow 11$	30.56
$13 \rightarrow 12$	28.75

The discrepancy between the energy level spacings between the parabolic well and truncated well increase with higher quantum states, since near the top of the well, the truncated potential energy function is a poor approximation to a parabola.

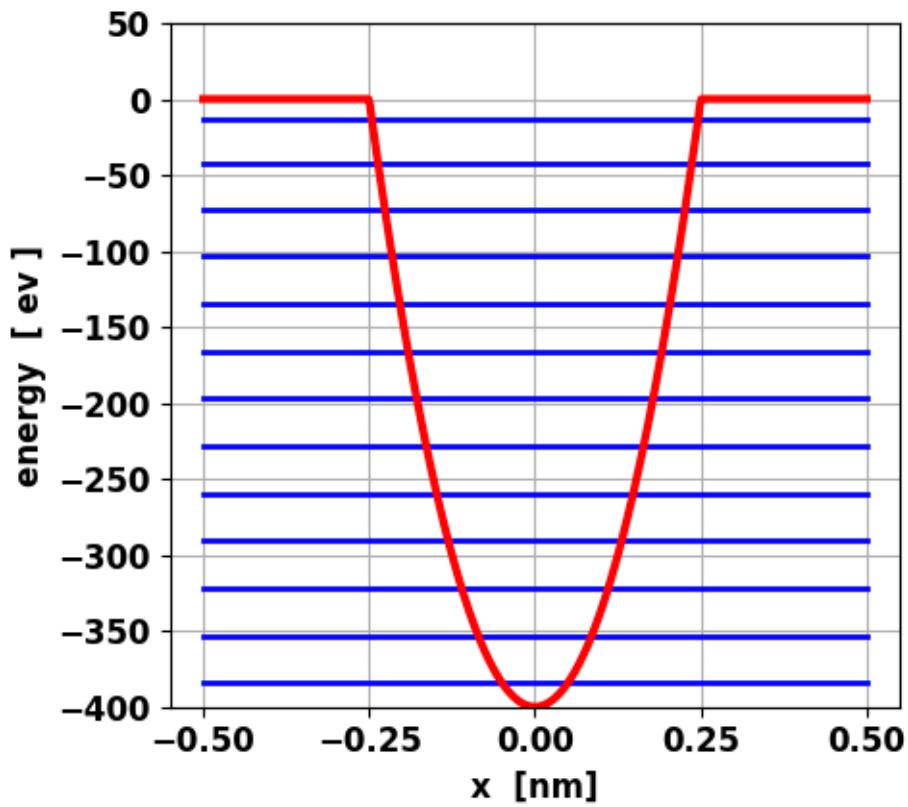


Fig. 3. Energy spectrum and truncated parabolic potential well. The well parameters are: width  $w = 0.500$  nm with depths  $U_0 = -400$  eV.  
Note: the even spacing of the energy levels.

## Eigenfunctions (eigenvectors)

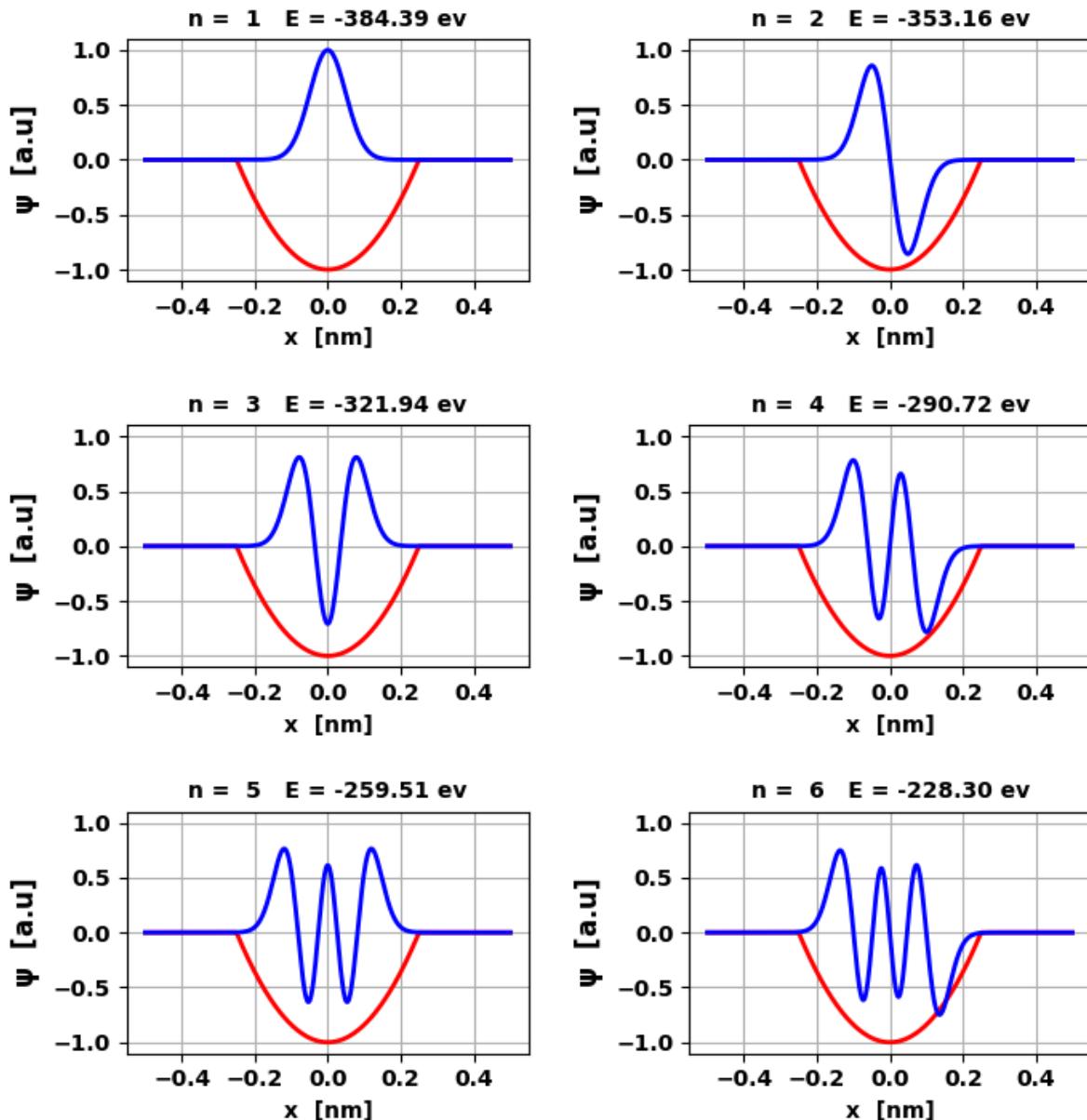


Fig. 4. Eigenfunctions for the **truncated parabolic potential well** at time  $t = 0$ . Each eigenfunction has been scaled by dividing each eigenfunction by the maximum of eigenfunction  $n = 1$ . Note: The peaks in the eigenfunctions increase in height as the potential energy increases with increasing  $|x|$ .

## Probability density functions

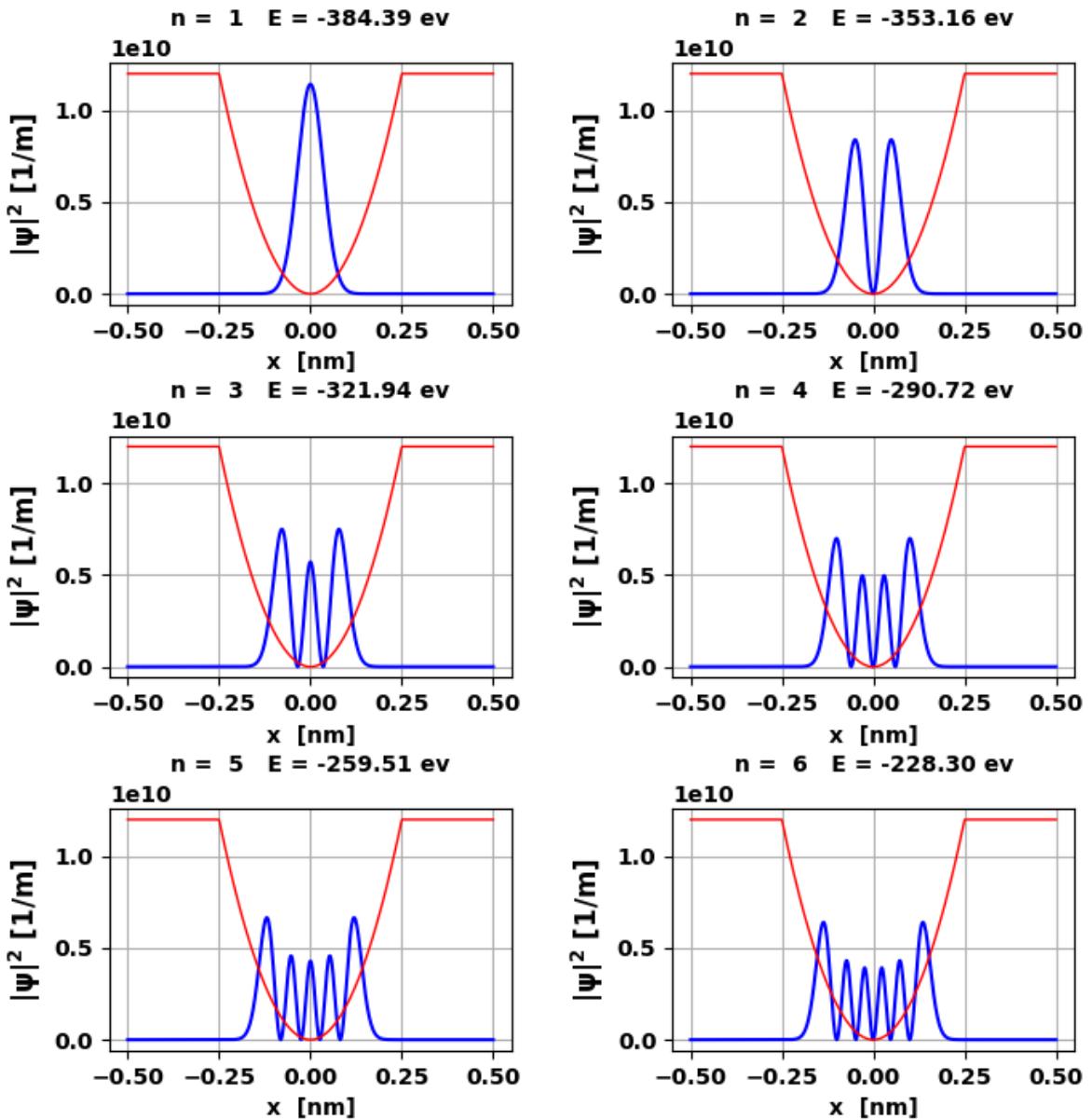


Fig. 5. Probability density function for the **truncated parabola potential well**. Area under curves is one since each eigenfunction has been normalized. Note: there is a finite probability of finding the electron beyond the classical limits of vibration.

In classical physics the largest probability of finding the electron at its extreme positions and minimum probability at the equilibrium position,  $x = 0$  (figure 6). Consider the eigenstate  $n = 1$ , the bound electron does not behave as a classical particle, since maximum probability of finding the electron is at the centre of the well and not at the extreme positions. However, the electron's behaviour is more like the classical particle at the highest quantum numbers for the bound electron as shown in figure 4 when  $n = 6$ .

For the states of higher energy, the probabilities predicted become more similar, in agreement with the principle that the quantum behaviour approaches classical behaviour under these conditions. This is known as the **correspondence principle**.

We can calculate the probability density function for a classical particle oscillating with simple harmonic motion between  $x_c = -1$  and  $x_c = +1$ . If the oscillator spends an infinitesimal amount of time  $dt$  in the vicinity  $dx$  of a given  $x$  value, then the probability  $p_D(x)dx$  of being in that vicinity will be  $p_D(x)dx = dt / (T / 2)$  where  $p_D(x)$  is the probability density for the classical particle moving from -1 to +1 in half a period  $T/2$ .

$$x = \sin(2\pi t / T)$$

$$dx = (2\pi / T) \cos(2\pi t / T) dt = (2\pi / T) \sqrt{1 - x^2} dt$$

$$dt = \frac{T dx}{(2\pi) \sqrt{1 - x^2}}$$

$$p_D dx = \frac{dt}{T / 2} = \frac{dx}{\pi \sqrt{1 - x^2}}$$

$$p_D = \frac{1}{\pi \sqrt{1 - x^2}}$$

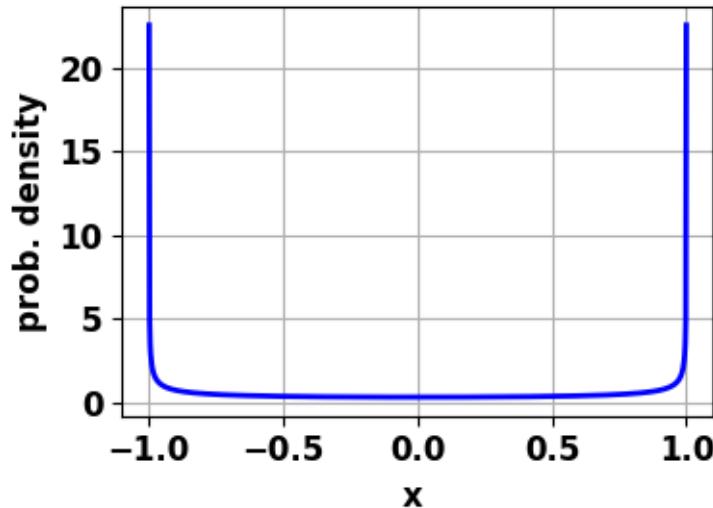


Fig. 6. Classical probability density function for a classical particle executing simple harmonic motion. The area under the curve is 1 since the function has been normalized.

## Quantum Interpretation

As the quantum number  $n$  increases, the maximum value in the amplitude of the eigenfunction shifts in the direction of higher potential energy and therefore, lower kinetic energy, lower momentum and longer wavelength (figures 4 and 5).

This can be shown by considering the eigenfunction and its slope at the boundary between two adjacent sections. We can consider the eigenfunction to be expressed as a sine function, then

$$\psi = A \sin\left(\frac{2\pi}{\lambda}x + \phi\right) \quad \frac{d\psi}{dx} = \left(\frac{2\pi}{\lambda}\right) A \cos\left(\frac{2\pi}{\lambda}x + \phi\right) = m$$

$$A \sin\left(\frac{2\pi}{\lambda}x + \phi\right) = \psi \quad A \cos\left(\frac{2\pi}{\lambda}x + \phi\right) = \frac{m}{2\pi} \lambda \quad m \neq 0$$

These equations can be squared and added to eliminate the phase  $\phi$  to give the equation for the maximum value of  $A$

$$A = \sqrt{\psi^2 + \frac{m^2}{4\pi^2} \lambda^2}$$

At the boundary of the two adjacent sections, the eigenfunction  $\psi$  and its slope  $m = d\psi / dx$  must be continuous function of  $x$ . So, at infinitesimal distances close to the boundary, the values of both  $\psi^2$  and  $m^2$  are equal in magnitude on either side, but the value of the

wavelength increases in the direction of higher potential. Therefore, the coefficient  $A$  increases with increasing wavelength, as shown in figure 4 for  $n = 6$ .

This result of greater amplitude with larger wavelength is important because any potential energy function can be approximated by a series of step functions. This implies that for any potential energy function, regions of smaller kinetic energy or smaller momentum and larger wavelength have a larger maximum value of the amplitude of the eigenfunction than adjacent regions of larger kinetic energy or momentum and smaller wavelength.

In nonuniform potential wells the wavefunctions are not sinusoidal, but over a small part of the cycle, the potential energy does not change much, and so we speak loosely of a local “wavelength”.

## Eigenstate explorations

In the input section of the Code for **qm044.py** you can enter the quantum number  $n$  for the state. In running the Code, a summary of the expectation values is shown in the Console Window as well you can test the Uncertainty Principle for the  $n^{\text{th}}$  state.

## Uncertainty Principle

$$\Delta x \Delta p \geq \hbar / 2 \quad HUP = 2 \Delta x \Delta p / \hbar > 1.$$

Plots of the potential well, the eigenfunction and probability density are displayed in Figure Windows. You will notice that the parameter  $HUP$  is always greater than 1 and gets larger as  $n$  increases.

## Eigenstate $n = 2$

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#### Expectation values and Uncertainty Principle

$$\langle x \rangle = -0.000 \text{ nm}$$

$$\Delta x \Delta X = 0.060 \text{ nm}$$

$$\langle p \rangle = 0.00 \text{ N.s} \quad \Delta x \Delta P = 2.61 \times 10^{-24} \text{ m}$$

$$HUP = 3.00 > 1$$

### Eigenstate energies

$$E_n = -353.16 \text{ eV}$$

$$\langle E \rangle = -353.16 \quad \langle K \rangle = 23.42 \quad \langle U \rangle = -376.58$$

$$\langle K \rangle + \langle U \rangle = -353.16$$

Execution time = 6 s

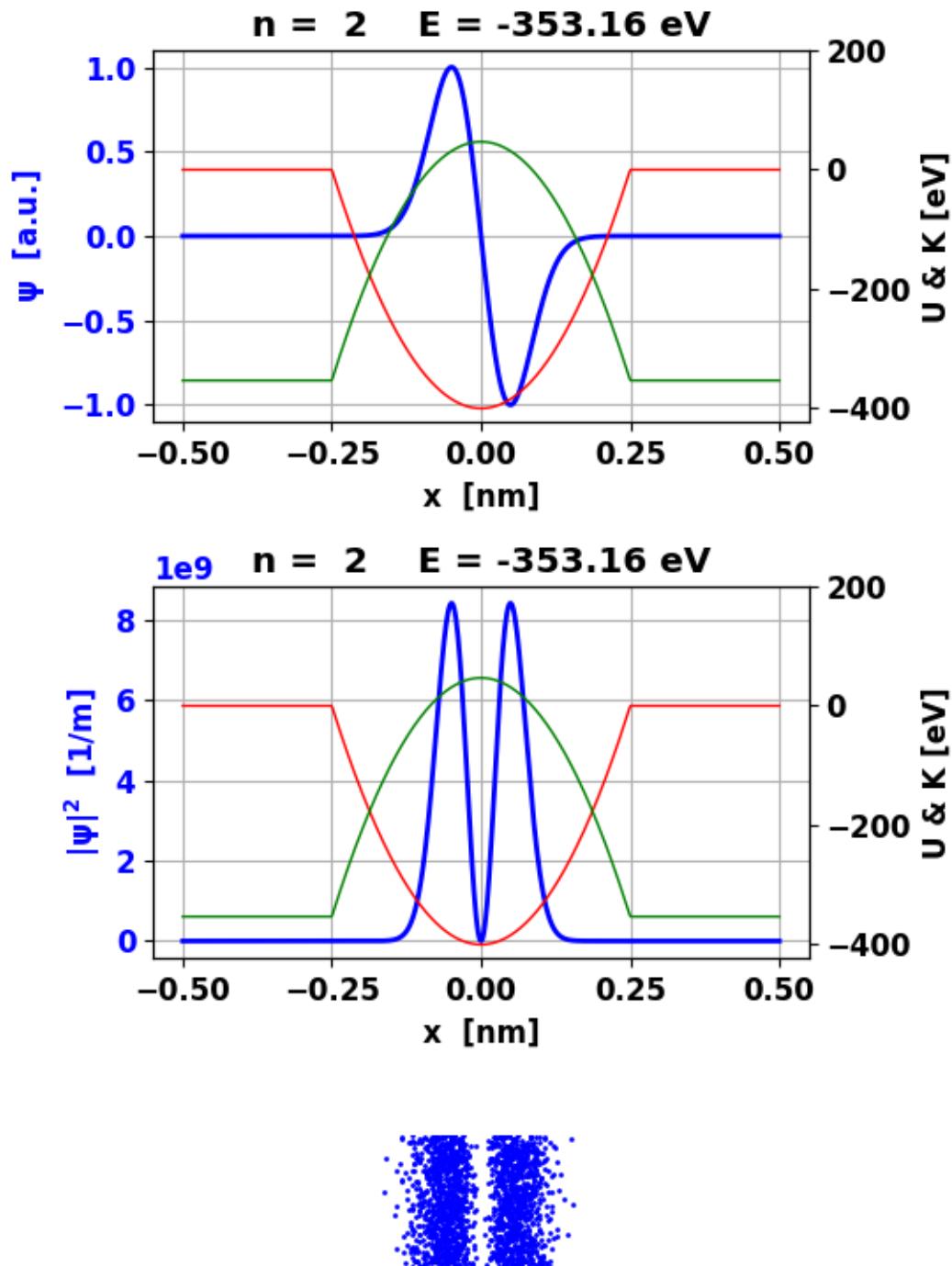
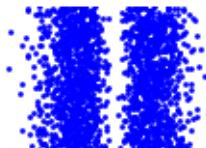


Fig. 7.  $n = 2$ : Plots of the eigenfunction, probability density and the potential energy function  $U$  and the kinetic energy function  $K$ .

In the region where  $K > 0$ , the eigenfunction is a sinusoidal function (highest probability of finding the electron) and in the regions where  $K < 0$ , the eigenfunction is an exponentially decreasing function (non-zero probability of finding the electron).

Image that you have 20 000 identical system in the state  $n = 2$ . You measure the position of the bound electron in each of the 20 000 identical systems. When you plot the result, you would get the figure shown below. Each point recorded is represented by a dot. There are region of high density corresponding to high probability of finding the electron. But, more surprisingly is that there is zero probability of finding the electron at the centre of the well. Therefore, we can no longer think of the electron in this situation as a moving particle, but have to accept that the electron has to be described by a wavefunction that is a solution to the Schrodinger equation.



## Eigenstate n = 6

Expectation values and Uncertainty Principle

$$\langle x \rangle = -0.000 \text{ nm}$$

$$\Delta x \Delta X = 0.116 \text{ nm}$$

$$\langle p \rangle = 0.00 \text{ N.s} \quad \Delta p = 5.01 \times 10^{-24} \text{ m}$$

$$\text{HUP} = 11.00 > 1$$

Eigenstate energies

$$E_n = -228.30 \text{ eV}$$

$$\langle E \rangle = -228.30 \quad \langle K \rangle = 85.88 \quad \langle U \rangle = -314.18$$

$$\langle K \rangle + \langle U \rangle = -228.30$$

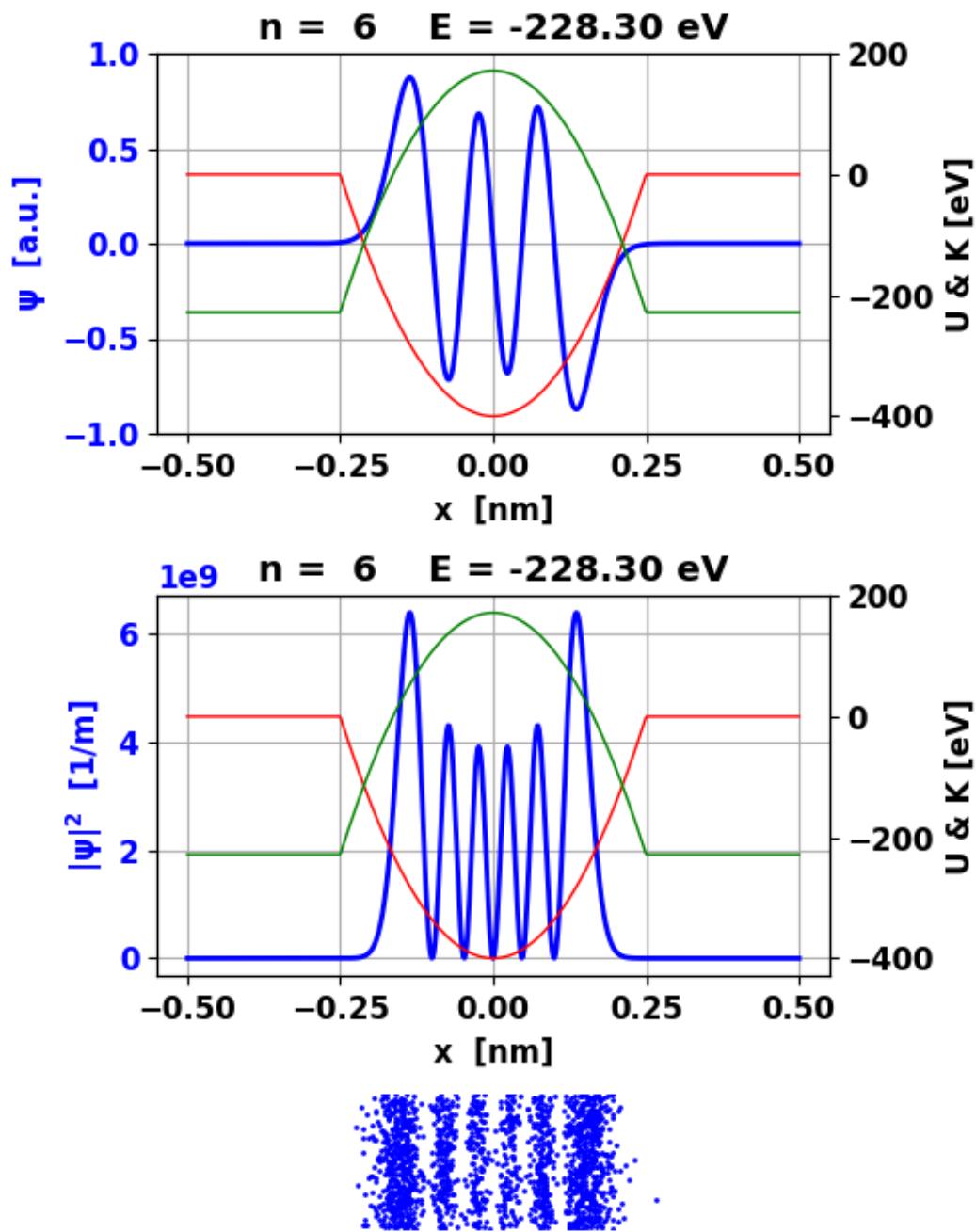


Fig. 8.  $n = 6$ : Plots of the eigenfunction, probability density and the potential energy function  $U$  and the kinetic energy function  $K$ . In the region where  $K > 0$ , the eigenfunction is a sinusoidal function (highest probability of finding the electron) and in the regions where  $K < 0$ , the eigenfunction is an exponentially decreasing function (non-zero probability of finding the electron).

## Eigenstate n = 13

Expectation values and Uncertainty Principle

$$\langle x \rangle = 0.000 \text{ nm}$$

$$\Delta x dX = 0.193 \text{ nm}$$

$$\langle p \rangle = 0.00 \text{ N.s} \quad \Delta p = 6.91 \times 10^{-24} \text{ m}$$

$$\text{HUP} = 25.23 > 1$$

Eigenstate energies

$$E_n = -13.24 \text{ eV}$$

$$\langle E \rangle = -13.24 \quad \langle K \rangle = 163.68 \quad \langle U \rangle = -176.92$$

$$\langle K \rangle + \langle U \rangle = -13.24$$

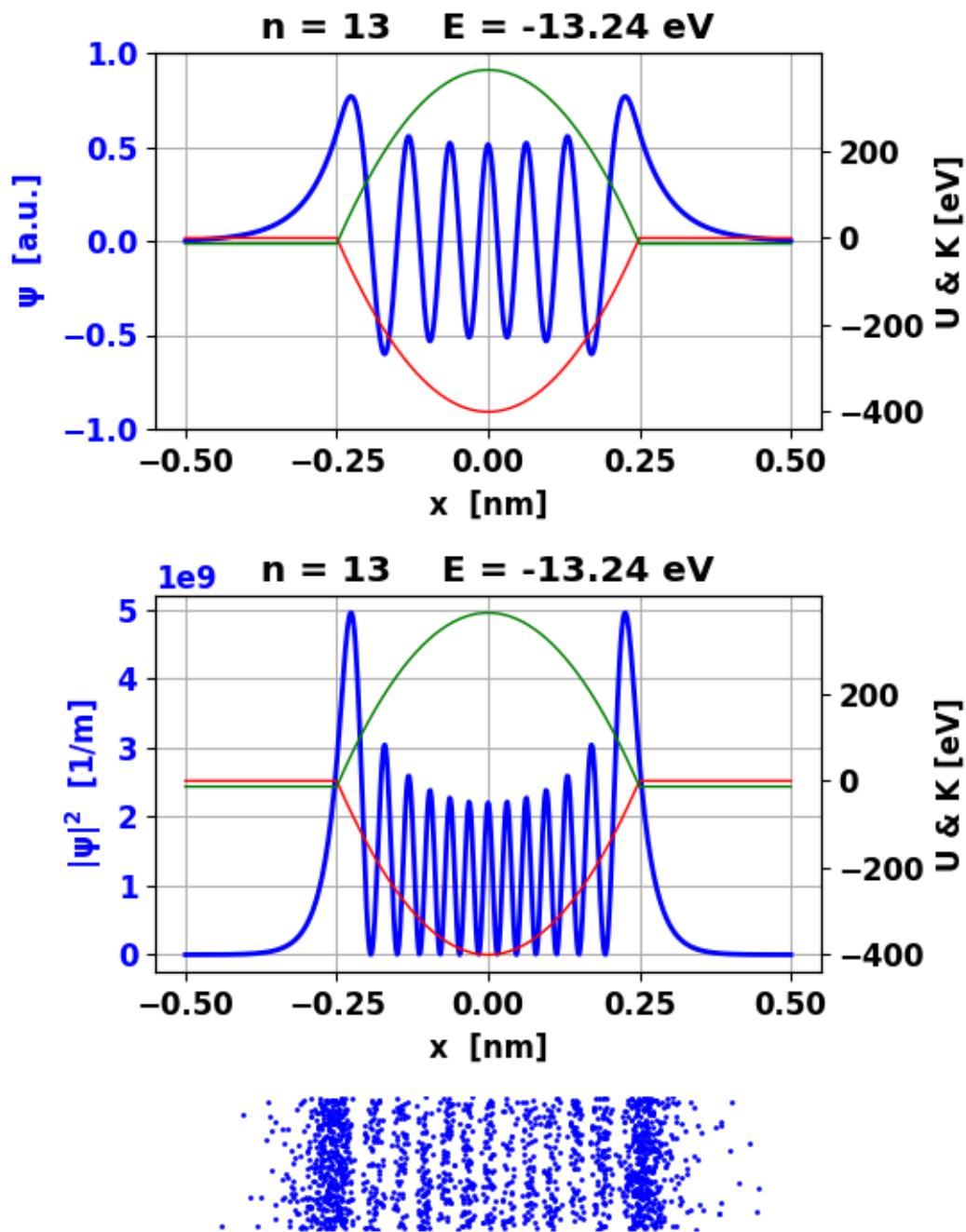


Fig. 9.  $n = 13$ : Plots of the **eigenfunction**, **probability density** and the **potential energy function  $U$**  and the **kinetic energy function  $K$** . In the region where  $K > 0$ , the eigenfunction is a sinusoidal function (highest probability of finding the electron) and in the regions where  $K < 0$ , the eigenfunction is an exponentially decreasing function (non-zero probability of finding the electron).