

# Quantum Mechanics with Python I: Time-Independent Schrödinger Equation

Rittik Mandal\*

E-mail: rittikhtml@gmail.com

## Introduction

The following is a tutorial style article about the time independent Schrödinger equation and how to solve it numerically using Python 3. For simplicity, we will consider simple systems like a one-dimensional harmonic oscillator, a particle in a 1d box and, we will end with a 1d Hydrogen atom. We will also investigate the first few wavefunctions of each of these different systems and how they look like when we plot them. Also, we will look into the shape of the probability distribution function of the first few energetic eigen-states.

Let's start with the time independent Schrödinger equation itself, which is as follows.

$$H\psi(x) = E\psi(x)$$

The above can also be rewritten as,

$$-\frac{\hbar^2}{2m}\nabla^2 + V\psi(x) = E\psi(x)$$

Now, for a one dimensional system the operator  $\nabla^2$  will be,

$$\nabla^2 \rightarrow \frac{\partial^2}{\partial x^2} \tag{1}$$

∴ For a system, which is one dimensional, the time independent Schrödinger equation is as follows.

$$H\psi(x) = E\psi(x) \quad (2)$$

$$\text{or, } -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V\psi(x) = E\psi(x) \quad (3)$$

Here,  $\psi(x)$  is a wave function,  $H$  is an operator and,  $E$  is the possible energy eigenvalue of the system. The operator  $H$  is known as the Hamiltonian operator, which is a type of Hermitian operator. The Hamiltonian operator is associated with the kinetic and the potential energy of a system. Let's assume that,  $T$  and  $V$  are the kinetic and the potential energy of the operator  $H$  respectively.

Then,  $H$ ,  $T$  and,  $V$  are related to each other in the following way,

$$H = T + V \quad (4)$$

$$= -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) \quad (5)$$

$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \text{ (for a 1-dimensional system)} \quad (6)$$

From the above equations, we can say, what the Hamiltonian operator does is it calculates the kinetic energy of a system and then multiplies it with a constant  $-\frac{\hbar^2}{2m}$  and then adds it with the potential energy of that system.

Also, note that the time independent Schrödinger equation is an eigenvalue problem. By that we mean, there are certain functions on which when the operator  $H$  operates, the only modification that the original function suffers is multiplication by a constant. For example, Assuming that  $\Omega$  is a operator and  $f(x)$  is a function and  $c$  is a constant then for an eigenvalue problem,

$$\Omega f(x) = cf(x)$$

In the above example,  $c$  is commonly referred as the eigenvalue and the function  $f(x)$  associated with it is referred as the eigenfunction.<sup>1</sup> For the time independent Schrödinger equation, the operator  $H$  results in a group of functions  $\psi(x)$  and a constant  $E$  associated with it. Or in other words, when  $H$  operates on the function  $\psi(x)$ , the function suffers the only modification of multiplication by a constant  $E$ . Clearly,  $E$  is the eigenvalue and the corresponding eigenfunction is  $\psi(x)$ .

Now that we have an insight about the time independent Schrödinger equation, let's rewrite it using Dirac's bra-ket notation.

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \quad (7)$$

Just like  $|V\rangle$  is a vector in a complex vector space, in Quantum Mechanics  $|\psi_n\rangle$  is a vector within a complex Hilbert space. It represents the state of a system. This state vector also has the information about the probabilities of all the possible outcomes of that system.

In general, the wave-function  $\psi(x)$  or the state vector  $|\psi\rangle$  stores all the information available about the system to the observer unlike a classical system.<sup>1</sup> To acquire the physical property there exists an operator which operates on the state vector  $|\psi\rangle$  and results in eigenvalues which are respective physical properties of that operator. For example, the Hamiltonian operator  $\hat{H}$  operates on the state vector  $|\psi\rangle$  and results in eigenvalues which are possible energy states of that system, and the same way the momentum operator  $\hat{p}$  operates on the vector  $|\psi\rangle$  and results the eigenvalues which are possible momentum of that system.

In other words, the time independent Schrödinger equation is an eigenvalue problem which results in eigenvalues which are the possible energy states of the system and the corresponding eigenfunctions which are the corresponding Quantum states  $|\psi_n\rangle$  of that system.

Just like mentioned earlier, the purpose of this article is to solve the time independent Schrödinger equation numerically, by discretizing the continuous spectrum to a certain extent, so that it would return the results with a negligible amount of error.

## Method

Before we dive deep into each of the systems we can make a generalized solution for the Hamiltonian. As we already know,

$$\hat{H} = \hat{T} + \hat{V}$$

By examining the above equation we can clearly see that a good place to start would be solving the kinetic energy  $\hat{T}$  and, the potential energy  $\hat{V}$  separately. Once that is done we can find the Hamiltonian with the above relation.

## Computing Potential Energy Operator

Let's start with the potential energy  $\hat{V}$  first. Note that  $V$  is a function of the position operator  $\hat{x}$ , that is why it can be represented in a matrix form in the following way,<sup>1</sup>

$$V(\hat{x}) = \langle x_i | V(\hat{x}) | x_j \rangle = V(x_j) \delta_{ij}$$

$$\text{because, } \hat{x} | x_j \rangle = x_j | x_j \rangle$$

This is true for any function that is solely a function of  $\hat{x}$ . This can be explained by expanding an arbitrary function  $f(\hat{x})$  in a Taylor series.

$$f(\hat{x}) = \sum_n c_n \hat{x}^n$$
$$\text{or, } f(\hat{x}) | x_j \rangle = \sum_n c_n \hat{x}^n | x_j \rangle = \left( \sum_n c_n x_j^n \right) | x_j \rangle = f(x_j) | x_j \rangle$$

And now because  $V(\hat{x}) = V(x_j)\delta_{ij}$ , the potential energy will be placed diagonally along the matrix, as  $\delta_{ij}$  is the Kronecker delta function which is defined as,

$$\delta_{ij} = \begin{cases} 1 & \text{for } [i = j] \\ 0 & \text{for } [i \neq j] \end{cases} \quad (8)$$

$$(9)$$

Therefore, the matrix representation of the operator  $\hat{V}$  will look like,

$$\hat{V} = \begin{bmatrix} V_{00} & 0 & 0 & \cdots \\ 0 & V_{11} & 0 & \cdots \\ 0 & 0 & V_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (10)$$

Also note that, the above matrix is a  $N \times N$  matrix, where  $N$  is the number of grid points chosen within the boundary. We will discuss more on grid points in the next section when we are calculating the kinetic energy matrix elements.

## Computing Kinetic Energy Operator

There are numerous methods for calculating the kinetic energy matrix  $\hat{T}$ . Now, it is important to mention that there is an obstacle in calculating the kinetic energy matrix of a system on a computer program. Let's discuss the problem concisely. Suppose that, a particle exists on a one dimensional axis within a boundary of say,  $[-10, 10]$ . The particle here can of course exist at any given point within this interval and hence, the position of the particle is a continuous spectrum within this given boundary. That is why we will have to consider the position of this particle to be a discrete spectrum instead of a continuous spectrum. When discretizing a continuous spectrum and working with it we will always get an error associated with the result. However, if we take a large number of grid points  $N$  in between the given interval then, the error associated with the result will be negligible and that is when we can conclude that, the result is a good approximation of the original. There exists

various methods for computing Kinetic energy matrix elements within grid basis.

Here we use the Fourier Grid Hamiltonian<sup>2</sup> approach for calculating the kinetic energy matrix  $\hat{T}$  in the grid basis. All we need to know about it is, the value that needs to be assigned in the  $\hat{T}_{ij}$ th position of the matrix  $\hat{T}_{ij}$  will be as follows.<sup>2</sup>

$$\hat{T}_{ij} = \begin{cases} \frac{\hbar^2}{2m} \frac{K^2}{3} (1 + \frac{2}{N^2}) & \text{for } [i = j] \end{cases} \quad (11)$$

$$\hat{T}_{ij} = \begin{cases} \frac{\hbar^2}{2m} \frac{2K^2}{N^2} \frac{-1^{j-i}}{\sin^2 \pi \frac{j-i}{N}} & \text{for } [i \neq j] \end{cases} \quad (12)$$

Here,  $K = \frac{\pi}{\Delta x}$ , and  $\Delta x$  is the distance between each the discrete points. With the above method we will get a matrix which will look similar to the one below,

$$\hat{T} = \begin{bmatrix} T_{00} & T_{01} & T_{02} & \cdots \\ T_{10} & T_{11} & T_{12} & \cdots \\ T_{20} & T_{21} & T_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (13)$$

## Computing the Hamiltonian operator

As we previously discussed,

$$\hat{H} = \hat{T} + \hat{V}$$

Calculating the matrix representation of the Hamiltonian operator  $\hat{H}$  is rather straightforward, given that we have already know the matrix representation of  $\hat{T}$  and  $\hat{V}$ . However, it is quite challenging to acquire the eigenvalues and their corresponding eigenvectors from the matrix  $\hat{H}$ . Let's discuss the process by which we can obtain the energy eigenvalues from the Hamiltonian. The Hamiltonian matrix  $\hat{H}$  is a Hermitian matrix. By that we mean, the transpose conjugate of that matrix is the matrix itself, i.e.  $H_{ij} = H_{ji}^*$ . It has been proven for a Hermitian matrix that, there exists at least a basis consisting of its orthonormal eigenvec-

tors, and also the operator's matrix representation itself is diagonal in this eigenbasis and has its eigenvalues as its diagonal entries.

So, it is clear that, to solve the eigenvalue problem we have to find the eigenbasis on which the operator's matrix representation is diagonal, and once we have done that we have the possible eigenvalues of the system. And since, the operator that we are operating on the state vector  $|\psi_n\rangle$  is the Hamiltonian operator  $\hat{H}$  (from Eq. 7), the eigenvalues that result will be nothing but the possible energy states of the system. In other words, we have to transform the basis in such a way that we diagonalize the matrix. To do this we can either do an active transformation or a passive transformation. In an active transformation we transform the vectors and in a passive transformation we transform the matrix representation of the operator and consequently the basis on which it is defined is transformed passively.

Say,  $\{|V_i\rangle\}$  is a set of vectors from a linear vector space. Let's write  $\hat{\Omega}$  in this arbitrary basis,  $\{|V_i\rangle\}$ ,  $\hat{\Omega} = \sum_{i,j} \langle V_j | \hat{\Omega} | V_i \rangle |V_j\rangle \langle V_i|$ . If  $\{|\Omega_k\rangle\}$  are the eigenstates of  $\hat{\Omega}$  we can write,

$$\Omega_k \delta_{kk'} = \langle \Omega_k | \hat{\Omega} | \Omega_{k'} \rangle = \sum_{i,j} \langle \Omega_k | V_i \rangle \langle V_i | \hat{\Omega} | V_j \rangle \langle V_j | \Omega_{k'} \rangle \quad (14)$$

$$= \sum_{ij} U_{ki}^\dagger \hat{\Omega}_{ij} U_{jk'} \quad (15)$$

$$= [U^\dagger \times \hat{\Omega} \times U]_{kk'} \quad (16)$$

where we have introduced  $\hat{U}$  that have matrix elements  $U_{jk} = \langle V_j | \Omega_k \rangle$ . Consequently, the matrix elements of  $\hat{U}^\dagger$  are  $U_{jk}^\dagger = \langle V_j | \Omega_k \rangle^\dagger = \langle \Omega_k | V_j \rangle$ . We have to find an Unitary matrix  $\hat{U}$  in such a way that, operator  $\hat{\Omega}$  is diagonalized. Once, we have diagonalized it, we can claim that, we have solved the eigenvalue problem of the operator  $\hat{\Omega}$ , since we already know that, diagonalizing an operator is equivalent to solving the eigenvalue problem.

However, finding the eigenbasis on which the operator  $\hat{\Omega}$  diagonalizes is not as simple as it sounds. Usually it involves iterative algorithms.

For now let's assume we have diagonalized it, and now the matrix representation of the Hamiltonian operator will look similar to the one below.

$$\hat{H} = \begin{bmatrix} \omega_0 & 0 & 0 & \cdots \\ 0 & \omega_1 & 0 & \cdots \\ 0 & 0 & \omega_2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (17)$$

Here, as we already know, the diagonal entries  $\omega_1, \omega_2, \omega_3, \dots$  are nothing but the eigenvalues of the Hamiltonian operator  $\hat{H}$  and, the corresponding eigenstates are  $|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle, \dots$

And with that, we have solved the eigenvalue problem of the Hamiltonian operator  $\hat{H}$ . And with this approach we can solve the time independent Schrödinger equation for different systems which what we are going to do next.

## 1-dimensional Harmonic Oscillator

Our first system, for which we are solving the time independent Schrödinger equation is a 1d harmonic oscillator, which is a particle oscillating back and fourth within a boundary of say, -10 to 10 with it's equilibrium point at 0. The particle can therefore exist at any point given that falls within the boundary of  $[-10, 10]$ . Therefore, it is a continuous spectrum, the problem which we discussed earlier. We also discussed that we can manipulate this problem by taking  $N$  number of grid points within the interval  $[-10, 10]$ . Here the distance between the each of the successive discrete points are,

$$\Delta x = \frac{10 - (-10)}{N}$$

or,  $\Delta x = x_1 - x_0 = x_2 - x_1 = x_3 - x_2 = \dots$



Now, let's take a look at the time independent Schrödinger equation.

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle$$

$$\text{or, } -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) |\psi_n\rangle = E_n |\psi_n\rangle$$

As we discussed in the previous sections, we can first calculate the potential energy matrix and the kinetic energy matrix separately and then find the Hamiltonian.

### Potential Energy Matrix Element

For a 1d harmonic oscillator, the potential energy for the particle which is oscillating is  $\frac{1}{2}m\omega^2 R^2$ .

Where,  $m$  is the mass of particle,  $\omega$  is the angular frequency of the particle and  $R$  is the distance of the particle from the equilibrium point at a given instance.

For simplicity, suppose that,  $\omega$  and  $m$  are both 1.

Then, all of the potential energy of each of these points can be written in a matrix where each of these potential energies will be placed diagonally along a  $N \times N$  matrix.

$$\hat{V}_{ij} = \begin{bmatrix} \frac{1}{2}m\omega^2 R_0^2 & 0 & 0 & \cdots \\ 0 & \frac{1}{2}m\omega^2 R_1^2 & 0 & \cdots \\ 0 & 0 & \frac{1}{2}m\omega^2 R_2^2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (18)$$

### Kinetic Energy Matrix Element

Now, that we have the potential part solved, we can move on and solve the kinetic energy matrix. Just like, we wrote the potential energy in a  $N \times N$  matrix, we can write the kinetic energy in a  $N \times N$  matrix. However, we don't need to recalculate it as, we have already calculated it in earlier sections. That is why we can conclude the Kinetic energy matrix element will be same as it is in equation no.13.

## Matrix representation of the Hamiltonian

Since,

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V} \\ &= \begin{bmatrix} \frac{1}{2}m\omega^2 R_0^2 & 0 & 0 & \cdots \\ 0 & \frac{1}{2}m\omega^2 R_1^2 & 0 & \cdots \\ 0 & 0 & \frac{1}{2}m\omega^2 R_2^2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} + \begin{bmatrix} T_{00} & T_{01} & T_{02} & \cdots \\ T_{10} & T_{11} & T_{12} & \cdots \\ T_{20} & T_{21} & T_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \\ &= \begin{bmatrix} T_{00} + \frac{1}{2}m\omega^2 R_0^2 & T_{01} & T_{02} & \cdots \\ T_{10} & T_{11} + \frac{1}{2}m\omega^2 R_1^2 & T_{12} & \cdots \\ T_{20} & T_{21} & T_{22} + \frac{1}{2}m\omega^2 R_2^2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}\end{aligned}$$

As we already discussed in the General Sections that, the Hamiltonian operator is a Hermitian operator and we further discussed that the problem of diagonalizing the matrix representation of these operators are equivalent to solving the eigenvalue problem of the system. And once we have diagonalized it, we can find energy eigenvalues placed diagonally along the matrix  $\hat{H}$ . Therefore, we can claim that we have solved the time independent Schrödinger equation for 1d quantum harmonic oscillator, all that is left to do is to code it up on Python.

## Implementation in Python

Let's start by importing all the necessary libraries.

```
import math
import numpy as np
import matplotlib.pyplot as plt
```

Now we can define all the necessary constants to simplify our equations. This part is optional but it would help if we want to change the constants later on.

```
h_bar,m,w      = 1, 1, 1
```

Now, we have to discretize the continuous spectrum within the given interval  $[-10, 10]$ . It is clear that, the more grid points we have within this interval the more accurate the wave function will be. However, after a certain number of grid points, the accuracy of our model will converge to a point where there will be a negligible amount of error. Therefore, we can say, after a certain number of grid points within a given interval, it is pointless to increase the number of grid points to increase the accuracy of our model by a tiny fraction with a relatively large amount of computational resources and time. We will try and find the optimal number of grid points later on. For now, let us discretize the given interval with the following line of codes.

```
def R(N):
    Rmax, Rmin = -10, 10
    return np.linspace(Rmax,Rmin,N)
```

Now we can start computing the Hamiltonian itself.

Computing the potential energy matrix of the Hamiltonian first would be a good place to start. As we discussed earlier,  $\hat{V}(R)$  will be a  $N \times N$  matrix where, the potential energy of the particle at a point within the given interval will be placed diagonally along the matrix. We can do it in this in the following way,

```
def V(R):
    return np.diag(0.5 * m * w**2 * R**2 )
```

We now have the potential energy matrix of the Hamiltonian, it is now time for us to compute the kinetic energy matrix,  $\langle x_i | \hat{T} | x_j \rangle$  of the Hamiltonian. As we have seen in the general sections, the value that needs to be assigned for  $\hat{T}_{ij}$ th position is,

$$\hat{T}_{ij} = \begin{cases} \frac{\hbar^2}{2m} \frac{K^2}{3} \left(1 + \frac{2}{N^2}\right) & \text{for } [i = j] \\ \frac{\hbar^2}{2m} \frac{2K^2}{N^2} \frac{-1^{j-i}}{\sin^2 \pi \frac{j-i}{N}} & \text{for } [i \neq j] \end{cases} \quad (19)$$

The pseudo code for doing this is as follows.

```
def T(R):
    n = len(R)
    h2m = h_bar**2/2*m
    k = np.pi/(R[1]-R[0])
    T = np.zeros((n,n))
    pi = math.pi
    for i in range(n):
        T[i,i] = h2m * ((k**2)/3)*(1+(2/(n**2)))
        for j in range(i+1,n):
            T[i,j] = h2m * (2*k**2*(-1)**(j-i))/(n**2 * (np.sin(pi*(j-i)/n))**2)
            T[j,i] = T[i,j]
    return T
```

Now that we have both the kinetic energy matrix and the potential energy matrix of the Hamiltonian, we can calculate to find Hamiltonian itself, and then diagonalize it for the eigenvalues and the respective eigenvectors.

```
def H(N):
    #since  $\hat{H} = \hat{T} + \hat{V}$ 
    H = T(R(N)) + V(R(N))
    E, psi = np.linalg.eigh(H)
    return E, psi
```

We now have solved the eigenvalue problem of the time independent Schrödinger equation for a 1d harmonic oscillator and have acquired the possible energy states  $E_n$  and the corresponding state vectors  $|\psi_n\rangle$  for this system. In fact, we can now take a look at the energy eigenvalues for a certain number of grid points within the given interval.

For 10 grid points the energy eigenvalues of the Hamiltonian  $\hat{H}$  for this system are,

*#Code:*

H(10)[0]

*#Output:*

0.74323775, 1.15090087, 5.86563745, 5.93486264, 15.75307369,  
15.79399286, 30.5573967, 30.61756851, 50.13166319, 50.55298136

For a 1d harmonic oscillator the energy eigenvalues are,<sup>3</sup>

$$E_n = (n + \frac{1}{2})\hbar\omega \quad (21)$$

$$n = 1, 2, 3, 4, \dots \quad (22)$$

Therefore, the difference between two successive energy states for a particle with  $\hbar = 1$  and  $\omega = 1$  is 0.5. Therefore, our output has a considerable amount of error.

Now, instead of 10 grid points let's take 100 grid points and then observe the results.

*#Code:*

H(100)[1]

*#Output:*

0.5	,	1.5	,	2.5	,	3.5	,
4.5	,	5.5	,	6.5	,	7.5	,
8.5	,	9.5	,	10.5	,	11.5	,
12.5	,	13.5	,	14.5	,	15.5	,
16.5	,	17.5	,	18.5	,	19.5	,
20.5	,	21.5	,	22.5	,	23.5	,
24.5	,	25.5	,	26.5	,	27.5	,...

Clearly, here the difference between each of the successive energy eigenvalues are 0.5. That is why, we can claim that the error is negligible for a 100 grid points within the given boundary. Now, we can take a look at the first few wavefunctions of the system by plotting them. We can do this in the following way,

```
def plot1dWave(n,i):
    psi = H(n)[1]
    for j in range(0,i+1):
        plt.plot(R(n),psi[:,j])
```

The above function takes two arguments, the first one is the number of chosen grid points and, the second one is the number of wave functions we want to plot.

To plot the first 3 wavefunctions for a 1000 grid points in between the given interval  $[-10, 10]$  we can just call the previous function. To check the result refer to Figure 1.<sup>4</sup> We can also

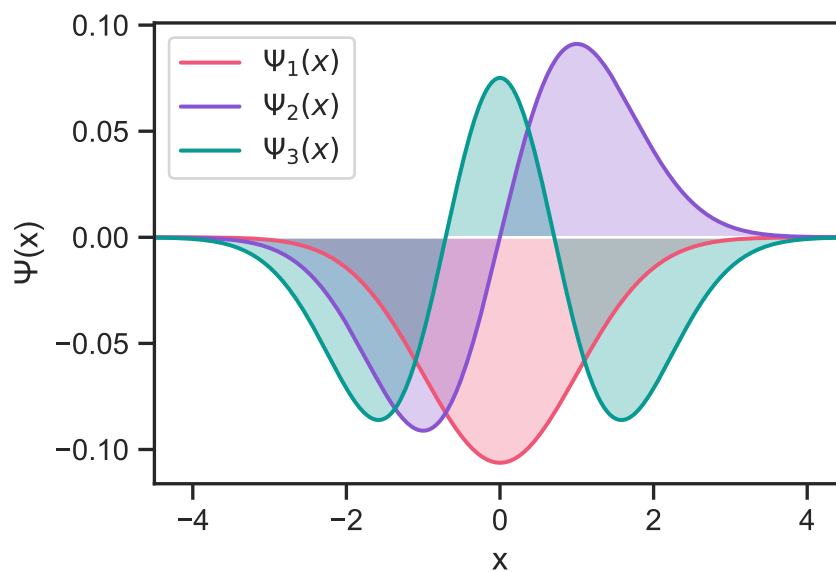


Figure 1: First three wave-functions of a 1D Harmonic oscillator

plot the probability density function of the corresponding energy states and at the same time plot the potential energy of the system.

```
def plotProbDensity(div,num):
    Rmax, Rmin, N = 10, -10, div
    R = np.linspace(Rmax,Rmin,N)
```

```

E    = H(div)[0]
psi = H(div)[1]
mlt.plot(R,0.5 * m * w**2 * R**2)
mlt.ylim(0,num)
mlt.xlim(-10,10)
for i in range(num):
    mlt.plot(R,E[i]+np.conjugate(psi[:,i]) * psi[:,i])

```

The above function takes two arguments, the first one is the number of grid points within the given interval and the second is the number of energetic states and their corresponding probability density function that we want to plot.

Now, to plot the first three energy states and their corresponding probability distribution and the potential energy we can call the above function. To check the result, please refer to Figure 2.<sup>4</sup>

Let's take a moment to discuss about the properties of Figure 2. As we can see from the figure, the lowest energy state is at 0.5, this is also commonly referred as the zero-point energy. It also contradicts with the classical mechanics since the lowest energy state of the system is at a finite point which is not 0. For a classical system, the energy of that system starts from 0 but here clearly it doesn't. Also, another property that we can notice from the figure is that for the first energy eigenstate the probability density has one peak, for second energy eigenstate the probability density has two peaks and, for third energy eigenstate the probability density has three peaks. So, for the  $n$ th energy eigenstate the corresponding probability distribution function will contain  $n$  peaks. It is also unexpected for the particle to have a near zero probability for a range near the node and have high probability for it being at the two opposite sides of the node. Also, the energy gap between two successive energy states is constant. These are the results that we can observe from the figure.

We can also try and find the optimal number of grid points that we need within this given interval for an appreciable result. We can find the deviation( $\sigma$ ) of the first 5 energy eigenvalues

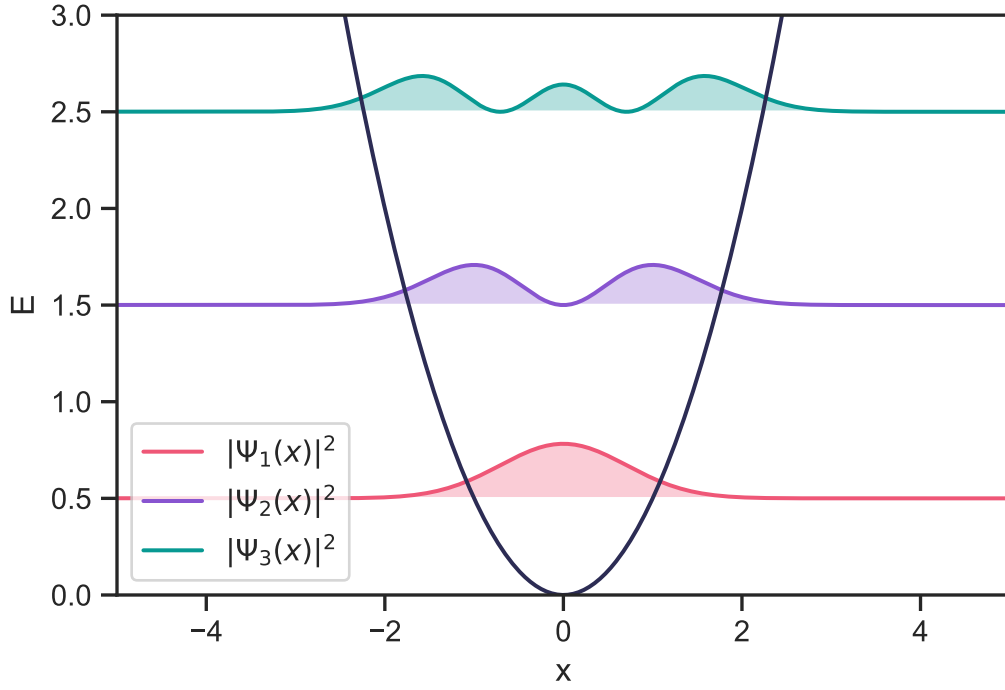


Figure 2: First three energy states and their probability distribution function

from the actual energy.

$$\sigma_i = \left| E_i - \left( n + \frac{1}{2} \right) \right| \quad (23)$$

where  $E_i$  is the  $i$ th energy eigenvalue and  $n = 0, 1, 2, 3, \dots$

Now, we can calculate this for a specific number of grid points in between the given interval and then plot them to find an optimal point.

First let's calculate the deviation from 0.5 for first 5  $E_i$  for a specific number of discrete points in between the given interval.

```
def std_dev(N):
    Rmax, Rmin = 10, -10
    R = np.linspace(Rmax, Rmin, N)
    Nmax = 5
```



```

E = H1dho(N)[0][:Nmax]
Error = E - np.arange(0.5, Nmax + 0.5)
return np.abs(Error)

```

Now we can call this function and calculate and plot the deviation for a given range of grid points.

```

def plotStdDev():
    nmax = 5
    Nrange = np.arange(10,100,1)
    error = np.zeros((len(Nrange),nmax))
    for i in range(len(Nrange)):
        error[i,:] = std_dev(Nrange[i])
    fig, ax = plt.subplots()
    for j in range(nmax):
        ax.plot(Nrange, np.log(error[:,j]), label = f'$E_{j}$')
    ax.legend(loc= 'upper right')
    plt.xlabel('N')
    plt.ylabel('$log(\sigma)$')

```

Now, let's plot it till a 100 grid points and observe the nature of the curve(Figure 3).<sup>4</sup> Clearly, from the graph we can conclude 100 grid points is a good enough optimal point where it will take less computational time and resources; and at the same time give a low deviation  $\sigma$  from 0.5 for the first 5 energy eigenvalues.

And with that, we have solved the Time independent Schrödinger equation for a 1d quantum harmonic oscillator and can move on to the next system.

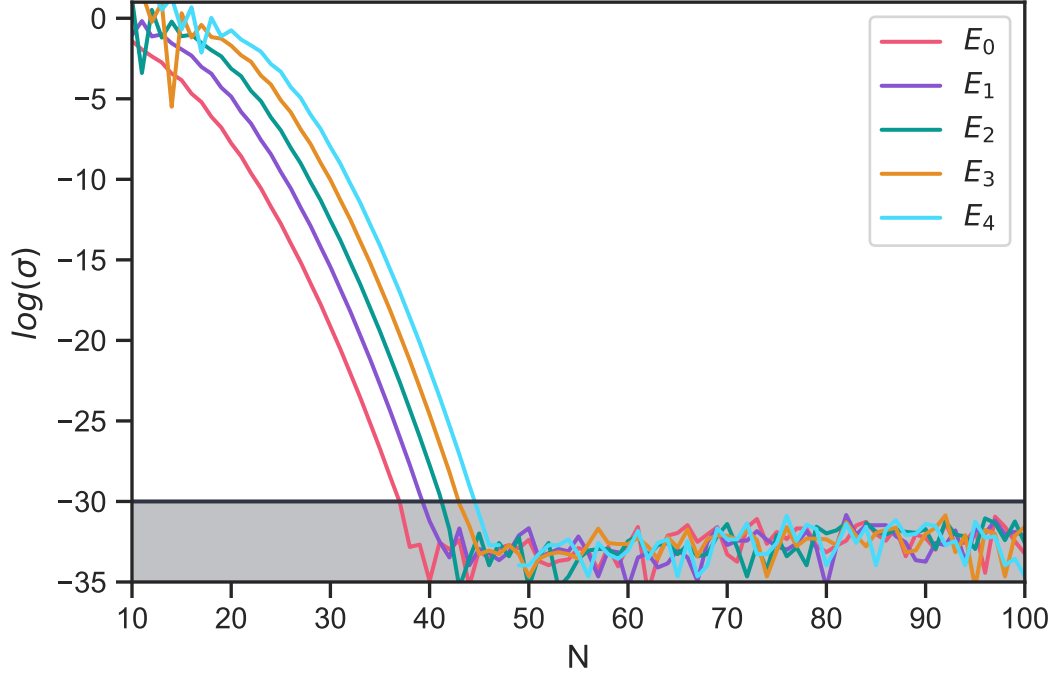


Figure 3: Deviation  $\sigma$  till 100 grid points

## Particle in a 1-Dimensional Box

Our second system for which we are going to solve the time independent Schrödinger equation is a particle in a one dimensional box. This system consists of a particle which can move freely but it is enclosed in a small space which is surrounded by impenetrable walls. Just like our previous system we will consider the particle to be enclosed within a boundary of  $[-10, 10]$ , within which the particle can move freely and, the system will be enclosed in a boundary of say  $[-20, 20]$ . We will use the same method of discretizing this continuous spectrum until we get a result which has a negligible amount of error associated with it. Now, let's solve the time independent Schrödinger equation for this system.

### Potential Energy Matrix Element

Potential energy of the particle within this box is supposed to be 0 and at the walls and outside the walls is supposed to be  $\infty$  so that there is a 0 probability for the particle to be

outside or at the walls.<sup>3</sup>

$$\hat{V}(x) = \begin{cases} 0 & \text{for } [Within\ the\ box] \\ \infty & \text{for } [At\ the\ walls\ and\ Outside\ the\ box] \end{cases} \quad (24)$$

$$(25)$$

However, we can't assign the potential to be  $\infty$  on a computer program, that is why we suppose it to be a finite number say, 10.

$$\hat{V}(x) = \begin{cases} 0 & \text{for } [Within\ the\ box] \\ 10 & \text{for } [At\ the\ walls\ and\ Outside\ the\ box] \end{cases} \quad (26)$$

$$(27)$$

Therefore, the potential energy for a particle in a 1d box is a step function, which will look like Figure 4. We can now calculate the potential energy matrix just like we did for the

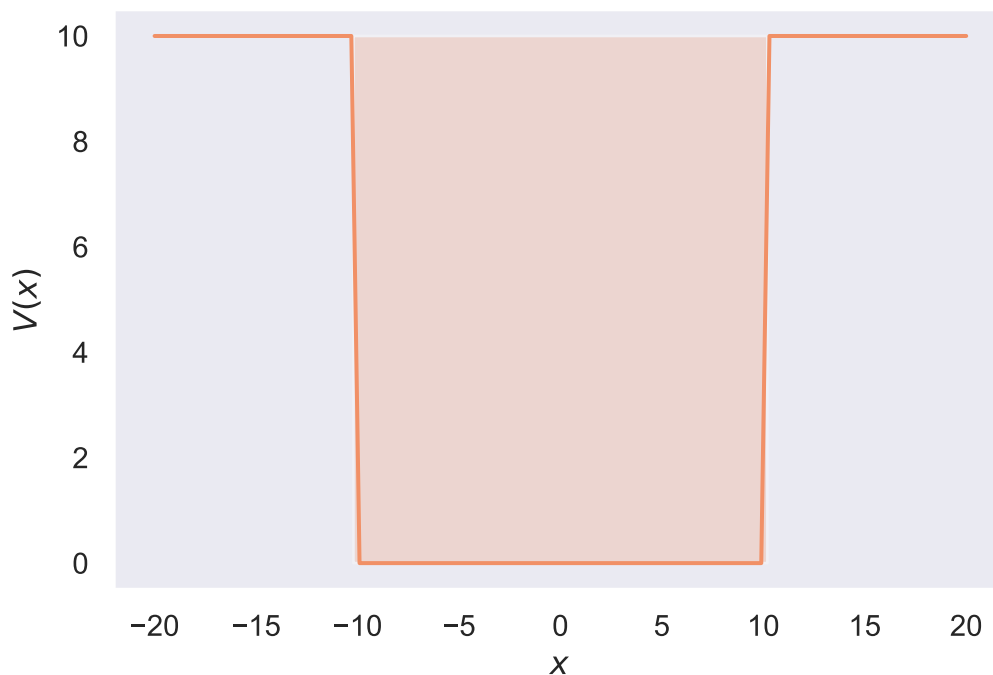


Figure 4: Potential energy of a particle in a 1d box

previous system. The potential energy at a given point of the particle within the boundary

of  $[-20, 20]$  will be 0 for the particle when it is within the box and 10 everywhere else.

$$\therefore \hat{V} = \begin{bmatrix} V_{00} & 0 & 0 & \cdots \\ 0 & V_{11} & 0 & \cdots \\ 0 & 0 & V_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

### Kinetic Energy Matrix Element

To find the kinetic energy matrix we are going to use the same method as we did in the general sections. Refer to equation no.13 for the process on how we can solve and find the kinetic energy matrix  $\hat{T}$  for this system.

### Matrix representation of the Hamiltonian

As we already know,

$$\hat{H} = \hat{T} + \hat{V}$$

Therefore, computing the Hamiltonian Matrix is rather simple as it is nothing but the sum of the kinetic and the potential energy matrix. That is why we can represent the Hamiltonian in the following way.

$$\hat{H} = \begin{bmatrix} T_{00} + V_{00} & T_{01} & T_{02} & \cdots \\ T_{10} & T_{11} + V_{11} & T_{12} & \cdots \\ T_{20} & T_{21} & T_{22} + V_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

As we already know, the above matrix  $\hat{H}$  is a Hermitian matrix and once it is diagonalized the energy eigenvalues will be placed diagonally along the matrix.

We now do have prerequisite knowledge for implementing the time independent Schrödinger

equation for this system in Python.

## Implementation in Python

Let's assume we have already imported all the necessary libraries and we are ready to begin the calculation of the potential energy matrix, which can be computed in the following way.

```
def v1db(n):  
    Rmax, Rmin, N = 20, -20, n  
    V = np.zeros(N)  
    R = np.linspace(Rmax, Rmin, N)  
    for i in range(N):  
        if ((R[i]<10) and R[i]>-10):  
            V[i] = 0  
        else:  
            V[i] = 10  
    return np.diag(V),V
```

Now that we have the potential energy matrix computed, we can proceed and compute the kinetic energy matrix. However, the method for calculating it is same as it was for the previous system, that is why we can skip this part and calculate the Hamiltonian matrix directly. Now that we have both the kinetic and the potential energy matrix computed we can proceed and compute the Hamiltonian matrix.

```
def H1db(N):  
    Rmax, Rmin = 20, -20  
    R = np.linspace(Rmax,Rmin,N)  
    H = T(R) + v1db(N)[0]  
    E, psi = np.linalg.eigh(H)  
    return E, psi
```

We can now take a look at the number of grid point required to converge first 5 energy eigenvalues to the original energy. In other words, find an optimal point at which the error is negligible for the first 5 energy eigenvalues. To do this let us define the deviation  $\sigma_i$  of the  $E_i$  energy eigenvalue of the system.

It has been calculated in other ways that the energy eigenvalues for a particle in a one dimensional box is as follows.<sup>3</sup>

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (28)$$

Where,  $n = 1, 2, 3, \dots$  and  $\hbar = 1$  in atomic units and  $L$  is the length of the box and  $m$  is the mass of the particle, for simplicity, which we have assumed to be 1.

$\therefore$  Deviation  $\sigma$  will be defined as,

$$\sigma_i = \left| E_i - \left( \frac{n^2 \pi^2}{2L^2} \right) \right| \quad (29)$$

The length of the box  $L$  for our system is 20. Now, we can calculate the deviation with the help of the previous function that we defined earlier. We can plot it and observe the nature of the curve and find an optimal number of grid points at which the error associated with the resultant energy eigenvalue is negligible. However, we have done this before for our previous system that is why we are not repeating it and skipping this part. Now, we can write the following lines of codes to plot the first few wave functions of this system.

```
def plotP1dbWave(n,i):
    psi = H1db(n)[1]
    for j in range(i):
        plt.plot(np.linspace(-20,20,n),psi[:,j])
```

The first 3 wave functions for a 100 grid points in between the interval  $[-20, 20]$  will look like Figure 5.<sup>4</sup> Now, we can write the following line of codes which will plot the probability

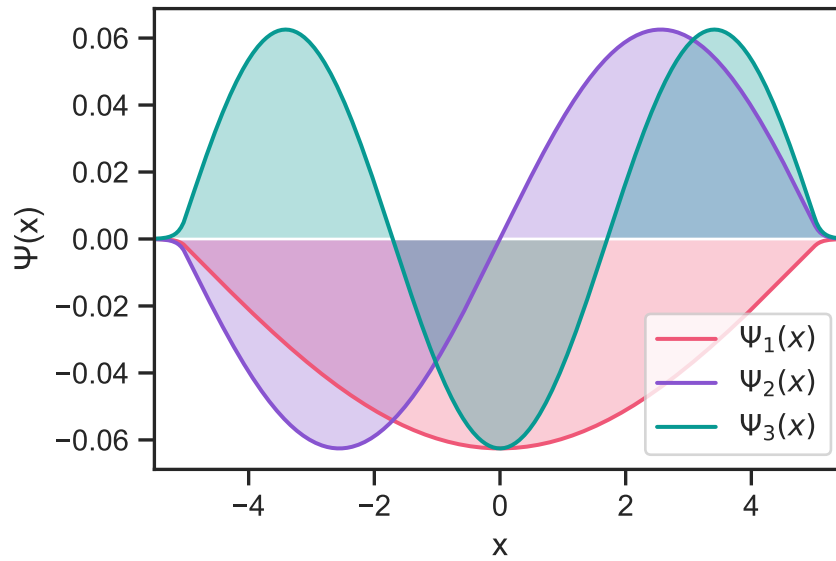


Figure 5: First three wave-functions of a particle in a 1d box

density function of the first few energetic states of the system.

```
def plotP1dbProbDensity(div,num):
    Rmax, Rmin, N = 20, -20, div
    R = np.linspace(Rmax,Rmin,N)
    E = H1db(div)[0]
    psi = H1db(div)[1]
    plt.plot(R ,np.diag(v1db(N)[0]))
    plt.xlim(-20,20)
    plt.ylim(0,num/10)
    for i in range(num):
        plt.plot(R,E[i]+np.conjugate(psi[:,i]) * psi[:,i])
```

Let's also take a look the at the first three energy states with their respective probability density function and how the potential energy is shaped around the system(Figure 6).<sup>4</sup>

Let's also take a moment to discuss about the properties that we can observe from Figure 6. The first thing that we can notice is that, the lowest energy state of the system, the zero-point energy is not at zero. This indicates that the particle in consideration can never be at rest and always has some minimum amount of energy associated with it. Also, we can notice that, at some points at which, for a specific energy state, the probability of finding the particle near a small given range near that point is almost zero. When discussing about our previous system we came across these points and mentioned these points as nodes. We can clearly see, a similar pattern that we observed from our previous system which is, for the  $n$ th energy eigenstate the number of nodes for the probability distribution function associated with that energy state is  $n$ . The energy gap between two successive energy states is not constant unlike the previous system. Also, the energy clearly is not a continuous spectrum, rather it comes in discrete values.

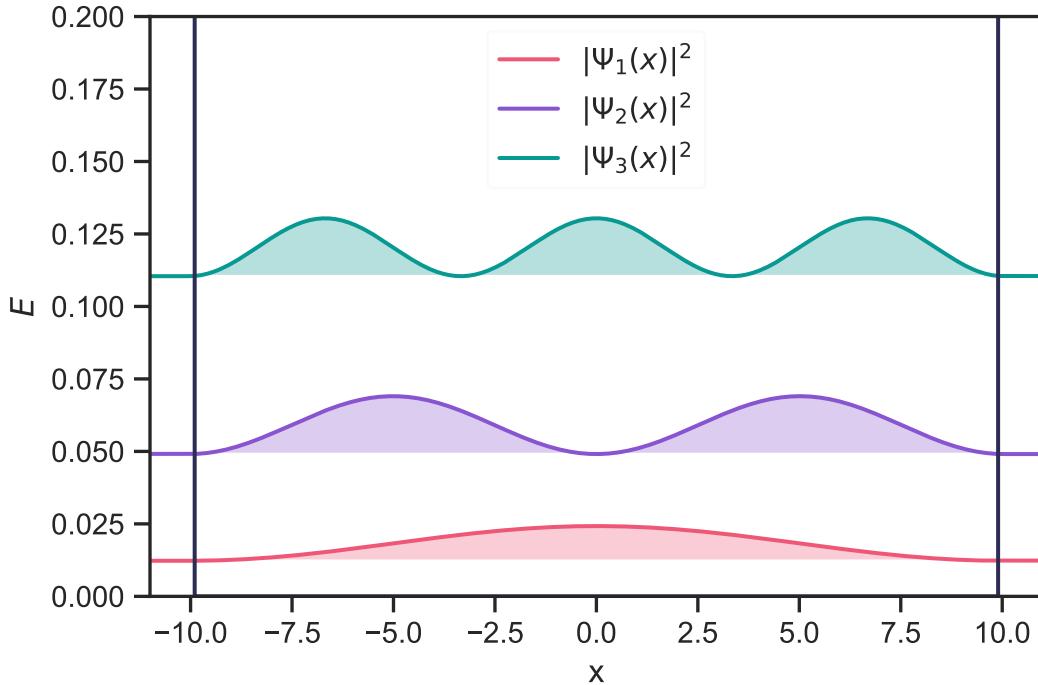


Figure 6: First three energy states and their probability distribution function

And, with that we have solved the time independent Schrödinger equation for a particle



in a 1d box. So now, we can move on to our next and final system which is a 1d Hydrogen atom.

## 1d Hydrogen Atom

While we proceed to our next and final system it is important that we keep in mind that this is more like a toy atom, since it is 1 dimensional. Now let's get acquainted with the structure of this system. This system consists of an electron and a nucleus, the electron can move around the nucleus and there is an electrostatic interaction between them since they are both charged particles. Let's assume that, the nucleus is at the position 0 and the electron can move around the nucleus with a maximum distance from it being 10. Therefore, the electron is a particle which can move around the boundary of -10 to 10. Now, that we have all the necessary information available about the system we can move on and solve the time independent Schrödinger equation for this system.

### Potential Energy Matrix Element

The potential energy of the particle in consideration which is the electron is as below.

$$\hat{V}_R = \frac{1}{4\pi\epsilon_0} \times \frac{-1}{r_0 - R} \quad (30)$$

where,

$$\frac{1}{4\pi\epsilon_0} = 1(\text{in atomic units})$$

$\hat{V}_R$  = Potential energy of the electron at position  $R$ ,

$r_0$  = The position of the Nucleus and,

$R$  = The position of the Electron

But there is complication with this, which will be easier to explain by plotting the potential which looks like Figure 7. As we can see from the graph, there is an infinite potential for the

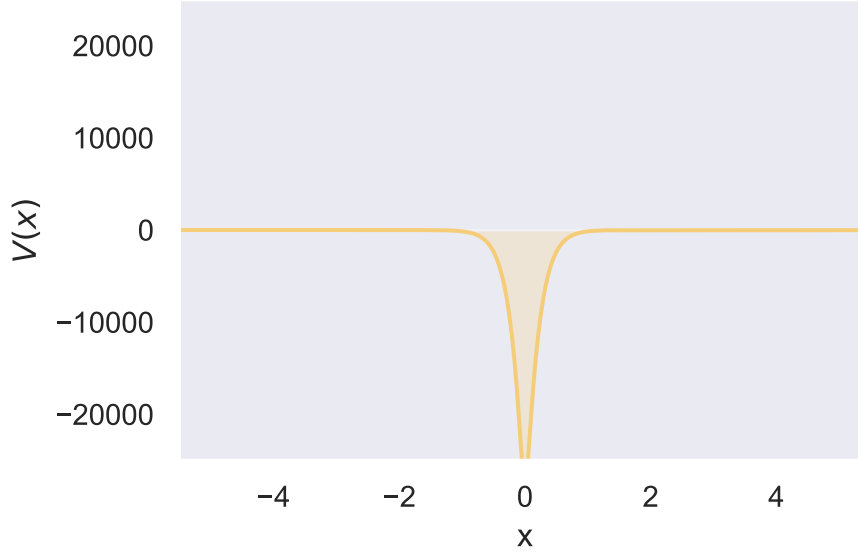


Figure 7: Potential energy of a 1d Hydrogen atom

electron at the 0 position. To mitigate this problem, we can add an extra term in the equation of the potential energy of the electron,  $\hat{V}_R$  say,  $\Delta$ .

$$\hat{V}_R = \frac{-1}{|r_0 - R| + \Delta} \quad (31)$$

We will treat  $\Delta$  as a constant with a rather small value assigned to it say, 0.001. What this will do is, it will not let the potential  $\hat{V}$  to be  $\infty$  by keeping the denominator  $|r_0 - R| + \Delta \neq 0$ . And, just like the other systems, this can be written in a  $N \times N$  matrix where the potential

energies will be placed diagonally.

$$\hat{V} = \begin{bmatrix} V_{00} & 0 & 0 & \cdots \\ 0 & V_{11} & 0 & \cdots \\ 0 & 0 & V_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

Now, we can proceed to the calculation of the kinetic energy matrix.

### **Kinetic Energy Matrix Element**

The calculation of the kinetic energy matrix remains unaltered and it will be calculated like the other two previous systems. For more details on this refer to the General Sections and equation no.13 in particular.

### **Matrix representation of the Hamiltonian**

As we already know,

$$\hat{H} = \hat{T} + \hat{V}$$

$$\therefore \hat{H} = \begin{bmatrix} T_{00} + V_{00} & T_{01} & T_{02} & \cdots \\ T_{10} & T_{11} + V_{11} & T_{12} & \cdots \\ T_{20} & T_{21} & T_{22} + V_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

We can diagonalize the above matrix and acquire the energy eigenvalues.

### **Implementation in Python**

Just like the other two systems, let's start by computing the potential energy matrix  $\hat{V}$ .

```

def v1da(n):
    Rmax, Rmin, N = 10, -10, n
    Delta = 0.001
    V = np.zeros(N)
    R = np.linspace(Rmax, Rmin, N)
    for i in range(N):
        V[i] = -1/(abs(-R[i])+0.001)
    return np.diag(V)

```

The calculation of the kinetic energy matrix will be same as the above systems, that is why we can just skip this part and calculate the Hamiltonian matrix at first hand. When calculating the matrix  $\hat{H}$  we can call the function  $T$  which calculates the kinetic energy matrix which we have defined previously for the above systems.

```

def H1db(N):
    Rmax, Rmin = 10, -10
    R = np.linspace(Rmax, Rmin, N)
    H = T(R) + v1db(N)
    E, psi = np.linalg.eigh(H)
    return E, psi

```

It has been calculated that the energy eigenvalues for a 1d Hydrogen atom are,<sup>5</sup>

$$E_n = -\frac{R}{\alpha^2} \quad (32)$$

Where,  $\alpha$  is the quantum number and  $R = \frac{\hbar^2}{2ma_0^2}$ , where again  $a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ . With these information in hand we can define the deviation  $\sigma$  in the following way,

$$\sigma_i = E_i - \frac{R}{\alpha^2} \quad (33)$$

We can now plot the deviation for the first 5 every states and find at optimal number of grid points at which the energy eigenvalues converge to their original results. However, we have done something similar like this for our first system that is why we can just skip this part. Now we are ready to plot the wave functions of the system as well as the probability density function of the different energetic states of the electron around the nucleus.

```
def plot1d_HydrogenWave(n,i):
    psi = H1da(n)[1]
    for j in range(i):
        plt.plot(np.linspace(-10,10,n),psi[:,j])
        plt.ylabel('Energy')

def plot1d_HydrogenProbDen(div,num):
    Rmax, Rmin, N = 10, -10, div
    R = np.linspace(Rmax,Rmin,N)
    E = H1da(div)[0]
    psi = H1da(div)[1]
    plt.plot(R ,np.diag(v1da(N)))
    plt.xlim(-10,10)
    plt.ylim(0,num)
    for i in range(num):
        plt.plot(R,E[i]+np.conjugate(psi[:,i]) * psi[:,i])
```

The first three wave function of the electron is shaped like as shown in Figure 8.<sup>4</sup> We can also take a look at the different energetic states of the electron and their corresponding probability density function around the nucleus(Figure 9). Let's also discuss about the properties of Figure 9 for a moment. The first thing that we can notice that the energy is a set of discrete points and is not continuous. Unlike, the previous two systems, for the  $n$ th energy eigenstate, it doesn't necessarily mean the number of nodes in the probability

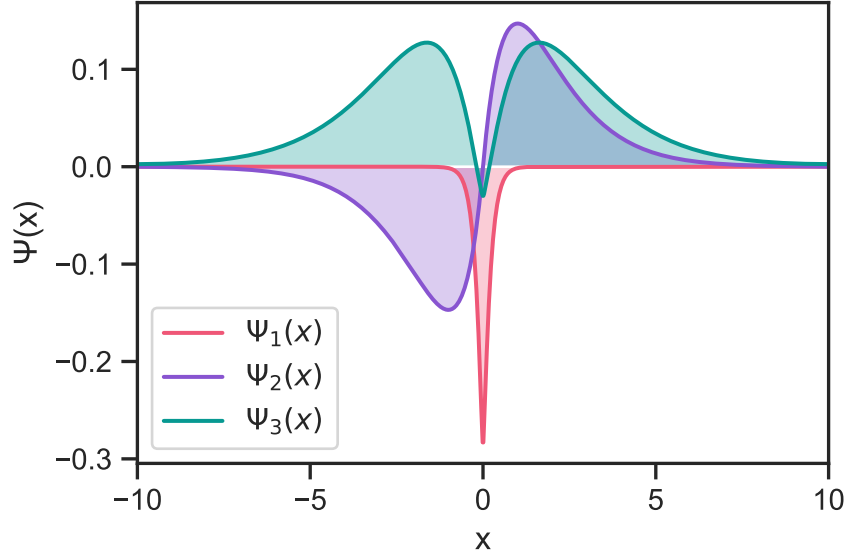
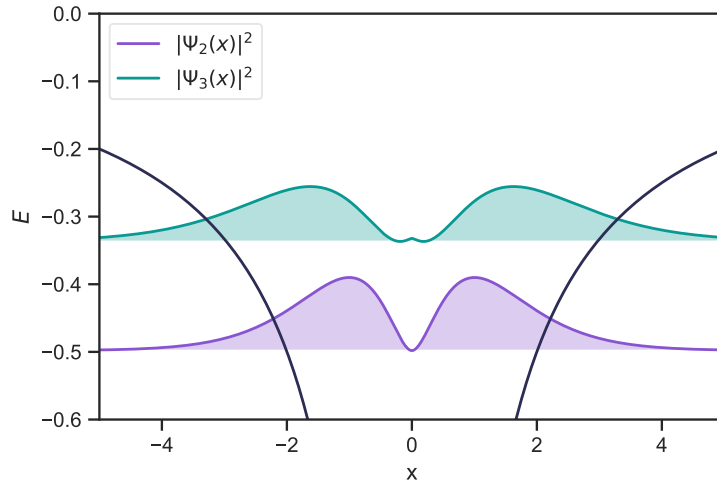


Figure 8: First three wave-functions of a 1d Hydrogen atom

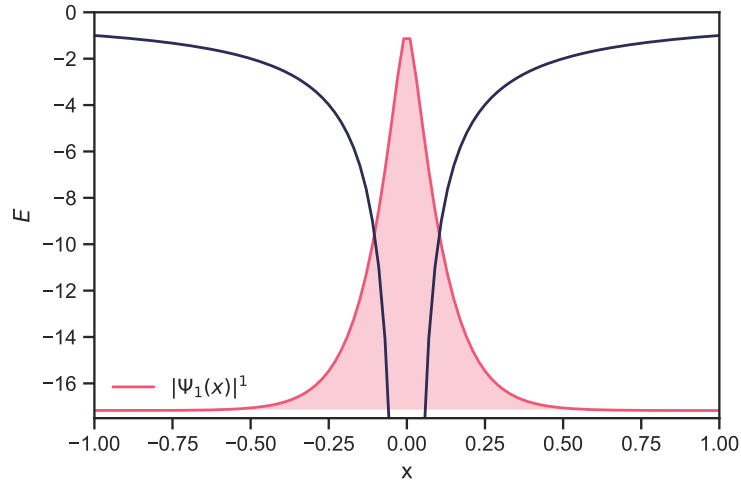
distribution function associated with it is  $n$ . Also, the distance between two energetic states is not constant which is similar to the previous system. And finally, the zero-point energy for this system too is not at 0, instead it is at some finite point which is greater than 0. This means, that the particle in consideration, which is the electron, always has a kinetic energy associated with it and can never be at rest. Also an interesting fact about the third energy state and its distribution function is that it is very similar to the  $d_{z^2}$  atomic orbital. And with that, we that we have solved the time independent Schrödinger equation for our final system, a 1d Hydrogen atom.

## Conclusion

To sum up, we discussed about the time independent Schrödinger equation and solved it for three different systems, which are, a 1d harmonic oscillator, a particle in a 1d box and, a 1d



(a) First two excited states and their probability distribution function of a 1d Hydrogen atom



(b) First energy state and its probability distribution function for a 1d Hydrogen atom

Figure 9: First 3 energy states and their probability distribution function

Hydrogen atom.

We also observed that, the energy for a quantum system comes in packets and is not a continuous spectrum. Also, the zero point energy for a quantum system is not at 0, this signifies that for a quantum system, the particle in consideration can never be at rest and always has some energy associated with it. Also, we found some dissimilarities for these three systems, like the energy gap for a 1d harmonic oscillator is constant but for a particle in a 1d box and a 1d Hydrogen atom it is not.

Also, it is important to mention that the figures that were used in this article, were plotted with different line of codes but for simplicity those were not included in this article, to take a look at how the plots were generated check the referred github repository.<sup>4</sup>

## References

- (1) Shankar, R. Principles of Quantum Mechanics. Plenum Press: New York and London **1994,1980**,
- (2) Tannor, D. Introduction to Quantum Mechanics: A Time-Dependent Perspective. University Science books: Mill Valley, U.S.A **2007**,
- (3) Anon, Particle in a 1-Dimensional box. 2020; <https://chem.libretexts.org/@go/page/1724>.
- (4) Mandal, R. Quantum Mechanics with Python I: Time-Independent Schrodinger Equation. <https://github.com/Rittik03/Code>, 2021.
- (5) Loudon, R. One-dimensional hydrogen atom. Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences **2016**, 472, 20150534.