An-Najah National University

Faculty of Graduate Studies

The Numerical Methods for Solving Schrödinger Equation

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This Thesis is Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Mathematics, Faculty of Graduate Studies, An-Najah National University, Nablus, Palestine.

2019

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Dedication

I dedicate this thesis to all my family members, to my parents, my husband Moath, to my sister, and my brothers, without their patience, understanding, support, and most of all love, this work wouldn't have been possible. I also dedicate this dissertation to my homeland Palestine.

Acknowledgement

At the beginning, I am greatful to God for the completion of this thesis, without whose mercy and clemency nothing would have been possible.

I am thankful to my supervisor, Prof. Naji Qatanani, for his encouragement and support to develop and understand the topic of my research.

My thanks also to my internal examiner Dr. Adnan Daraghmeh and my external examiner Dr. Abdelhalim Ziqan from Arab American University for their positive comments.

I take this opportunity to express gratitude to all my family members for their help and support. I also thank my parents and my husband for the unceasing encouragement, support and attention.

Finally, I offer my thanks and blessing to all of those who supported me in any respect during the completion of this thesis.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان :

The Numerical Methods for Solving Schrödinger Equation

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The Numerical Methods for Solving Schrödinger Equation

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Abstract

Schrödinger equation and its variants are one of the basic equations studied in the field of partial differential equations, and have various applications in geometry, spectral and scattering theory and integrable systems.

In this thesis we review some basic details of quantum mechanics such as Schrödinger equation of both types: these include time-dependent and time-independent Schrödinger equation. Moreover, we focus mainly on some analytical and numerical methods for solving Schrödinger equation and its variants. For the analytical solution of the Schrödinger equation, we use the separation of variables method and method of characteristics. For the numerical handling of this equation, we use the Finite Difference Method (FDM) and Pseudo-Spectral Method (PSM), for two cases of quantum mechanics: finite and infinite square well.

To test the efficiency of these methods, we consider some numerical test cases. Numerical results show clearly that Pseudo-Spectral Method is one of the most powerful numerical technique for solving time independent Schrödinger equation in comparison with the Finite Difference Method.

Introduction

At the beginning of the twentieth century, experimental evidence suggested that atomic particles were also wave-like in nature. For example, electrons were found to give diffraction patterns when passed through a double slit in a similar way to light waves. Therefore, it was reasonable to assume that a wave equation could explain the behavior of atomic particles [11,14].

Schrödinger equation is a type of differential equation known as a wave-equation, which serves as a mathematical model of the moment of waves. Solutions to Schrödinger's equation express not only molecular, atomic and subatomic systems but also macroscopic systems, perhaps even the whole universe. Schrödinger’s equation is central to all applications of quantum mechanics including quantum field theory which incorporate special relativity with quantum mechanics [14]. In mathematics, the Schrödinger equation and its variants are one of the basic equations studied in the field of partial differential equations, and have applications in geometry, spectral and scattering theory, and integrable systems.

In1924, de-Broglie suggested that every moving particle has a wave associated with it, which is also known as matter wave. Furthermore, Erwin Schrödinger, in continuation to de-Broglie’s hypothesis, constructed a differential wave equation of second order to rationalize the wave nature of matter and particle that correlates to wave [11]. Thus the equation is analogous to the equation for waves in optics, which assumes

that the particle behaves as wave and yields solution in terms of a function called the wave function. When this equation is solved, it generates two of the following; namely the wave function φ and the energy E, of the particle under consideration.

In 1926, Irwin Schrödinger inserted de Broglie's wave-like representation of particles into the conservation of energy equation (total energy = kinetic energy plus potential energy) and from this he derived an equation to describe their behavior— which has become known as the Schrödinger wave equation.

Once the wave function φ is known, then everything about the particle is known or can be deduced from the wave function. Thus, the wave function φ is the most important thing, which itself does not have any physical significance, however the absolute square of φ, i.e. $|\varphi|^2$gives the probability of finding the particle in a particular region of space at a particular instant of time [11,14].

A wave equation is an example of an 'equation of motion' which, as the name suggests, can be used to predict the motion of an object. In this case the object is a wave. In other words, if we know the amplitude and velocity of the wave at a given time and place, we can project forward (or backward) and predict the amplitude and velocity of the wave at some other time and place. For example, if one dropps a pebble into a pond it makes a wave of a given height (amplitude) which will decrease with time as the wave spreads. Knowing the rate at which the wave spreads and loses amplitude, we can predict what it will look like in ten seconds, twenty

seconds and so on. Or conversely, we can look at the circular wave pattern at a given time and run the whole thing in reverse to re-create the original pulse created by the pebble.

Essentially, Schrödinger equation has two forms: one consisting of time termed as time dependent equation and the other in which time factor is eliminated and hence named as time independent equation [37]. The solution of Schrödinger equation can be obtained analytically by using the exact solvable models developed by Makowski [22]. On the other hand, numerical methods play a very crucial rule in solving Schrödinger equation. Sandvik [34] has obtained a numerical solution of the Schrödinger equation by using Numerov's method. Marston [24] has described the Fourier grid Hamiltonian method for bound state eigenvalues and eigenfunctions. Monovasilis [28] studied the exponential-fitting symplectic methods for the numerical integration of the Schrödinger equation. Doescher and Rice, in their work [8] studied the infinite square well potential with a moving wall. Jackiewicz technique [17] is used to find the solutions by spectral collocation method and wave method form relaxation methods. Strikwerda [36] has obtained a numerical solution of the Schrödinger equation by using finite difference method. Aronstein and Stroud [1] implemented the general series for finite square-well energy levels for use in wave-packet studies. Robinson and Fairweather [33] have obtained an orthogonal spline collocation method for Schrödinger -type equation in one space variable. Gildener and Patrascioui [13] have shown that the energy spectrum of a one-dimensional system by using the pseudo

spectral contributions. The solution of the differential equations of chemical physics can be obtained by using the spectral difference methods by Mazziotti [26]. Orszag [29] made a comparison of pseudo-spectral and spectral approximation. Also, England and Savari [9] implemented pseudo-spectral method of solving linear ordinary differential equations. Furthermore, Bulirsch, Miele and Stoer [4] have used the direct collocation as numerical method to find the numerical solution of optimal control problems.

For the numerical handling of the Schrödinger equation, we employ the Finite Difference Method (FDM). In order to implement the FDM method, Schrödinger equation is first transformed into a diffusion equation by the imaginary time transformation. The resulting time-domain diffusion equation is then solved numerically by the FDM. In this method, we approximate derivatives using difference equation with errors of order $O(h^n)$ to solve differential equations numerically. This method was first developed by A. Thom in the 1920s [6]. Finite difference procedures approximate the derivative appearing in a partial differential equation by sums and differences of function values at a set of discrete points. These approximations are based on Talyor series expansions of a function of one or more variables [5,6,20,36].

In addition, we will solve the Schrödinger equation by the Pseudo-spectral method, which is a family of numerical methods for the solution of differential equations based on the expansion of basis functions defined on a set of grid points. A pseudo-spectral method is proposed for the

numerical solution of linear Schrödinger equation. The employed method is based on Chebyshev-Gauss-Lobbato quadrature points. Using the pseudo-spectral differentiation matrices, the problem identified is reduced to a system of nonlinear algebraic equations [13,26]. However, this method has already been implemented by England and Savari, in their work [9] studied the pseudo-spectral method of solving linear ordinary differential equations.

This thesis is organized as follows: In chapter one, we review some basic details of quantum mechanics such as Schrödinger equation of both types: these include time-dependent and time-independent Schrödinger equation. In chapter two, we use analytical methods to solve the time-independent Schrödinger equation for three cases, namely, the finite square well, the infinite square well and the harmonic oscillator. Two numerical techniques for solving Schrödinger equation are presented in chapter three, these techniques are finite difference method and pseudo-spectral method for two cases of quantum mechanics: finite and infinite square well. In chapter four, some numerical examples for solving Schrödinger equation including the finite square well and infinite square well are illustrated. Finally, Conclusion are drawn.

Chapter One
Introduction to Schrödinger Equation

Chapter One

Introduction to Schrödinger Equation

In this chapter, we investigate some important concepts related to Schrödinger equation including the derivation of two types of Schrödinger equation, namely: time-dependent and time-independent Schrödinger equation, also we introduce some properties of the solutions of the Schrödinger equation, probability, normalization, and expectation value.

1.1 Schrödinger Equation

For a general quantum system, the Schrödinger equation may be written into the form:

$$i\hbar \frac{\partial}{\partial t}\varphi(x,t) = \hat{H}\varphi(x,t) \tag{1.1}$$

where $\hbar = \frac{h}{2m}$ is the plank constant, $\varphi(x,t)$ is the wave function or state function, i is the imaginary unit, $i\hbar \frac{\partial}{\partial t}$ is the energy operator, and

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

is the Hamiltonian operator, where $V(x)$ represent the real function that illustrates the potential energy (input) of the method.

The Schrödinger equation has two types, in the first one, the time is obvious in the form with certain description and characterization that will show the wave function and how it will change with time. Therefore, the functional equation is known as time-dependent

Schrödinger (TDSE) wave equation for one dimension which can be written as:

$$i\hbar\frac{\partial}{\partial t}\varphi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\varphi(x,t) + V(x)\varphi(x,t) \quad (1.2)$$

or

$$i\hbar\frac{\partial}{\partial t}\varphi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\varphi(x,t), \quad (1.3)$$

where m indicates the mass of the element.

This is typically a second-order linear differential equation, where the visible expression on the left-hand side of the functional equation (1.3) denotes the total energy of the visible particle. The first part on the right-hand side sufficiently denotes the kinetic energy of the particle, while the second part on the right-hand side denotes the potential energy of the particle. There are three important properties of the solution for time-dependent Schrödinger functional equation as the following:

1. The time dependent Schrödinger equation is carefully consistent with energy reservation.

2. The time dependent Schrödinger equation has linear and singular value solution, which suggest that solutions can be typically formed by superposition of two or more independent solutions.

3. The free-particle solution $V(x) = 0$ is harmonious, with a single wave of de Broglie.

The second type of the Schrödinger equation is the time-independent Schrödinger equation (TISE), which is suitable for finding energy values for a one-dimensional system, which can be written as:

$$E\varphi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\varphi(x) + \mathrm{V}(x)\varphi(x). \tag{1.4}$$

We will derive the two types of the Schrödinger equation:

1.2 Derivation of the Time-Independent Schrödinger Equation

We will start with the one-dimensional standard wave equation [10,14]

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{\mathrm{c}^2}\frac{\partial^2 u}{\partial t^2}. \tag{1.5}$$

Using separation of variables,

$$u(x,t) = \psi(x)f(t), \tag{1.6}$$

we have,

$$\frac{\partial^2 u}{\partial x^2} = \frac{\partial^2}{\partial x^2}\varphi(x)\, f(t)$$

$$\frac{\partial^2 u}{\partial t^2} = \psi(x)\frac{\partial^2}{\partial t^2} f(t)$$

then we obtain,

$$f(t)\frac{\partial^2}{\partial x^2}\psi(x) = \frac{1}{\mathrm{c}^2}\psi(x)\frac{\partial^2}{\partial t^2} f(t), \tag{1.7}$$

when we use a standard solution of the wave equation, $f(t) = e^{i\omega t}$, we obtain

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{-\omega^2}{\mathrm{c}^2}\psi(x). \tag{1.8}$$

We want to find the standard form of the Schrödinger equation by using the total energy which contains kinetic and potential energy[17]

$$E = \frac{p^2}{2m} + V(x), \tag{1.9}$$

finally, by using $\omega = 2\pi v$, $\mathrm{c} = v\lambda$, and $h = p\lambda$ we have

$$\frac{\omega^2}{\mathrm{c}^2} = \frac{4\pi^2 v^2}{\mathrm{c}^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m[E-V(x)]}{\hbar^2}, \tag{1.10}$$

Combining equations (1.10) and (1.8) gives

$$\frac{\partial^2}{\partial x^2}\psi(x) = -\frac{2m[E-V(x)]}{\hbar^2}\,\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\psi(x) + \frac{2m[E-V(x)]}{\hbar^2}\,\psi(x) = 0 \tag{1.11}$$

Rearranging equation (1.11) it becomes

$$\frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2}\psi(x)E - \frac{2m}{\hbar^2}\,V(x)\psi(x) = 0, \tag{1.12}$$

Multiplying both side of equation (1.12) by $\frac{-\hbar^2}{2m}$ gives:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) - E\psi(x) + V(x)\psi(x) = 0$$

or

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\psi(x). \tag{1.13}$$

This is the time-independent Schrödinger Equation, which describes the state function of a particle with mass m and potential energy $V(x)$.

Functional equation (1.13) can be expanded sufficiently to the specific case of three dimensions [10]. That is,

$$\frac{-\hbar^2}{2m}\nabla^2\psi(x) + V(x)\psi(x) = E\psi(x) \tag{1.14}$$

where $\nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

Equation (1.14) may take the form [10]

$$\hat{H}\varphi(x) = E\varphi(x).$$

1.3 Derivation of the Time-dependent Schrödinger Equation

There is more than one method to derive time-dependent Schrödinger equation. We will derive it by using the time-independent Schrödinger equation.

The Schrödinger's time-independent equation is:

$$\frac{\partial^2}{\partial x^2}\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \tag{1.15}$$

We assume that a wave function represented as (see [9,36]):

$$\psi = A \cdot e^{-i\omega t} \tag{1.16}$$

where A is the amplitude of the wave, ω is an angular frequency which equal $2\pi v$, and t is the time period.

Differentiating equation (1.16) with respect to t,

$$\frac{\partial\psi}{\partial t} = -i\omega A e^{-i\omega t} = -i(2\pi v)Ae^{-i\omega t} \tag{1.17}$$

since $E = hv$

$$\frac{\partial\psi}{\partial t} = -i\left(\frac{2\pi E}{h}\right)A \cdot e^{-i\omega t} = -i(\frac{2\pi E}{h})\psi$$

$$E\psi = \frac{-h}{2\pi i} \cdot \frac{\partial\psi}{\partial t} = \frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = i\hbar\frac{\partial\psi}{\partial t} \tag{1.18}$$

Substituting equation (1.18) into equation (1.15) gives,

$$\frac{\partial^2}{\partial x^2}\psi + \frac{2m}{\hbar^2}\cdot i\hbar\frac{\partial\psi}{\partial t} - \frac{2mV}{\hbar^2}\psi = 0$$

$$\frac{2mi}{\hbar}\cdot\frac{\partial\psi}{\partial t} = \frac{2mV}{\hbar^2}\psi - \nabla^2\psi \qquad (1.19)$$

Multiplying equation (1.19) by $\frac{\hbar^2}{2m}$, we get

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = V\psi(x,t) - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) \qquad (1.20)$$

this is time-dependent Schrödinger equation with the term:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V = H$$

as the Hamiltonian operator.

Equation (1.20) takes the form [10, 37]

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\varphi(x,t)$$

1.4 Schrödinger's operators

An operator is a rule for construction one function from another. In quantum mechanics, we have just seen that the momentum becomes associated with an operator related to the spatial derivative.

For any function: $f(x) \xrightarrow{\hat{D}}$ another function of x

or

$$\hat{D}\varphi = \acute{\varphi},$$

where $\widehat{D}$ is an operator. Every operator in quantum mechanics can be typically structured from the fundamental factors of both position and momentum.

$$\hat{x}\varphi = x\varphi$$

$$\hat{p}_x\varphi = -i\hbar\frac{d}{dx}\varphi.$$

Definition $(\mathbf{1}.\mathbf{1})$[11,14]: For an operator $\widehat{D}$, if

$$\widehat{D}f(x;D) = Df(x;D)$$

for a given $D \in \mathbb{C}$ where c denotes any complex number, then $f(x)$ denotes an eigenfunction of the operator $\widehat{D}$ and D is the corresponding eigenvalue.

Operators act on the eigenfunctions in a way identical to multiplying the eigenfunction by a constant number as seen in definition (1.1).

To every observable quantity, there is associated corresponding operator. For instance, the momentum operator is

$$\hat{p} = -i\hbar\frac{d}{dx},$$

the position operator is

$$\hat{x} = x$$

the energy operator is

$$\hat{E} = \frac{\hat{p}^2}{2m} + V(\hat{x}) = i\,\hbar\frac{\partial}{\partial x}$$

and so on.

Note that the operator order is important. For instance,

$$\hat{p}\hat{x}f(x) = \hat{p}\big(xf(x)\big) = -i\hbar\frac{d}{dx}\big(xf(x)\big) = -i\hbar\left(f(x) + x\frac{df(x)}{dx}\right), \quad (1.21)$$

while,

$$\hat{x}\hat{p}f(x) = \hat{x}\left(-i\hbar\frac{df(x)}{dx}\right) = -i\hbar x\frac{df(x)}{dx}. \quad (1.22)$$

To measure the importance of order, we define the commutator of two operators $\hat{A}$ and $\hat{B}$ as [11,14]

$$\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}.$$

Subtracting equation (1.21) from equation (1.22) we get

$$\hat{x}\hat{p}f(x) - \hat{p}\hat{x}f(x) = i\hbar f(x) \quad (1.23)$$

1.5 Linear Operators

Definition $(\mathbf{1.1})$[11]: An operator $\hat{A}$ is said to be linear if

$$\hat{A}\big(cf(x)\big) = c\hat{A}f(x) \quad (1.24)$$

and

$$\hat{A}\big(f(x) + g(x)\big) = \hat{A}f(x) + \hat{A}g(x) \quad (1.25)$$

where $f(x)$ and $g(x)$ are any two appropriate functions and c is a complex constant.

Examples: the operators $\hat{x}, \hat{p}, and\ \hat{H}$ are all linear operators.

1.6 Wave function

The wave function defined as a variable quantity that describes the wave characteristics of a particle mathematically.

Note that wave function, denoted by the Greek letter, φ, may be thought of as an expression for the amplitude of the particle wave. The wave function φ must be single-valued, continuous, and finite.

Also, the probability of finding the particle described by a specific wave function φ at a given point and time is proportional to the value of φ^2.

$p(x) = |\varphi(x)|^2$ determines the probability that an object in the state $\varphi(x)$ will be found at position x. The total probability is the probability of the particle that must be unity [11,14,37],

$$\int_{-\infty}^{\infty} |\varphi(x)|^2 \, dx = 1 \qquad (1.26)$$

and this is the normalization requirement which can be satisfied only if the wave function, $\varphi(x)$, does not diverge to infinite.

1.7 Equation of motion of the wave function

Moving to another operator called the Hamiltonian operator which plays an essential part in quantum mechanics. The Hamiltonian operator corresponds to the total energy observable for a free particle of mass m moving in 1-dimension in a potential $V(x)$. The Hamiltonian operator may take the form

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x). \qquad (1.27)$$

In three dimensions, equation (1.27) may take the form [37]:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \qquad (1.28)$$

For many-particle systems, we need to explain the expression for the total energy which includes the kinetic energy of the particles and the potential energy of the system. For two particles in 3-dimensions, functional equation (1.28) may take the form [37]:

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla_1{}^2 - \frac{\hbar^2}{2m}\nabla_2{}^2 + V(\vec{r_1},\vec{r_2}) \quad (1.29)$$

where

$$\nabla_1{}^2 = \frac{\partial^2}{\partial x_1{}^2} + \frac{\partial^2}{\partial y_1{}^2} + \frac{\partial^2}{\partial z_1{}^2}$$

and

$$\nabla_2{}^2 = \frac{\partial^2}{\partial x_2{}^2} + \frac{\partial^2}{\partial y_2{}^2} + \frac{\partial^2}{\partial z_2{}^2}$$

The Hamiltonian operator typically plays an essential role in the time-dependent development of the wave function. time- dependent wave function will have its equation of motion given by the time-dependent Schrödinger equation (TDSE):

$$i\hbar\frac{\partial\varphi}{\partial t} = \widehat{H}\varphi.$$

This obtain a basic equation that describes the movement of a quantum mechanical system.

1.8 Properties of the solutions of the time-independent Schrödinger equation

Considering a free particle where V(x)= 0, the wave function solution can be carefully inserted in the form of a plane wave

$$\varphi(x,t) = Ae^{ikx-i\omega t} \quad (1.30)$$

which as a complex function can be expanded sufficiently in the form

$$\varphi(x,t) = A\cos(kx-\omega t) + iA\sin(kx-\omega t) \quad (1.31)$$

where A is the amplitude of the wave , ω is an angular frequency and t is the time period. The free particle wave function is associated with a known momentum:

$$p = \frac{h}{\lambda} = \frac{hK}{2\pi} = \hbar \mathrm{K}.$$

The time-independent Schrödinger equation is beneficial for finding energy values for a one dimensional system

$$E\varphi(x) = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial x^2}\varphi(x,t) + \mathrm{V}(x)\varphi(x,t). \qquad (1.32)$$

From equation (1.32) we obtain the normalized eigenfunctions:

$$\varphi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x \qquad n = 1,2,3, \ldots. \qquad (1.33)$$

which we will explore it in chapter two.

The solutions of the time-independent Schrödinger equation (TISE) have the following three properties:

1. **Continuity**: The possible solutions to the time-independent Schrödinger equation $\varphi(x)$ and its first derivative $\acute{\varphi}(x)$ must be naturally extended for all values of x (the latter holds for finite potential $V(x)$).
2. **Normalizable**: The possible solutions to the time-independent Schrödinger equation must typically square integrable, i.e. the functional integral of the modulus squared of the wave function over all space must be a finite constant so that the wave function can be normalized to give $\int_{-\infty}^{\infty}|\varphi(x)|^2\,dx = 1$.
3. **Linearity**: Owing to the linearity of the time-independent Schrödinger equation, given two independent solutions $\varphi_1(x)$ and $\varphi_2(x)$, we can construct other solutions by taking an appropriate superposition of these: $\varphi(x) = \alpha_1\varphi_1(x) + \alpha_2\varphi_2(x)$, where $|\alpha_1|^2 + |\alpha_2|^2 = 1$ to ensure normalization.

1.9 Basis of quantum mechanics

Corollary $(\mathbf{1.1})$ **[10,36]**: The function $\varphi(x,t)$ denotes the state of a quantum mechanical system, which depends on space and time coordinates of the particle. This function, called the wave function or state function.

Corollary $(\mathbf{1.2})$ **[11,37]**: To every observable, A, in classical mechanics (e.g energy, position and momentum), there corresponds a linear Hermitian operator, $\hat{A}$ in quantum mechanics.

Corollary $(\mathbf{1.3})[\mathbf{11,37}]$: In any measurement of the observable associated with operator $\hat{A}$, the only values that will ever be available are the eigenvalues (a), which satisfy the eigenvalue equation:

$$\hat{A}\,\varphi_a = a\,\varphi_a, \tag{1.34}$$

where φ_a is the eigenfunction corresponding, respectively, with the eigenvalue a of the operator $\hat{A}$. An arbitrary state can be expanded in the complete set of eigenvectors of $\hat{A}$ ($\hat{A}\varphi_a = a\varphi_a$) as [11,14,37]:

$$\varphi = \sum_a^n c_a\,\varphi_a \tag{1.35}$$

in this specific situation , we only know that the specific measurement of the observable A will be typically yield one of the values (a) with a probability $|c_a|^2$.

Corollary $(\mathbf{1.4})[\mathbf{11,14,37}]$**:** If a system is in a state which is typically related by a normalized wave function φ, then the average value of the observable corresponding to $\hat{A}$ is given by:

$$\langle\hat{A}\rangle = \int_{-\infty}^{\infty} \varphi^*(x)\,\hat{A}\varphi(x)dx \tag{1.36}$$

and

$$\Delta A \equiv \sqrt{\langle A^2\rangle - \langle A\rangle^2}$$

1.10 Stationary States

By separation the space and time dependence of the Schrödinger equation as

$$\varphi(x,\mathrm{t})= \varphi(x)\mathrm{g}(\mathrm{t})$$

then the concept of a stationary state arises naturally. It then turns out that the separation of the partial differential Schrödinger equation is possible only if

1- $\widehat{H}$ is time independent,

2- $\varphi(x)$ is an eigenfunction of $\widehat{H}$,

that is, φ must be a solution of the time-independent Schrödinger equation, $\widehat{H}\varphi(x) = E\varphi(x)$.

It is then easy to find $g(t)$. We consider the time-dependent Schrödinger equation [36]:

$$i\hbar\frac{\partial}{\partial \mathrm{t}}\varphi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \mathrm{V}(x)\right)\varphi(x,t) = \widehat{H}\varphi(x,t) \qquad (1.37)$$

We assume that the potential energy in the Hamiltonian operator in equation (1.37) to be time-independent, i.e ($V = V(x)$).

To solve equation (1.37) we use the separation of variables method. Let

$$\varphi(x,\mathrm{t}) = \mathrm{g}(\mathrm{t})\varphi(x)$$

Inserting the above equation into equation (1.37) yields:

$$i\hbar\varphi(x)\frac{\partial g(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\varphi(x)}{\partial x^2}g(t) + V(x)\varphi(x)g(t) \qquad (1.38)$$

Dividing both sides of equation (1.38) $by\ \varphi(x)g(t)$ gives:

$$i\hbar\frac{1}{g(t)}\frac{\partial g(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{1}{\varphi(x)}\frac{\partial^2\varphi(x)}{\partial x^2} + V(x). \qquad (1.39)$$

Both sides of equation (1.39) must be equal to a constant, since the left-hand side is only dependent on t and the right-hand side only on x, which we can denote E. Thus we have two separated sides as:

$$i\hbar\frac{1}{g(t)}\frac{\partial g(t)}{\partial t} = E \quad \Rightarrow \frac{dg}{g} = -\frac{i}{\hbar}Edt$$

$$\ln(g) = -\frac{i}{\hbar}Et + const. \quad \Rightarrow g(t) = const.\, e^{-iEt/\hbar} \qquad (1.40)$$

So, we have

$$\varphi(x,t) = \varphi(x)\, e^{-iEt/\hbar}$$

This is called a stationary solution of the Schrödinger equation, because:

- The probability density is time-independent

$$|\varphi(x,t)|^2 = \varphi^*(x)\varphi(x)e^{iEt/\hbar}e^{-iEt/\hbar} = |\varphi(x)|^2 \qquad (1.41)$$

The spatial part of the wave function satisfies the time-independent Schrödinger equation.

- all operators which do not depend explicitly on time, like $x, p_x, E\ etc$, have time-independent expectation values in the stationary state $\varphi(x,t)$. Thus, if $A = A(x,p_x)$, then

$$\langle A(x,p_x)\rangle = \int \varphi^*(x)e^{iEt/\hbar}\, A(x, -i\hbar\frac{d}{dx})\varphi(x)e^{-iEt/\hbar}\, dx$$

$$= \int \varphi^*(x)\, A(x, -i\hbar\tfrac{d}{dx})\varphi(x)dx = \text{constant.} \qquad (1.42)$$

Theorem $(\mathbf{1.1})[\mathbf{37}]$: **(Time-independent Schrödinger equation)**

$$\hat{\mathrm{H}}\varphi(x) = \mathrm{E}\varphi(x)$$

where $\hat{H} = -\frac{\hbar^2}{2m}\nabla + V(x)$ is the Hamiltonian.

Definition $(\mathbf{1.2})[\mathbf{11}, \mathbf{14}, \mathbf{37}]$: A state is called stable if it is performed by the wave function:

$$\varphi(x, \mathrm{t}) = \varphi(x)\, e^{-iEt/\hbar}$$

Corollary $(\mathbf{1.5})[\mathbf{11}, \mathbf{14}]$: As a direct result, the eigenvalues of the Hamiltonian, which represent the potential energy levels of the system, are clearly time-independent.

To see this, just take $\hat{H}(x, p_x)$ instead of $A(x, p_x)$ in equation (1.42) and use the time-independent Schrödinger equation (Theorem 1.1)

$$\langle \hat{H}(x, p_x) \rangle = \int \varphi^*(x)\, H\, \varphi(x)\, dx = \int \varphi^*(x)\, E\, \varphi(x) dx =$$

$$E\left(\int \varphi(x)\varphi^*(x) dx\right). \qquad (1.43)$$

The value of this integration is finite.

Chapter Two
Analytical Methods

Chapter Two

Analytical Methods

2.1 Introduction

In this chapter we attempt to solve the time-independent Schrödinger equation analytically. This include the following three cases: the infinite potential well, the finite potential well and the quantum harmonic oscillator.

2.2 Infinite square well

Regarding the infinite square well, the particle exists only in the finite interval [0, L]. Such that [8],

$$V(x) = \begin{cases} 0, & x \in [0, L] \\ \infty, & else \end{cases} \tag{2.1}$$

which sufficiently indicate that the quantum object is carefully restricted to a specific area between $x = 0$ and $x = L$ it moves freely but cannot escape. Therefore, mathematically we have.

outside region: $\varphi(x) = 0 \quad for\ x \notin [0, \mathrm{L}]$ (2.2)

inside region: $\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2} = E\varphi$, this is time-independent Schrödinger equation.

and,

$$\psi(0) = 0 \text{ and } \psi(L) = 0 \tag{2.3}$$

this because φ must be continuous.

Taking into Consideration any sample point $\psi(x_k)$, $x_k \notin [0, \mathrm{L}]$, there is no $\psi(x_k)$ will visible in the system of linear equations, since each $\psi(x_k) = 0$.

The wave functions, ψ, are eigenvectors of the Hamiltonian operator, and satisfy equation:

$$\hat{H}\psi = E\psi \tag{2.4}$$

we recall that the Hamiltonian is simply the sum of the kinetic and potential energies, so equation (2.4) becomes

$$\hat{\mathrm{H}}\psi = E\psi$$

$$\left[\hat{K} + \hat{V}\right]\psi = E\psi \tag{2.5}$$

we know that the kinetic energy of the particle is

$$K = \frac{\sqrt{2mE}}{\hbar}, K^2 = \frac{2mE}{\hbar^2} \tag{2.6}$$

Substituting equation (2.6) into equation (2.5), we get [24]

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x) = \frac{K^2\hbar^2}{2m}\,\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\psi(x) = -K^2\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\psi(x) + K^2\psi(x) = 0 \tag{2.7}$$

Equation (2.7) has the general solution:

$$\psi(x) = a\sin(Kx) + b\cos(Kx) \tag{2.8}$$

a and b are two constants that are being specified by the boundary conditions

$$\psi(0) = 0 \text{ and } \psi(L) = 0 \,, \tag{2.9}$$

beginning with $\psi(0) = 0$,

$$\psi(0) = a\sin(0) + b\cos(0) = 0 \quad \Rightarrow \quad b = 0 \tag{2.10}$$

from the second boundary condition $\psi(L) = 0$ then implies

$$\psi(L) = a\sin(KL) = \ 0 \tag{2.11}$$

it is assumed that $a \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear. The condition that $\sin KL = 0$ implies that

$$KL = n\pi \quad \Rightarrow \quad K = \frac{n\pi}{L}, \tag{2.12}$$

where $n = 1,2,3,\ldots$ can be any natural number.

Substituting equation (2.12) into equation (2.6) to obtain

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}\,, \tag{2.13}$$

from equation (2.13) we can see that:

1. the energy is finite [7],
2. $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$, $E_2 = \frac{4\pi^2\hbar^2}{2mL^2} = 4E_1$, $E_3 = \frac{9\pi^2\hbar^2}{2mL^2} = 9E_1$, …..
3. $E_{min} = E_1 \neq 0$ $(zero\ point\ energy)$.
4. As $L \to \infty, E_{min} = 0$.

5. As $m \to \infty, E_{min} = 0$.

6. We know that $K = \frac{n\pi}{L} = \frac{2\pi}{\lambda}$, so $L = \frac{n\lambda}{2}$.

The eigenfunctions in equation (2.8) with $b = 0$ and $K = \frac{n\pi}{L}$, is given by:

$$\psi_n(x) = a \sin\frac{n\pi x}{L}, \qquad n = 1,2,3, \ldots \qquad (2.14)$$

Finally, we get the value of the constant (a) from the normalization of the wave function.

$$\int_0^L |\psi_n|^2 dx = 1 \qquad (2.15)$$

the integration running over the domain of the particle, $0 \leq x \leq L$. Substituting equation (2.14) into equation (2.15)[9,12,30],

$$|a|^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx = |a|^2 \frac{L}{n\pi} \int_0^{n\pi} \sin^2\theta \; d\theta = |a|^2 \frac{L}{2} = 1. \qquad (2.16)$$

We have made the substitution $\theta = \frac{n\pi x}{L}$ and used the fact that the average value of $\sin^2\theta$ over an integral of half wavelengths equals $\frac{1}{2}$. From equation (2.16) we can identify the normalization constant $a = (\frac{2}{L})^{1/2}$ for all values of n. Thus, we obtain the normalized eigenfunctions:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \cos(\frac{n\pi}{L}x), \qquad n = 1,3,5, \ldots \qquad (2.17)$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right), \qquad n = 2,4,6 \ldots \qquad (2.18)$$

For $n = 1$ we get the bound state of the energy E_1 and wave function ψ_1, for $n > 1$ are named excited states.

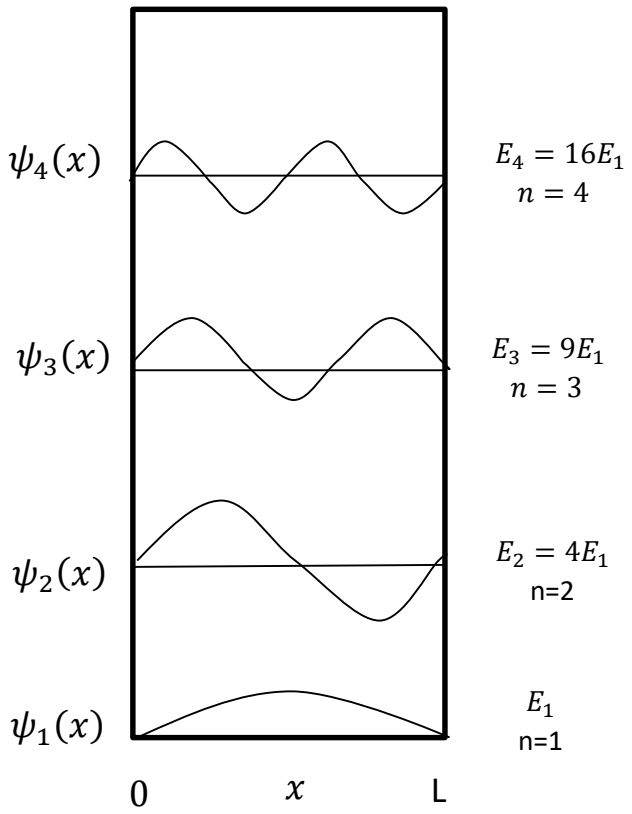


Figure 1.1: Eigenfunctions and the energy for a particle in a box

2.3 Finite square well

In this section we want to solve the finite square well. Consider the potential shown in

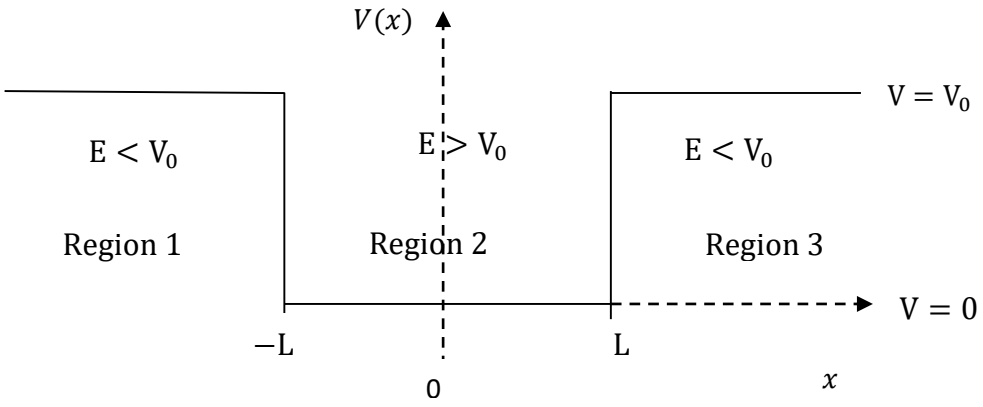


Figure 1.2: A finite square well, depth V_0, width 2L.

Since we have a symmetric well, we must focus on the positive half of the x -axis since we know $\varphi(-x) = \varphi(x)$ for the even parity states such as (ground, second excited, and forth exited state) and $\varphi(-x) = -\varphi(x)$ for odd parity states (such as for the first excited, third excited, and fifth excited state) [1].

2.3.1 Bound states

Region 1:

$x \leq -L, V(x) = V_0$,

similarly, to region 3, the solutions are:

$\psi(x) = Fe^{\alpha x} + Qe^{-\alpha x}$,

but since $\psi \to 0$ as $x \to -\infty$, $Q = 0$

we get $\psi = Fe^{\alpha x}$ for region 1.

Region 2:

$-L < x < L, V(x) = 0.$

substituting into these equation:

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x) = E\,\psi(x) \Rightarrow \frac{\partial^2}{\partial x^2}\psi(x) = -\frac{2m}{\hbar^2}E\,\psi(x)$$

meaning

$$\frac{\partial^2}{\partial x^2}\psi(x) = -K^2\,\psi(x) \text{ with } K^2 = \frac{2mE}{\hbar^2}.$$

The solutions to this equation is [1]

$$\psi(x) = A\sin(Kx) + B\cos(Kx)$$

Region 3:

$x \geq \mathrm{L}, V(x) = V_0$, the Schrödinger equation becomes:

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi + V_0\psi(x) = E\,\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\psi = \frac{2m}{\hbar^2}(V_0 - E)\psi \qquad (2.19)$$

yielding

$\frac{\partial^2}{\partial x^2}\psi = \alpha^2\psi$, with $\alpha^2 = \frac{2m}{\hbar^2}(V_0 - E) > 0$

So,

$\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$, which is real.

The solutions to this differential equation are:

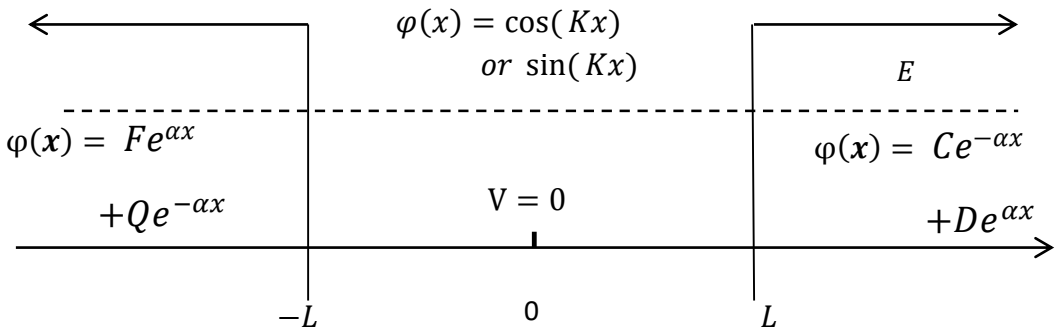
$$\psi(x) = Ce^{-\alpha x} + De^{\alpha x},$$

but since $\psi \to 0$ as $x \to \infty$, $D = 0$

we get $\psi = Ce^{-\alpha x}$ for region 3.

We want to determine the value of the energy E and the other coefficients (C, D, F, Q) The symmetry of the well allow us to choose even or odd functions, which means cosine or sine solution in the central region depending on which n state we want.

The parity condition $\varphi(x) = \pm\varphi(-x)$ allows us to join the coefficients in the area $x \leq -L$ to the coefficients in the area $x \geq L$ [1]. Here is a graphic summery of which solutions apply in which regions.



This leaves us with three unknowns: $(E, C, D)$and right now we have three boundary conditions to consider: the continuity of the wave function and the continuity of its derivative. The last boundary condition is that the wave function must have a sensible behavior at infinity [1,23]. That is, $\varphi(x)$ is finite at infinity, we require $\varphi(x)$ to be finite as $x \to \pm\infty$.

The finite behavior at infinity is a powerful condition since it tells us that $D = 0$ and we must have $\varphi(x) = Ce^{-\alpha x}$ in the region $x \geq L$. For the even parity states we select a cosine function for the well center point. We start with the wave function continuity condition which requires

$$\varphi(L)_{left} = \varphi(L)_{right}$$

$$\cos(KL) = Ce^{-\alpha L} \tag{2.20}$$

To apply the continuity of the derivative condition, we begin by taking the derivative of the wave functions [33]:

$$\frac{\partial \cos(\mathrm{K}x)}{\partial x}_{x=\mathrm{L}} = -\mathrm{K}\sin(\mathrm{K}x)_{x=\mathrm{L}} = -\mathrm{K}\sin(\mathrm{KL})$$

$$\frac{\partial \mathrm{Ce}^{-\alpha x}}{\partial x}_{x=\mathrm{L}} = -\alpha \mathrm{Ce}^{-\alpha x}{}_{x=\mathrm{L}} = -\alpha \mathrm{Ce}^{-\alpha \mathrm{L}},$$

hence the condition $\frac{\partial \varphi(\mathrm{L})}{\partial x}_{\text{left}} = \frac{\partial \varphi(\mathrm{L})}{\partial x}_{\text{right}}$ gives :

$$-K\sin(KL) = -\alpha Ce^{-\alpha L} \tag{2.21}$$

From equations (2.20) and (2.21) we obtain:

$$K\tan(KL) = \alpha,$$

inserting expressions for K and α as a function of E we have,

$$\sqrt{\frac{2mE}{\hbar^2}}\,\tan(L\sqrt{\frac{2mE}{\hbar^2}}) = \sqrt{\frac{2m(V-E)}{\hbar^2}},$$

taking out the common factor of $\sqrt{\frac{2m}{\hbar^2}}$ leaves us with the transcendental equation:

$$\sqrt{E}\,\tan(L\sqrt{\frac{2mE}{\hbar^2}}) = \sqrt{V-E} \qquad (2.22)$$

We want to solve equation (2.22) by graphing the left and right sides of the equation on a semilog graph. Logical solutions happened at the intersection of the two plots. We take V= 50 eV.

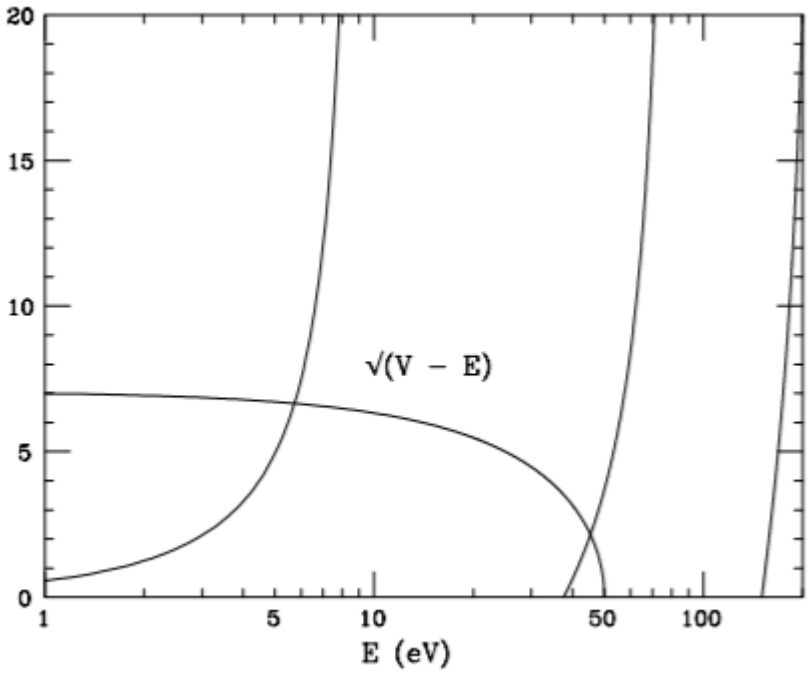


Figure 1.3: A semilog graph for the energy of finite square well.

There are precisely two intersections, as a result, there are two even bound states in the well n = 1 and n = 3. One of the even bound states happens at $E = 5.72\ eV$, the other happens near the peak of

the well at a power of $E = 45.4\ eV$. There is an odd bound state corresponding respectively to $n = 2$ at roughly $20\ eV$.

2.4 The quantum harmonic oscillator

The quantum harmonic oscillator is very important in quantum mechanics, is a very useful solution in both approximations and in exact solutions of various problems.

The harmonic oscillator is described by the Hamiltonian**:**

$$\widehat{H} = \frac{\hat{\mathrm{p}}^2}{2m} + \frac{1}{2}\mathrm{k}\hat{x}^2 = \frac{\hat{\mathrm{p}}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2, \qquad (2.23)$$

where m is the particle's mass, k is the force constant, $\omega = \sqrt{\frac{k}{m}}$ is the angular frequency of the oscillator, $\hat{x}$ is the position operator (given by x), and $\hat{\mathrm{p}}$ is the momentum operator (given by $\hat{\mathrm{p}} = -i\,\hbar\frac{\partial}{\partial x}$). The initial concept in the Hamiltonian intentionally introduces the kinetic energy of the fundamental particle [7], and the second key concept introduces its potential energy.

First, we have to sufficiently identify what is meant by the energy eigenstate of the possible solution of the Schrödinger equation.

The energy quantity = $\hbar\omega = \frac{\hbar^2}{m\,a^2} = m\omega^2 a^2$,

thus $a^4 = \frac{\hbar^2}{m^2\,\omega^2} \rightarrow a^2 = \frac{\hbar}{m\ \omega}$, where a is the length.

The Schrödinger equation of the harmonic oscillator is:

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2} + \frac{1}{2}m\omega^2 x^2\varphi = E\varphi \qquad (2.24)$$

with boundary condition:

$$\varphi(x) \to 0 \text{ as } |x| \to \infty \,. \tag{2.25}$$

Multiplying equation (2.24) by $\frac{2}{\hbar\omega}$, we get:

$$-\frac{\hbar}{m\omega}\frac{d^2\varphi}{dx^2} + \frac{m\omega}{\hbar}x^2\varphi = \frac{2E}{\hbar\omega}\varphi \,, \tag{2.26}$$

let $\varepsilon = \frac{2E}{\hbar\omega}$ be the dimensionless value of the energy, so equation (2.26) takes the form:

$$-\frac{\hbar}{m\omega}\frac{d^2\varphi}{dx^2} + \frac{m\omega}{\hbar}x^2\varphi = \varepsilon\varphi, \tag{2.27}$$

let, $$x = au \,, \tag{2.28}$$

where a is the length and u is the new variable of differential equation.

Differentiating both sides of equation (2.28) with respect to x,

$$\frac{d}{dx} = \frac{1}{a}\frac{d}{du} \to \frac{d^2}{dx^2} = \frac{1}{a^2}\frac{d^2}{du^2}$$

so, equation (2.27) may take the form :

$$-\frac{d^2\varphi}{du^2} + u^2\varphi = \varepsilon\varphi \tag{2.29}$$

when $\varepsilon \to \infty$, the equation becomes $\acute{\varphi} = u^2\varphi$,

let $\varphi = u^{\mu}e^{\alpha u^2/2}$, where α is any number.

$$\acute{\varphi} = \alpha u u^{\mu}e^{\alpha u^2/2} + \mu u^{\mu-1}e^{\alpha u^2/2},$$

$$\acute{\phi} = (\alpha u)^2 u^{\mu}\, e^{\alpha u^2/2} + \ldots\ldots\ldots\ldots$$

$$\acute{\phi} = \alpha^2 u^2 u^{\mu}\, e^{\alpha u^2/2}\left[1 + \frac{2\mu+1}{\alpha}\frac{1}{u^2} + \frac{\mu(\mu-1)}{\alpha^2}\frac{1}{u^4}\right]$$

$$= \alpha^2 u^2 \varphi\, \left[1 + \frac{2\mu+1}{\alpha}\frac{1}{u^2} + \frac{\mu(\mu-1)}{\alpha^2}\frac{1}{u^4}\right].$$

When $u \to \infty, \alpha^2 = 1$ since $\acute{\phi} = u^2\varphi$.

$$\varphi(u) = Au^{\mu}\, e^{-u^2/2} + Bu^{\mu}\, e^{u^2/2}, \qquad (2.30)$$

In equation (2.30) , $B = 0$ for $|u| \to \infty$.

Let, $\varphi(u) = h(u)e^{-u^2/2}$, (2.31)

where $h(u)$ an arbitrary function.

Substituting equation (2.31) into equation (2.29) to obtain:

$$\frac{d^2h}{du^2} - 2u\frac{dh}{du} + (\varepsilon - 1)h = 0, \qquad (2.32)$$

solving equation (2.32) by a power series expansions, so,

$$h(u) = \sum_{j=0}^{\infty} a_j u^j, \qquad (2.33)$$

$$\frac{dh}{du} = \sum_{j=0}^{\infty} j\, a_j u^{j-1}, \qquad (2.34)$$

$$\frac{d^2h}{du^2} = \sum_{j=0}^{\infty} j(j-1)a_j u^{j-2} = \sum_{j=2}^{\infty} j(j-1)a_j u^{j-2}, \qquad (2.35)$$

Suppose that, $j = \acute{j} + 2$, equation (2.35) become:

$$\frac{d^2h}{du^2} = \sum_{\acute{j}=0}^{\infty} (\acute{j}+2)(\acute{j}+1)a_{\acute{j}+2}u^{\acute{j}} = \sum_{j=0}^{\infty} (j+2)(j+1)a_{j+2}u^{j}, \qquad (2.36)$$

Substituting equations (2.33), (2.34), (2.35) and (2.36) into equation (2.32), we get:

$$\sum_{j=0}^{\infty}((j+2)(j+1)\,a_{j+2} - 2ja_j + (\varepsilon - 1)a_j)u^j = 0$$

$$\sum_{j=0}^{\infty}((j+2)(j+1)\,a_{j+2} - (2j+1-\varepsilon)a_j)u^j = 0, \quad (2.37)$$

from equation (2.37), we get this relation:

$$a_{j+2} = \frac{(2j+1-\varepsilon)}{(j+2)(j+1)}\,a_j. \quad (2.38)$$

Possible solutions fixed by given a_0, a_1 $\left(h(0), \acute{h}(0)\right)$, where from a_0 we can properly fixed a_2, a_4, ... even solutions, and from a_1 we can fixed a_3, a_5, ... odd solutions.

Now, to terminate the series we can choose

$$2j + 1 - \varepsilon = 0, \quad (2.39)$$

this will make $a_{j+2} = 0$.

So the solution $h(u) = a_j u^j + a_{j-2}u^{j-2} + \cdots$

call $j = n$, we get $h(u) = a_n u^n + a_{n-2}u^{n-2} + \cdots$

equation (2.39) become:

$$2n + 1 - \varepsilon_n = 0, \quad (2.40)$$

from equation (2.40), we get

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

where E_n is the energy of the harmonic oscillator

$$E_n = \frac{\hbar\omega}{2}(2n+1) = \hbar\omega\left(\mathrm{n} + \frac{1}{2}\right) \quad (2.41)$$

$$H_n(u) = 2^n u^n + O(u^{n-2}) \qquad (2.42)$$

Here, $H_n(u)$ is a polynomial of degree *n* called *a* Hermite polynomial. The first four Hermite polynomials are

$$H_0(u)=1$$

$$H_1(u) = 2u$$

$$H_2(u) = 4u^2 - 2$$

$$H_3(u) = 8u^3 - 12u$$

A few sample wave functions are given in Figure 1.3. As the value of the principal number increases, the solutions alternate between even functions and odd functions about *x*=0.

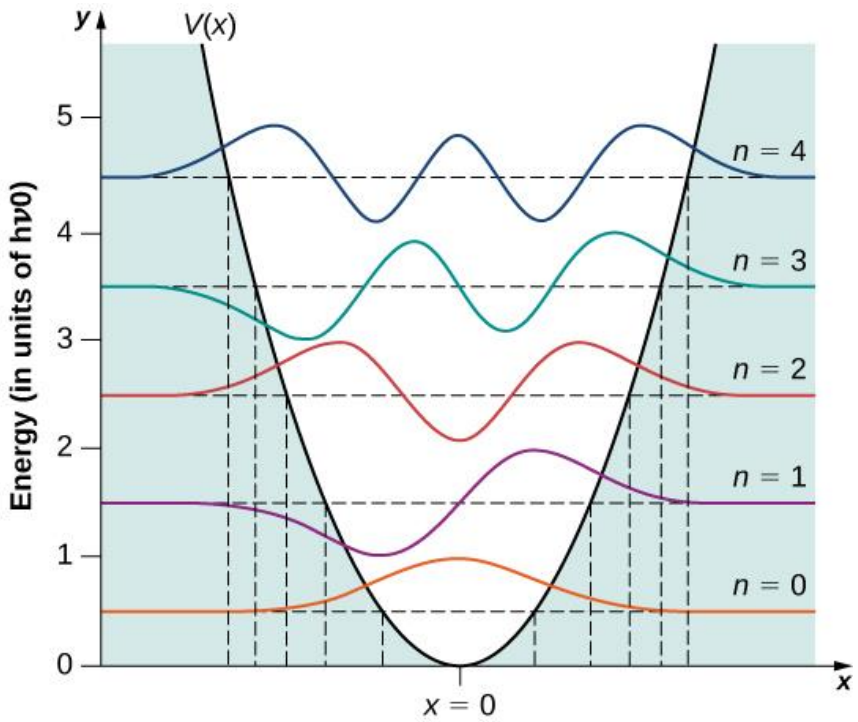


Figure 1.4: The first five wavefunctions of the quantum harmonic oscillator.

The solution of the quantum harmonic oscillator is:

$$\varphi_n = H_n(u)e^{-u^2/2}$$

$$\varphi_n(x) = H_n\left(\frac{x}{a}\right)e^{-x^2/2a^2}$$

Chapter Three
Numerical Techniques for Solving Schrödinger Equation

Chapter Three

Numerical Techniques for Solving Schrödinger Equation

In this chapter, we attempt to solve the Schrödinger equation and its variants numerically. This involves using the finite difference and the pseudo-spectral methods.

3.1 Finite Difference Method (FDM)

This method replaces the partial derivatives of the dependent variable (unknown function) with a partial differential equation using finite difference approximations with errors.

This procedure transforms the region (where the independent variables in PDE are defined on) to a mesh grid of points where the dependent variables are approximated [5,20,36]. The possible replacement of partial derivatives with various approximation formulas depends on Taylor's Theorem. Hence, Taylor's Theorem is presented.

3.2 Taylor's Theorem [5,36]

Let $\varphi(x)$ has $n \in N$ continuous derivatives over the interval (a, b). Then, for $a < x_0, x_0 + h < b$, we can write the value of $\varphi(x)$ and its derivatives nearby the point $x_0 + h$ as follows:

$$\varphi(x_0 + \Delta x) = \varphi(x_0) + \frac{\acute{\varphi}(x_0)}{1!}(x - x_0) + \frac{\acute{\acute{\varphi}}(x_0)}{2!}(x - x_0)^2 + \frac{\acute{\acute{\acute{\varphi}}}(x_0)}{3!}(x - x_0)^3 + ..$$

$$\varphi(x_0 + h) = \varphi(x_0) + h\acute{\varphi}(x_0) + \frac{h^2}{2!}\acute{\acute{\varphi}}(x_0) + \frac{h^3}{3!}\acute{\acute{\acute{\varphi}}}(x_0) + .. + \frac{h^{n-1}}{(n-1)!}\varphi^{(n-1)}(x_0) + O(h^n) \quad (3.1)$$

which can be written in the more compact notation as

$$\sum_{n=0}^{\infty} \frac{\varphi^{(n)}(x_0)}{n!}(x - x_0)^n + O(h^n)$$

where

1. $\acute{\varphi}(x_0)$ is the first derivative of φ with recognition to x at the specific point x_0.
2. $\varphi^{(n-1)}(x_0)$ is the $n - 1^{th}$ derivative of φ with respect to x at the point x_0.
3. $O(h^n)$ denotes an unknown error term that satisfies the property: for $\varphi(h) = O(h^n)$

$$\lim_{h \to 0} \frac{\varphi(h)}{h^n} = c, \text{ for any nonzero constant c.}$$

When we eliminate the error term, $O(h^n)$, from the right-hand side of functional equation (3.1), we get an approximation to $\varphi(x_0 + h)$. the forward–difference formula for approximating $\acute{\varphi}(x_0)$

$$\acute{\varphi}(x_0) \cong \frac{\varphi(x_0 + \Delta x) - \varphi(x_0)}{\Delta x} + O(\Delta x),$$

The backward−difference formula

$$\acute{\varphi}(x_0) = \frac{\varphi(x_0) - \varphi(x_0 - \Delta x)}{\Delta x} + O(\Delta x),$$

and the central–difference formula

$$\acute{\varphi}(x_0) = \frac{\varphi(x_0 + \Delta x) - \varphi(x_0 - \Delta x)}{2\Delta x} + O(\Delta x)^2,$$

and we have also

$$\acute{\acute{\varphi}}(x_0) \cong \frac{\varphi(x_0 + \Delta x) - 2\varphi(x_0) + \varphi(x_0 - \Delta x)}{\Delta x^2} + O(\Delta x)^2.$$

To find the numerical solution to partial differential equation with finite difference method, we discretize the domain D of the given problem [5,20,36,37].

3.3 Strategy of Discretization

We start implementing the finite difference method to Schrödinger equation (3.2),

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x_i, t_j) + V(x_i, t_j)\psi(x_i, t_j) = i\hbar\frac{\partial}{\partial t}\varphi(x_i, t_j), \text{ for}(x, t) \in R \quad (3.2)$$

The rectangular domain $R = \{(x, t)|a < x < b, c < t < d\}$ and $\varphi(x, t) = g(x, t)$ for any $(x, t) \in S$, where: S denotes the boundary of a region R, $g(x, t)$ is continuous on S.

Now, we will use the finite difference algorithm for solving the time-independent Schrödinger equation [5,35]:

The Finite Difference Algorithm

Step 1: Choose positive integers N and M.

Step 2: Define $\Delta x = h = \frac{b-a}{N}$ and $\Delta t = k = \frac{d-c}{M}$.

This step partitions the interval [a, b] into N equal parts of width h and partitions the interval [c, d] into M equal parts of width k as step 3 illustrates.

Step 3: Define the mesh point (x_i, t_j) as

$$x_i = a + ih, \quad i = 0,1,2,\ldots\ldots,N$$

$$t_j = jk, \quad j = 0,1,2,\ldots\ldots,M$$

Step 2 and step 3 are illustrated in figure 1.4.

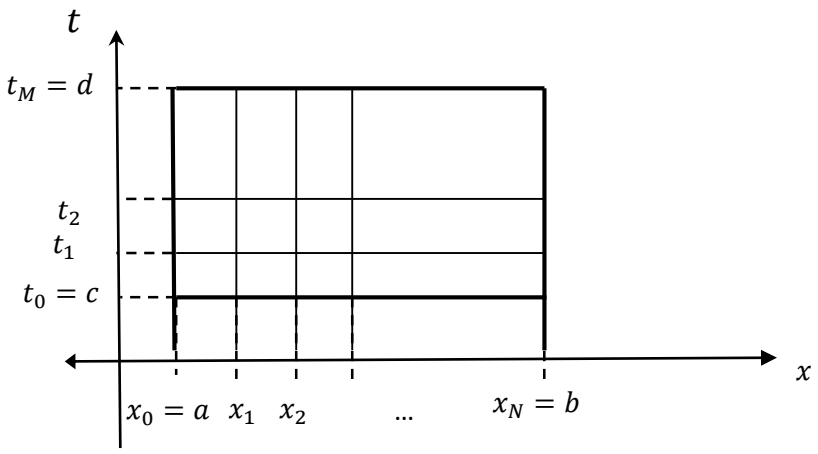


Figure 1.5: Grid lines and mesh points of the grid using Finite difference method.

It is clear from figure 1.5 that we obtain horizontal and vertical lines inside the rectangle R. These lines are called "grid lines" and

their intersections are named "mesh points" of the grid. For each mesh point inside the grid, (x_i, t_j), $i = 1,2,\dots,N-1$ and $j = 1,2,\dots,M-1$ [2,5]. We use Taylor series in the variable x about t to generate the central-difference formula:

$$\frac{\partial^2}{\partial x^2}\varphi(x_i,t_j) = \frac{\varphi(x_{i+1},t_j)-2\varphi(x_i,t_j)+\varphi(x_{i-1},t_j)}{\hbar^2} - \frac{\hbar^2}{12}\cdot\frac{\partial^4}{\partial x^4}\varphi(\xi_i,t_j) \qquad (3.3)$$

$where\ \xi_i \in (x_{i-1}, x_{i+1})$.

In addition, we use Taylor series in the variable t about x to generate the forward-difference formula [2,5]:

$$\frac{\partial}{\partial t}\varphi(x_i,t_j) = \frac{\varphi(x_i,t_{j+1})-\varphi(x_i,t_j)}{\tilde{k}} - \frac{\tilde{k}}{2}\frac{\partial^2}{\partial t^2}\varphi(x_i,\xi_j) \qquad (3.4)$$

where $(x_i, \xi_j) \in (t_j, t_{j+1})$.

Substituting equation (3.3) and equation (3.4) into equation (3.2), we get:

$$i\hbar\frac{\varphi(x_i,t_{j+1})-\varphi(x_i,t_j)}{k} - \frac{k}{2}\cdot\frac{\partial^2}{\partial t^2}\varphi(x_i,\xi_j) =$$

$$\frac{-\hbar^2}{2m}\frac{\varphi(x_{i+1},t_j)-2\varphi(x_i,t_j)+\varphi(x_{i-1},t_j)}{h^2} - \frac{h^2}{12}\cdot\frac{\partial^4}{\partial x^4}\varphi(\xi_j,t_j) + V(x_i)\varphi(x_i,t_j) \qquad (3.5)$$

For each $i = 1,2,3,\dots,n-1$ and $j = 1,2,3,\dots\dots,m-1$.

Rearranging equation (3.5), we get:

$$\frac{-i\hbar\varphi(x_i,t_j)}{k} - \frac{\hbar^2}{m}\cdot\frac{\varphi(x_i,t_j)}{h^2} - V(x_i)\varphi(x_i,t_j) + \frac{i\hbar\varphi(x_i,t_{j+1})}{k} +$$

$$\frac{\hbar^2}{2m}\cdot\frac{\varphi(x_{i+1},t_j)+\varphi(x_{i-1},t_j)}{h^2} = \frac{k}{2}\cdot\frac{\partial^2}{\partial t^2}\varphi(x_i,\xi_j) - \frac{h^2}{12}\cdot\frac{\partial^4}{\partial x^4}\varphi(\xi_i,t_j)$$

or it can simply be written as

$$[\frac{-i\hbar}{k} - \frac{\hbar^2}{mh^2} - V(x_i)]\varphi(x_i,t_j) + i\hbar\frac{\varphi(x_i,t_{j+1})}{k} + \frac{\hbar^2}{2m}\cdot\frac{\varphi(x_{i+1},t_j)+\varphi(x_{i-1},t_j)}{h^2} = \frac{k}{2}\cdot$$
$$\frac{\partial^2}{\partial t^2}\varphi(x_i,\xi_j) - \frac{h^2}{12}\cdot\frac{\partial^4}{\partial x^4}\varphi(\xi_i,t_j)$$

Multiplying both sides by $-h^2$, we get :

$$[\frac{i\hbar h^2}{k}+\frac{\hbar^2}{m}+h^2V(x_i)]\varphi(x_i,t_j)-\frac{i\hbar h^2}{k}\varphi(x_i,t_{j+1})-\frac{\hbar^2}{2m}\cdot[\varphi(x_{i+1},t_j)+\varphi(x_{i-1},t_j)]=-h^2[\frac{k}{2}\cdot\frac{\partial^2}{\partial t^2}\varphi(x_i,\xi_j)-\frac{h^2}{12}\cdot\frac{\partial^4}{\partial x^4}\varphi(\xi_i,t_j)].$$

Clarifying the last equation and typically let $\varphi_{i,j}$ approximate $\varphi(x_i,t_j)$, we form[2,5]:

$$[\frac{i\hbar h^2}{k}+\frac{\hbar^2}{m}+h^2V(x_i)]\varphi_{i,j}-\frac{i\hbar h^2}{k}\varphi_{i,j+1}-\frac{\hbar^2}{2m}\cdot\left[\varphi_{i+1,j}+\varphi_{i-1,j}\right]=0 \quad (3.6)$$

for each $i=1,2,3,\dots,n-1$ and $j=1,2,3,\dots\dots,m-1$.

3.4 Eigenvalue Problem

The wave functions, ψ, are eigenvectors of the Hamiltonian operator, and satisfy equation [16]:

$$\hat{\mathrm{H}}\psi=E\psi \quad (3.7)$$

where $\hat{\mathrm{H}}$ is the Hamiltonian operator, and the eigenvalues E represents the energies of a particle with wave function ψ. In the one dimensional situation, ψ is dependent only on the spatial coordinate x, and the one dimensional Hamiltonian is performed by

$$\hat{H}=\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}+V(x)$$

where ħ is a stable constant, m denotes the mass of the particle, and $V(x)$ determine the potential energy function of the particle. Note that H is dependent upon via x the $V(x)$ term. To give a dimensionless interpretation, we establish $\hbar^2=2m$, so that

$$\widehat{H} = -\frac{\partial^2}{\partial x^2} + V(x) \tag{3.8}$$

Let the points: x_j j = 0, 1, 2...n.

At each point x_j, equation (3.7) holds [16], so that

$$\widehat{H}_j\psi(x_j) = E\psi(x_j)$$

Where $\widehat{H}_j$ is the Hamiltonian operator evaluated at $V(x_j)$. Taking into Consideration that each of the points x_j makes the structure of equations:

$$\widehat{H}_0\psi(x_0) = E\psi(x_0)$$

$$\widehat{H}_j\psi(x_j) = E\psi(x_j) \tag{3.9}$$

….

$$\widehat{H}_n\psi(x_n) = E\psi(x_n)$$

Using equation (3.8), system (3.9) can be written as[16]:

$$-\psi''(x_0) + V(x_0)\psi(x_0) = E\psi(x_0)$$

$$-\psi''(x_1) + V(x_1)\psi(x_1) = E\psi(x_1) \tag{3.10}$$

….

$$-\psi''(x_n) + V(x_n)\psi(x_n) = E\psi(x_n)$$

We now have a system (3.10) of n equations relating the wave function of a particle to its fundamental energy.

$$-\psi''(x) + [V(x) - E]\psi(x) = 0 \tag{3.11}$$

]We will limit our analysis the evaluation of $\varphi\,(x)$ in the case of the infinite square well, and for scattering states within a finite interval[5,16].

We now select to approximate $\acute{\phi}(x)$ in equation (3.11) using finite difference scheme for $\acute{\phi}(x)$, such that:

$$\acute{\phi}(x) = \left(\frac{1}{h^2}\right)\left(A\varphi\left(x_{j-n}\right) + B\varphi\left(x_{j-n+1}\right) + \cdots + C\varphi\left(x_j\right) + \cdots + D\varphi\left(x_{j+n-1}\right) + G\varphi\left(x_{j+n}\right)\right)$$

where A, B, C, D, and G determined constants, h denotes the step size, and n is an integer.

In the second order, the centered finite difference approximation:

$$\acute{\phi}\left(x_j\right) \approx \left(\frac{1}{h^2}\right)\left(\varphi\left(x_{j-1}\right) - 2\varphi\left(x_j\right) + \varphi\left(x_{j+1}\right)\right)$$

Substituting the approximation for $\acute{\varphi}(x)$ system (3.10) becomes

$$\left(-\left(\tfrac{1}{h^2}\right)\varphi(x_{-1}) + \tfrac{2}{h^2}\varphi(x_0) - \tfrac{1}{h^2}\varphi(x_1)\right) + V(x_0).\varphi(x_0) = E\varphi(x_0),$$

Simplifying,

$$-\left(\frac{1}{h^2}\right)\varphi(x_{-1}) + \left[V(x_0) + \frac{2}{h^2}\right]\varphi(x_0) - \left(\frac{1}{h^2}\right)\varphi(x_1) = E\varphi(x_0)$$

$$-\left(\frac{1}{h^2}\right)\varphi(x_0) + \left[V(x_1) + \frac{2}{h^2}\right]\varphi(x_1) - \left(\frac{1}{h^2}\right)\varphi(x_2) = E\varphi(x_1)$$

$$\cdots\cdots\cdots$$

$$-\left(\frac{1}{h^2}\right)\varphi(x_{n-2}) + \left[V(x_{n-1}) + \frac{2}{h^2}\right]\varphi(x_{n-1}) - \left(\frac{1}{h^2}\right)\varphi(x_n) = E\varphi(x_{n-1})$$

$$-\left(\frac{1}{h^2}\right)\varphi(x_{n-1}) + \left[V(x_n) + \frac{2}{h^2}\right]\varphi(x_n) - \left(\frac{1}{h^2}\right)\varphi(x_{n+1}) = E\varphi(x_n)$$

now we define the vector

$$\varphi = \begin{bmatrix} \varphi(x_0) \\ \varphi(x_1) \\ \dots \\ \varphi(x_{n-1}) \\ \varphi(x_n) \end{bmatrix}$$

Employing a suitable finite differencing scheme, as well as using a boundary conditions, the system of linear equations may be expressed only in terms of the sample points $u(x_j)$ such that j = 0, 1, ..., n (excluding $u(x_{-1}), \dots., u(x_{n+1}), u(x_{n+2}), \dots$)[5,16].

In this case, system (3.11) can be written as

$$H\vec{\varphi} = E\vec{\varphi}$$

where H is a matrix containing the coefficients of each $\varphi(x_j)$ in the system of linear equations. E is the energy of eigenvector $\vec{\varphi}(x_j)$ at each sample points x_j, and is an eigenvalue of H.

$$E\varphi = \left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2\varphi}{\partial x^2} + V(x)\varphi$$

$$E\begin{bmatrix} \varphi_1 \\ \varphi_2 \\ . \\ . \\ \varphi_n \end{bmatrix} = \begin{bmatrix} H \\ N \times N \end{bmatrix}\begin{bmatrix} \varphi_1 \\ \varphi_2 \\ . \\ . \\ \varphi_n \end{bmatrix}$$

The eigenvalues of the N by N matrix (H) can be evaluated. There will be N eigenvalues and N eigenvectors. For a large value of N, Matlab can be used to find eigenvalues and eigenvectors.

$$[V, D] = eig\ (H)$$

where D has the eigenvalues of H as its diagonal elements. V has normalized eigenvectors of H as its columns [16,24].

3.5 Finite Difference Method for infinite square well

In this part, we need to find the solution to the free time-independent Schrödinger equation with the boundary conditions [22]

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x) = E\,\psi(x) \qquad (3.12)$$

Using the second order centered finite difference approximation:

$$\acute{\varphi}(x_j) \approx \left(\frac{1}{h^2}\right)\left(\varphi(x_{j+1}) - 2\varphi(x_j) + \varphi(x_{j-1})\right)$$

each linear combination will have the form

$$-\left(\frac{1}{h^2}\right)\left(\varphi(x_{j+1}) - 2\varphi(x_j) + \varphi(x_{j-1})\right) + V(x_j)\varphi(x_j) = E\varphi(x_j)$$

$$-\left(\frac{1}{h^2}\right)\varphi(x_{j-1}) + \left[V(x_j) + \frac{2}{h^2}\right]\varphi(x_j) - \left(\frac{1}{h^2}\right)\varphi(x_{j+1}) = E\varphi(x_j),$$

where $\varphi(x_k) = 0, \forall\, x_k \notin [0, \mathrm{L}]$.

Thus, the matrix H will take a form

$$\begin{pmatrix} \frac{2}{\Delta x^2} + V_1 & -\frac{1}{\Delta x^2} & & & \\ -\frac{1}{\Delta x^2} & \frac{2}{\Delta x^2} + V_2 & -\frac{1}{\Delta x^2} & & \\ & \ddots & \ddots & \ddots & \\ & & -\frac{1}{\Delta x^2} & \frac{2}{\Delta x^2} + V_{n-1} & -\frac{1}{\Delta x^2} \\ & & & -\frac{1}{\Delta x^2} & \frac{2}{\Delta x^2} + V_n \end{pmatrix}$$

3.6 Finite difference method for finite square well

The bound states of the finite square well which shows in figure (1.2):

Region 2:

$-L < x < L, V(x) = 0.$

The equation is:

$$\frac{\partial^2}{\partial x^2}\psi(x) = -k^2\,\psi(x)$$

Use second-order centered difference formula for $\acute{\phi}(x_i)$, $i = 1,2,\ldots,9$ and drop the error term,

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = -k^2\varphi_i$$

where $k^2 = \frac{2mE}{\hbar^2}$.

Region 1 and 3 in figure $(\mathbf{1.2})$:

$\mathrm{x} \leq -\mathrm{L}\ or\ x \geq L, V(x) = V_0.$

The equation is:

$$\frac{\partial^2}{\partial x^2}\psi = \alpha^2\psi$$

where $\alpha^2 = \frac{2m}{\hbar^2}(V_0 - E)$.

Use second-order centered difference formula for $\acute{\phi}(x_i)$, $i = 1,2,\ldots,9$ and drop the error term,

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = \alpha^2\varphi_i.$$

When we use second-order centered difference formula for $\acute{\phi}(x_i)$, and drop the error term, we get

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = -E\varphi_i.$$

Each linear combination will have a form

$$-\left(\frac{1}{h^2}\right)\left(\varphi(x_{i+1}) - 2\varphi(x_i) + \varphi(x_{i-1})\right) = E\varphi(x_i)$$

$$-\left(\frac{1}{h^2}\right)\varphi(x_{i-1}) + \frac{2}{h^2}\varphi(x_i) - \left(\frac{1}{h^2}\right)\varphi(x_{i+1}) = E\varphi(x_i) \qquad (3.13)$$ for $x_i \le x_{\frac{N}{2}}, i = 1, \ldots., \frac{N}{2}$.

Thus, the matrix H takes the form

$$\begin{bmatrix} \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} \end{bmatrix}$$

Use second-order centered difference formula for $\acute{\varphi}(x_i)$, and drop the error term, we get

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = \alpha^2\varphi_i.$$

Each linear combination will have a form

$$\left(\frac{1}{h^2}\right)\left(\varphi(x_{i+1}) - 2\varphi(x_i) + \varphi(x_{i-1})\right) = \alpha^2\varphi(x_i) \qquad (3.14)$$

for $\frac{N}{2} \le i \le N + 1$.

Thus, the matrix H takes the form

$$\begin{bmatrix} -\frac{2}{h^2} & \frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{h^2} & -\frac{2}{h^2} \end{bmatrix}$$

Then we need to solve these systems.

3.7 Pseudo-spectral method

Another method used to solve the Schrödinger equation is the pseudo-spectral method, which based on the expansion of basis functions defined in a collection of grid points, a function is approximated as a weighted sum of smooth basis functions, which are often selected to be Legendre or Chebyshev polynomials. The pseudo-spectral method is proposed for the numerical solution of the nonlinear Schrödinger equation [9,26].

The fundamental concept of this method is to expand the solution function as a finite series of smooth basis functions [8],

$$\varphi: [-1,1] \to R$$

$$\varphi_n(x) = \sum_{n=0}^{N} c_n T_n(x), \qquad (3.15)$$

where, $T_n(x)$ typically represents Chebyshev or Legendre orthogonal polynomials defined on the interval $[-1,1]$ [9,25,31], and c_n represents the constant coefficients vector.

$$c_n = (c_0, c_1, \ldots\ldots, c_N)^T \in R^{N+1},$$

Which are computed from the formula

$$c_n = \frac{2}{N\tilde{c}_n} \sum_{j=0}^{N} \frac{1}{\tilde{c}_j} \varphi(x_j) \cos\left(\frac{\pi j n}{N}\right), n = 0,1,2, \ldots\ldots, N. \qquad (3.16)$$

Here, $\tilde{c}_0 = \tilde{c}_N = 2$, $\tilde{c}_n = 1,\ n = 1,2, \ldots\ldots, N-1,\ and\ x_j = \cos\left(\frac{\pi j}{N}\right)$,

$j = 0,1, \ldots\ldots, N$, are the Chebyshev-Gauss-Lobatto points.

Let recall the definition of a Chebyshev polynomial:

$$T_n(x) = \cos(n \cos^{-1}(x)) \qquad \text{, if } |x| \leq 1 \qquad (3.17)$$

Let:

$$\theta = \cos^{-1} x \qquad \Rightarrow \qquad x = \cos\theta$$

Then:

$$T_n(x) = \emptyset_n(\theta) = \cos(n\theta), \qquad \theta \in [-\pi, \pi] \qquad (3.18)$$

Using the identity defined a bove, equation (3.15) becomes:

$$\varphi(x) = \sum_{n=0}^{N} c_n \cos(n\theta) \qquad (3.19)$$

Deriving equation (3.19) with respect to x, we get:

$$\frac{\partial \varphi(x)}{\partial x} = \sum_{n=0}^{N} c_n \left(\frac{n \sin n\theta}{\sin\theta}\right) \qquad (3.20)$$

$$\frac{\partial^2 \varphi(x)}{\partial x^2} = \sum_{n=0}^{N} c_n \left(\frac{n \sin n\theta \ \cos\theta - n^2 \cos n\theta \ \sin\theta}{\sin^3\theta}\right) \qquad (3.21)$$

The basic equation is:

$$\frac{\partial^2}{\partial x^2}\varphi(x) = E\varphi(x) \tag{3.22}$$

Substituting equation (3.21) in equation (3.22), we get:

$$\sum_{n=0}^{N} c_n\left(\frac{n\sin n\theta\ \cos\theta - n^2\cos n\theta\ \sin\theta}{\sin^3\theta}\right) = E.\sum_{n=0}^{N} c_n\cos(n\theta)$$

Using boundary condition to find the coefficients of the vector c_n[24,36].

$$\varphi(0) = \sum_{n=0}^{N} c_n\,T_n(0) = \sum_{n=0}^{N} c_n\emptyset_n\left(\frac{\pi}{2}\right) = \sum_{n=0}^{N} c_n\left(\cos n\frac{\pi}{2}\right) = 0$$

$$\varphi(1) = \sum_{n=0}^{N} c_n\,T_n(1)$$

$$= \sum_{n=0}^{N} c_n\emptyset_n(0) = \sum_{n=0}^{N} c_n(\cos n0) = \sum_{n=0}^{N} c_n(1)^n = 0$$

So

$$\begin{bmatrix} \frac{1}{2} & 0 & -1 & 0 & 1 & 0 & -1 & 0 & 1 & 0 \\ \frac{1}{2} & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix}\begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{3.23}$$

These relations form a system with two equations and $N+1$ unknowns, to construct the remaining $N-1$ equations we collocate (3.15) at the zeros of $T_{N-1}(x)$, which are the interior points between 0 and 1, and are given as [8,24,30]

$$\theta_n = \frac{(2n-1)\pi}{N-1}\ ,\ \ n = 1, \ldots\ldots, N-1.$$

By using inverse Fourier transform we will find the wave function $\varphi(x)$

$$\varphi(x) = \sum_{n=0}^{N} c_n\cos(n\theta).$$

3.8 Pseudo-Spectral Algorithm

Step 1: Choose positive integer N.

Step 2: Define $\Delta x = \frac{L}{N+1}$.

Step 3: Define the mesh point x_i as $x_i = ih \qquad i = 0,1,2, \dots \dots, N+1$.

Step 4: Define $x = \cos\theta$, $\theta = \cos^{-1} x$.

Step 5: Define $\emptyset_n(x) = \emptyset_n(\theta) = \cos n\theta$.

Step 6: Define $\varphi(x) = \sum_{n=0}^{N} c_n \cos(n\theta)$.

Step7: Using boundary conditions to evaluate the coefficient of the vector c_n.

From the first boundary condition :

$$\varphi(x_0) = \sum_{n=0}^{N} c_n \emptyset_n(x_0),$$

from the second boundary condition:

$$\varphi(x_{N+1}) = \sum_{n=0}^{N} c_n \emptyset_n(x_{N+1}).$$

Step 8: Find the matrix of the coefficient of the vector $c_{n,}$ by using this formula

$$\theta_n = \frac{(2n-1)\pi}{N-1}, \qquad n = 1, \dots \dots, 8$$

Step 9: Using inverse Fourier transform to find the wave function $\varphi(x)$.

Chapter Four
Numerical Examples and Results

Chapter Four

Numerical Examples and Results

In this chapter, we implement the two numerical methods, namely, the finite difference and pseudo-spectral methods, for solving the Schrödinger equation and its variants.

4.1 Numerical solution for infinite square well of TISE

Example $(\mathbf{4.1})$:

Consider that for the infinite square well, the particle whose mass 0.5 g is only found in the infinite interval $[0,1]$, such that

$$V(x) = \begin{cases} 0 & x \in [0,1] \\ \infty & else \end{cases}$$

consider the free time- independent Schrödinger equation

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x) = E\,\psi(x) \tag{4.1}$$

with the boundary conditions

$$\psi(0) = 0 \text{ and } \psi(1) = 0 \tag{4.2}$$

the exact solution of (4.1) [8] is:

$$\varphi(x) = \sqrt{2}\,\sin(\pi x)$$

the following algorithm is applied to obtain the solution of the equation (4.1) using the finite difference method.

Algorithm $(\mathbf{4.1})$**: Finite Difference Method**

1- Find the general solution for the equation

$$\frac{\partial^2}{\partial x^2}\psi(x) + K^2\psi(x) = 0$$

2- Define b=0, $L = 1,\ \hbar^2 = 2m$.

3- Find k, a, where $K = \frac{n\pi}{L}, a = \sqrt{\frac{2}{L}}$.

4- Find the energy E

where $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$

5- Choose positive integers $N = 9$.

6- Clarify $h = \frac{L}{N+1} = \frac{1}{10}$, this act separates the interval [0,1] into 9 equal parts of width $\frac{1}{10}$.

7- Define the mesh point x_i as $x_i = ih \quad i = 0,1,2, \ldots \ldots, 10$.

the mesh points are

x_0	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}
0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0

8- Use second-order centered difference formula for $\acute{\phi}(x_i)$,

$i = 1,2, \ldots, 9$ and drop the error term, we get

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = -E\varphi_i.$$

Each linear combination will have a form

$$-\left(\frac{1}{h^2}\right)\left(\varphi(x_{i+1}) - 2\varphi(x_i) + \varphi(x_{i-1})\right) = E\varphi(x_i)$$

$$-\left(\frac{1}{h^2}\right)\varphi(x_{i-1}) + \frac{2}{h^2}\varphi(x_i) - \left(\frac{1}{h^2}\right)\varphi(x_{i+1}) = E\varphi(x_i), \qquad (4.3)$$

where $\varphi(x_i) = 0, \forall\ x_i \notin [0,1]$.

For $i = 1$, equation (4.3) becomes

$$-\left(\frac{1}{h^2}\right)\varphi(x_0) + \frac{2}{h^2}\varphi(x_1) - \left(\frac{1}{h^2}\right)\varphi(x_2) = E\varphi(x_1)$$

for $i = 2$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_1) + \frac{2}{h^2}\varphi(x_2) - \left(\frac{1}{h^2}\right)\varphi(x_3) = E\varphi(x_2)$$

for $i = 3$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_2) + \frac{2}{h^2}\varphi(x_3) - \left(\frac{1}{h^2}\right)\varphi(x_4) = E\varphi(x_3)$$

for $i = 4$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_3) + \frac{2}{h^2}\varphi(x_4) - \left(\frac{1}{h^2}\right)\varphi(x_5) = E\varphi(x_4)$$

for $i = 5$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_4) + \frac{2}{h^2}\varphi(x_5) - \left(\frac{1}{h^2}\right)\varphi(x_6) = E\varphi(x_5)$$

for $i = 6$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_5) + \frac{2}{h^2}\varphi(x_6) - \left(\frac{1}{h^2}\right)\varphi(x_7) = E\varphi(x_6)$$

for $i = 7$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_6) + \frac{2}{h^2}\varphi(x_7) - \left(\frac{1}{h^2}\right)\varphi(x_8) = E\varphi(x_7)$$

for $i = 8$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_7) + \frac{2}{h^2}\varphi(x_8) - \left(\frac{1}{h^2}\right)\varphi(x_9) = E\varphi(x_8)$$

for $i = 9$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_8) + \frac{2}{h^2}\varphi(x_9) - \left(\frac{1}{h^2}\right)\varphi(x_{10}) = E\varphi(x_9)$$

Thus, the matrix H takes the form

$$\begin{bmatrix} \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{h^2} & \frac{2}{h^2} \end{bmatrix}$$

Applying algorithm (4.1) for example (4.1). Table (4.1) contains both the exact and the numerical results using the finite difference method for example (4.1).

Table (4.1): The exact and the numerical solutions using finite difference method algorithm where *N*=9.

x_i	$\varphi_e = \varphi_{exact}$	$\varphi_{i=}\varphi_{numerical}$	Absolute error $\lvert\varphi_e - \varphi_i\rvert$
0	0	0	0
0.1	0.43701602	0.46701602	0.03000000
0.2	0.83125388	0.90015676	0.06890288
0.3	1.14412281	1.18543371	0.04131090
0.4	1.34499702	1.25307610	0.09192092
0.5	1.36500261	1.28863421	0.07636840
0.6	1.34499702	1.55307610	0.20807908
0.7	1.14412281	1.18543371	0.04131090
0.8	0.831253878	0.90015676	0.06890288
0.9	0.43701602	0.46701602	0.03000000
1.0	0	0	0

It can be observed that the maximum absolute error is 0.20807908.

The exact and approximate results of $\varphi(x)$ are shown in Fig. 4.1 (a) and the resulted error is shown in Fig. 4.1 (b).

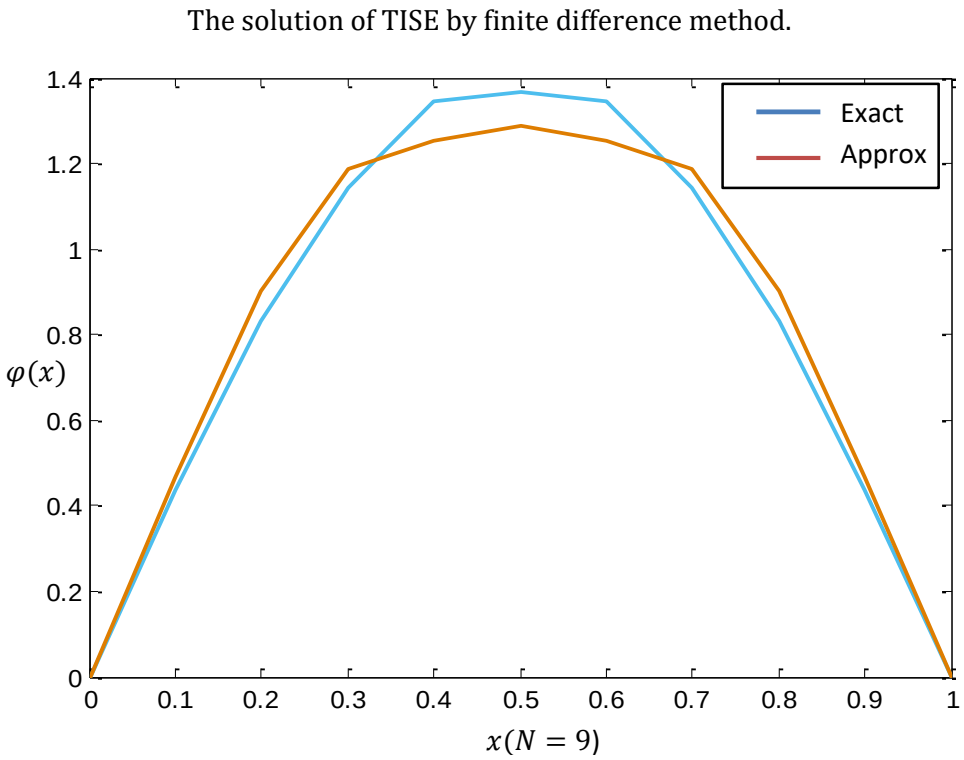


Fig. 4.1 (a): A comparison between the exact and approximate solution in example 4.1.

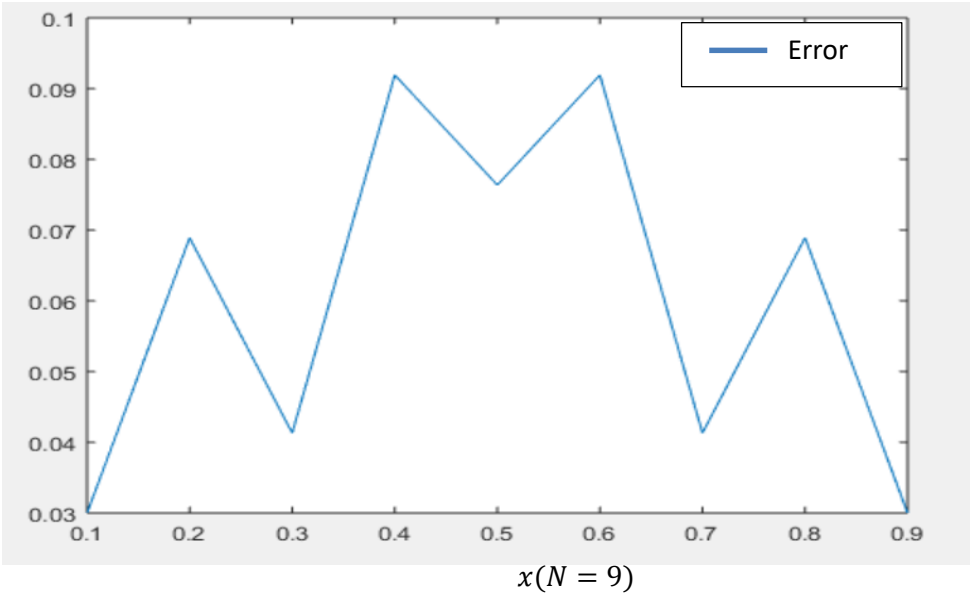


Fig. 4.1 (b): Absolute error between exact and numerical solution in example 4.1

Table (4.2) contains both the exact and the numerical results for the values of energy for example (4.1).

Table (4.2): The exact and the numerical solutions for the energy in example (4.1) where *N*=9.

N	E_{exact}	$E_{numerical}$	Absolute error $\lvert E_{exact}\text{-}E_{num}\rvert$
1	9.86960440	9.27431124	0.59529316
2	39.47841760	39.05884233	0.41957527
3	88.82643961	88.11904310	0.70739651
4	157.91367042	157.8754602	0.03821022
5	246.74011003	246.64312400	0.09698603
6	355.30575844	355.07313011	0.23262833
7	483.61061565	483.89924520	0.28862955
8	631.65468167	631.00001527	0.65466640
9	799.43795649	799.08054461	0.35741188

It can be observed that the maximum absolute error is 0.70739651.

The exact and approximate results of E_n are shown in Fig. 4.2 (a) and the resulted error is shown in Fig. 4.2 (b).

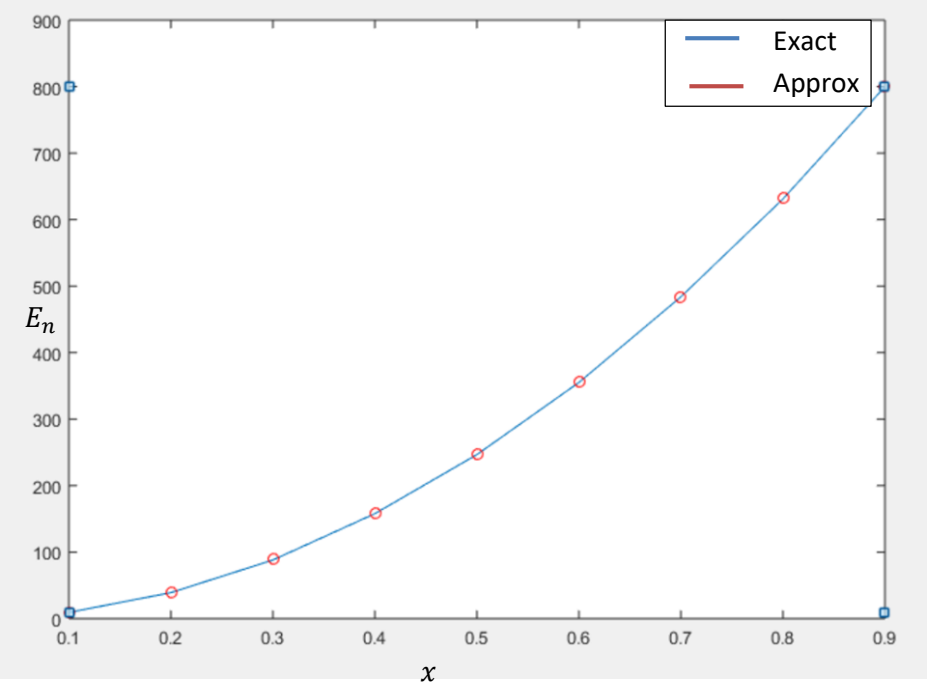


Fig 4.2 (a): A comparison between The exact and approximate results of $\mathbf{E_n}$.

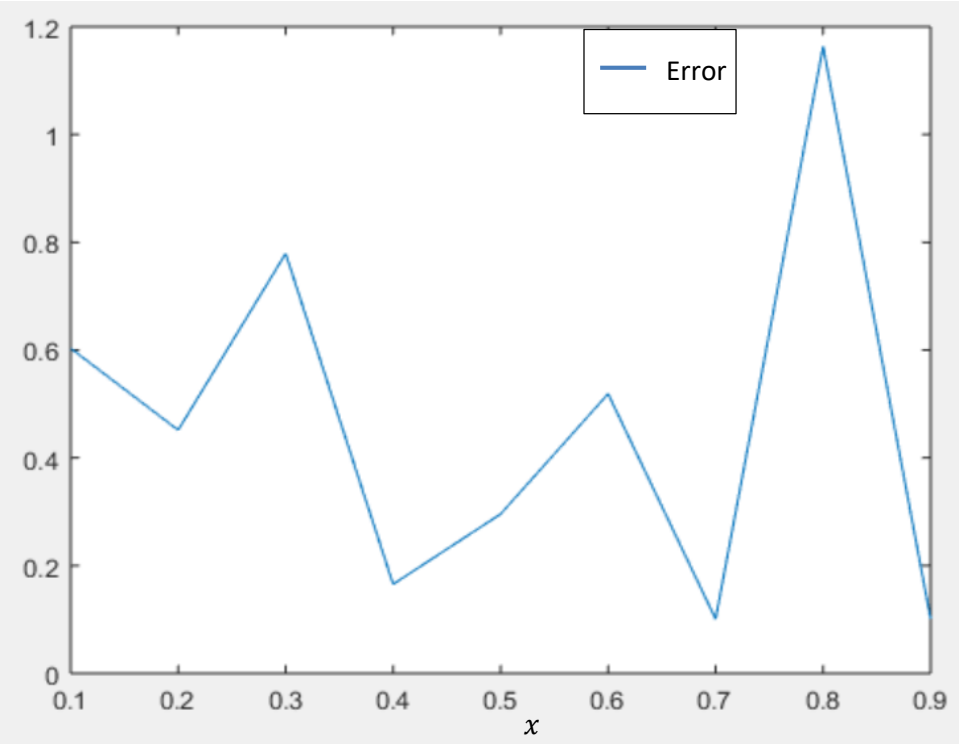


Fig 4.2 (b): Absolute error between The exact and approximate results of $\mathbf{E_n}$.

Pseudo-Spectral Method

Solving example (4.1) by the pseudo-spectral method.

Algorithm $(4.2)[4,13]$: The Pseudo- Spectral Method

1. Define L=1, m=0.5, n=1, $\theta \in [-\pi, \pi]$.
2. Choose positive integer N=9.
3. Define $\Delta x = \frac{L}{N+1} = \frac{1}{10}$.
4. Define the mesh point x_i as $x_i = ih \quad i = 0,1,2, \ldots \ldots, 10.$

   the mesh points are

x_0	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}
0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0

5. Define $x = \cos\theta, \theta = \cos^{-1} x.$

6. Define $\emptyset_n(x) = \emptyset_n(\theta) = \cos n\theta$.
7. Define $\varphi(x) = \sum_{n=0}^{N} c_n \cos(n\theta)$.
8. Using boundary conditions to evaluate the coefficient of the vector c_n.

From the first boundary condition:

$$\varphi(0) = \sum_{n=0}^{N} c_n \emptyset_n(0) = \sum_{n=0}^{N} c_n 0^n = 0$$

From the second boundary condition:

$$\varphi(1) = \sum_{n=0}^{N} c_n \emptyset_n(1) = \sum_{n=0}^{N} c_n 1^n = 0$$

9. Find the matrix of the coefficient of the vector $c_{n,}$by using this formula

$$\theta_n = \frac{(2n-1)\pi}{N-1}, \qquad n = 1, \dots\dots, 8$$

10. Using inverse Fourier transform to find the wave function $\varphi(x)$.

Applying algorithm (4.2) for example (4.1). Table (4.3) contains both the exact and the numerical results using the pseudo-spectral method for example (4.1).

Table (4.3): The exact and the numerical solutions using pseudo-spectral method algorithm where *N*=9.

x_i	$\varphi_e = \varphi_{exact}$	$\varphi_i = \varphi_{numerical}$	Absolute error$\lvert\varphi_e$-$\varphi_i\rvert$
0	0	0	0
0.1	0.31880021	0.40000852	0.08120831
0.2	0.60775210	0.72194022	0.11418812
0.3	0.83703748	0.98861174	0.15157426
0.4	0.98442201	1.02520004	0.10026000
0.5	1.03530001	1.08468201	0.04938200
0.6	0.98483305	1.01227759	0.02744454
0.7	0.83780103	0.90463332	0.06683229
0.8	0.60870000	0.65430703	0.04560703
0.9	0.32000000	0.37000032	0.05000032
1	0	0	0

It can be observed that the maximum absolute error is 0.15157426.

The exact and approximate results of $\varphi(x)$ are shown in Fig. 4.3 (a) and the resulted error is shown in Fig. 4.3 (b).

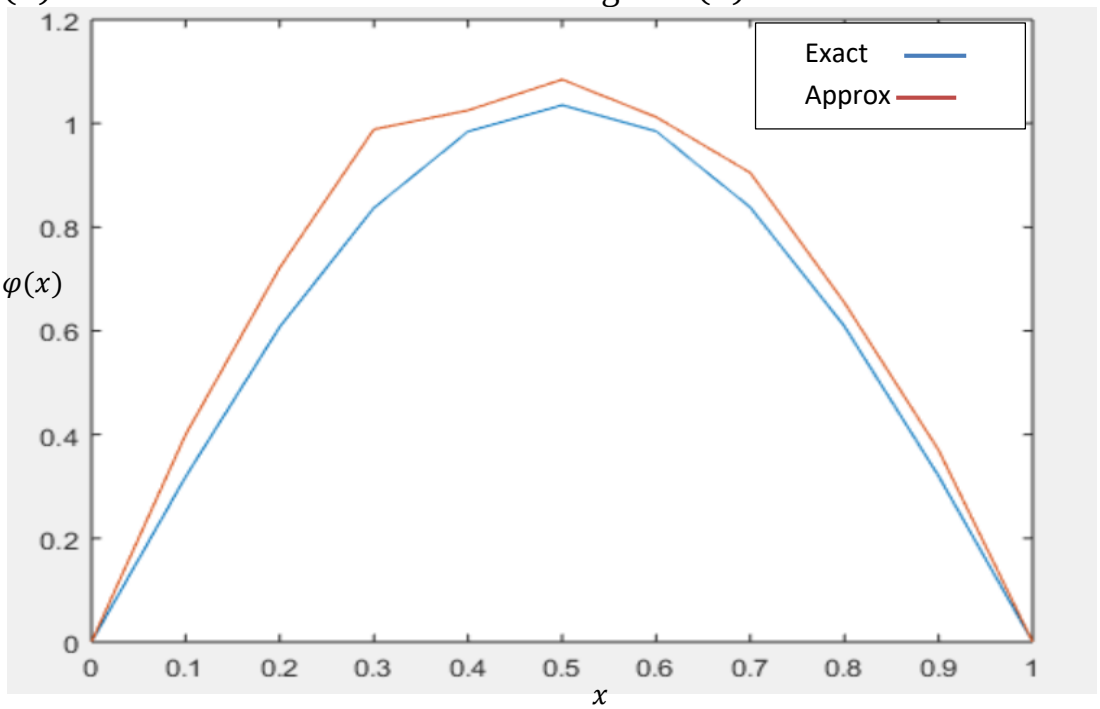


Fig 4.3 (a): A comparison between exact and numerical solution in example 4.1.

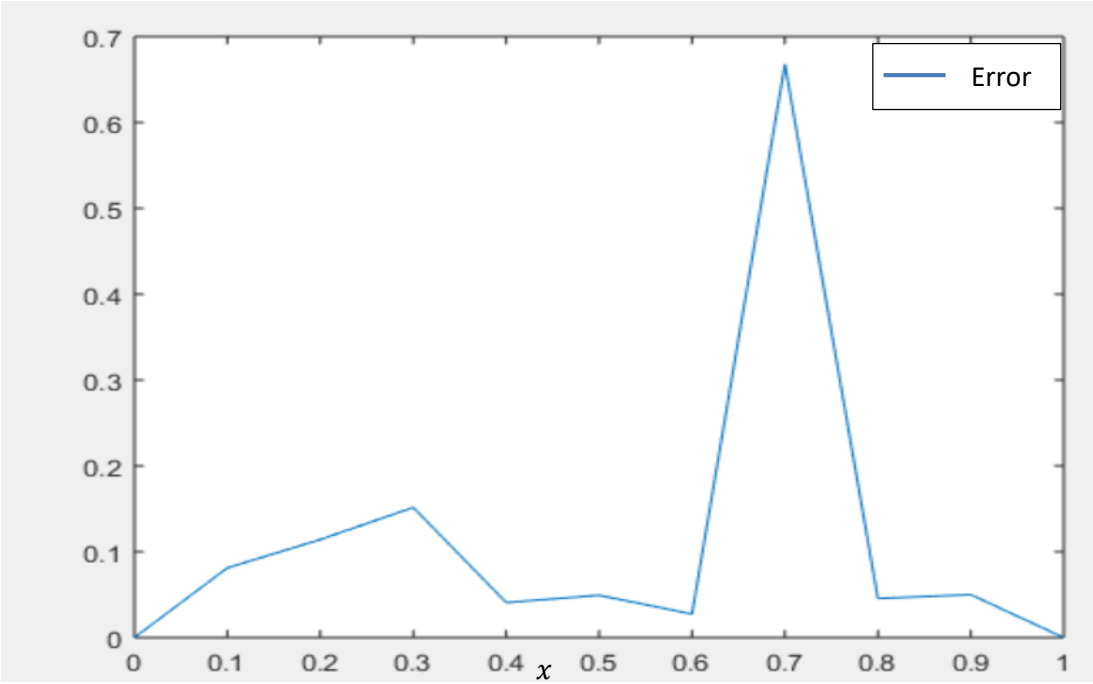


Fig 4.3 (b): Absolute error between exact and numerical solution in example 4.1.

Second case of quantum mechanics: the finite square well.

4.2 Numerical solution for finite square well

Region 2 in figure (1.2):

$-L < x < L, V(x) = 0.$

The equation is:

$$\frac{\partial^2}{\partial x^2}\psi(x) = -k^2\,\psi(x)$$

Use second-order centered difference formula for $\acute{\varphi}(x_i)$, $i = 1,2,\dots,9$ and drop the error term,

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = -k^2\varphi_i$$

where $k^2 = \frac{2mE}{\hbar^2}$.

Region 1 and 3 in figure (1.2):

$$\mathrm{x} \leq -\mathrm{L}\ or\ x \geq L, V(x) = V_{0.}$$

The equation is :

$$\frac{\partial^2}{\partial x^2}\psi = \alpha^2\psi$$

where $\alpha^2 = \frac{2m}{\hbar^2}(V_0 - E)$,

Use second-order centered difference formula for $\acute{\varphi}(x_i)$, $i = 1,2,\dots,9$ and drop the error term,

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = \alpha^2\varphi_i.$$

Example (4.2):

Consider that for the finite square well 1 nm, the particle with mass =0.5 g is found in the interval $[0,1]$, such that $V(x) = V_0 = 50\ eV$, consider the free time independent Schrödinger equation:

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\ \psi(x) \qquad (4.4)$$

with the boundary conditions

$$\psi(x) \to 0\ \ as\ |x| \to \infty \qquad (4.5)$$

the exact solution of (4.4) [1,23] is:

$$\varphi(x) = c\ e^{-\alpha x}$$

the following algorithm is applied to obtain the solution of the equation (4.4) using the finite difference method.

Algorithm (4.3): Finite Difference Method

1- Find the general solution for the equation

$$\frac{\partial^2}{\partial x^2}\psi(x) - \alpha^2\psi(x) = 0$$

2- Define $L = 1\,nm,\ \hbar^2 = 2m, V_0 = 50.$

3- Define $\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$

4- Find the energy E, where $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$

5- Choose positive integers $N = 3$.

6- Clarify $h = \frac{L_2 - L_1}{N+1} = \frac{1}{4} = 0.25$, this act separates the interval [0,1] into 4 equal parts of width 0.25.

7- Define the mesh point x_i as $x_i = ih,\ i = 0,1,2,3.$

The mesh points are

x_0	x_1	x_2	x_3	x_4
0	0.25	0.5	0.75	1

8- Use second-order centered difference formula for $\acute{\phi}(x_i)$, $i = 1,2$ and drop the error term, we get

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = -E\varphi_i.$$

Each linear combination will have a form

$$-\left(\frac{1}{h^2}\right)\left(\varphi(x_{i+1}) - 2\varphi(x_i) + \varphi(x_{i-1})\right) = E\varphi(x_i)$$

$$-\left(\frac{1}{h^2}\right)\varphi(x_{i-1}) + \frac{2}{h^2}\varphi(x_i) - \left(\frac{1}{h^2}\right)\varphi(x_{i+1}) = E\varphi(x_i) \qquad (4.6)$$

where $\varphi(x_i) = 0, \forall\ x_i \notin [0,1]$.

For $i = 1$, equation (4.6) becomes

$$-\left(\frac{1}{h^2}\right)\varphi(x_0) + \frac{2}{h^2}\varphi(x_1) - \left(\frac{1}{h^2}\right)\varphi(x_2) = E\varphi(x_1)$$

for $i = 2$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_1) + \frac{2}{h^2}\varphi(x_2) - \left(\frac{1}{h^2}\right)\varphi(x_3) = E\varphi(x_2)$$

9- Use second-order centered difference formula for $\acute{\acute{\varphi}}(x_i)$, $i = 3,4$ and drop the error term, we get

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = \alpha^2\varphi_i.$$

Each linear combination will have a form

$$\left(\frac{1}{h^2}\right)\left(\varphi(x_{i+1}) - 2\varphi(x_i) + \varphi(x_{i-1})\right) = \alpha^2\varphi(x_i)$$

for $i = 3$,

$$\left(\frac{1}{h^2}\right)\varphi(x_2) - \frac{2}{h^2}\varphi(x_3) + \left(\frac{1}{h^2}\right)\varphi(x_4) = \alpha^2\varphi(x_3)$$

for $i = 4$,

$$\left(\frac{1}{h^2}\right)\varphi(x_3) - \frac{2}{h^2}\varphi(x_4) + \left(\frac{1}{h^2}\right)\varphi(x_5) = \alpha^2\varphi(x_4)$$

Thus, for $i = 1,2$ the matrix H will take form

$$\begin{pmatrix} \frac{2}{h^2} & -\frac{1}{h^2} \\ -\frac{1}{h^2} & \frac{2}{h^2} \end{pmatrix}$$

and for $i = 3,4$ the matrix H will take form

$$\begin{pmatrix} -\frac{2}{h^2} & \frac{1}{h^2} \\ \frac{1}{h^2} & -\frac{2}{h^2} \end{pmatrix}$$

Applying algorithm (4.3) for example (4.2). Table (4.4) contains both the exact and the numerical results using the finite difference method for example (4.2).

Table (4.4): The exact and the numerical solutions using finite difference method algorithm where N=3.

N	$\varphi_e = \varphi_{exact}$	$\varphi_i = \varphi_{numerical}$	Absolute error $\lvert\varphi_e - \varphi_i\rvert$
1	0.18945941	0.18945027	0.00000914
2	0.25428327	0.24638761	0.00789566
3	0.58497260	0.58556111	0.00058851
4	0.90483742	0.90097764	0.00385978

It can be observed that the maximum absolute error is 0.00789566.

The exact and approximate results of $\varphi(x)$ are shown in Fig. 4.4 (a) and the resulted error is shown in Fig. 4.4 (b).

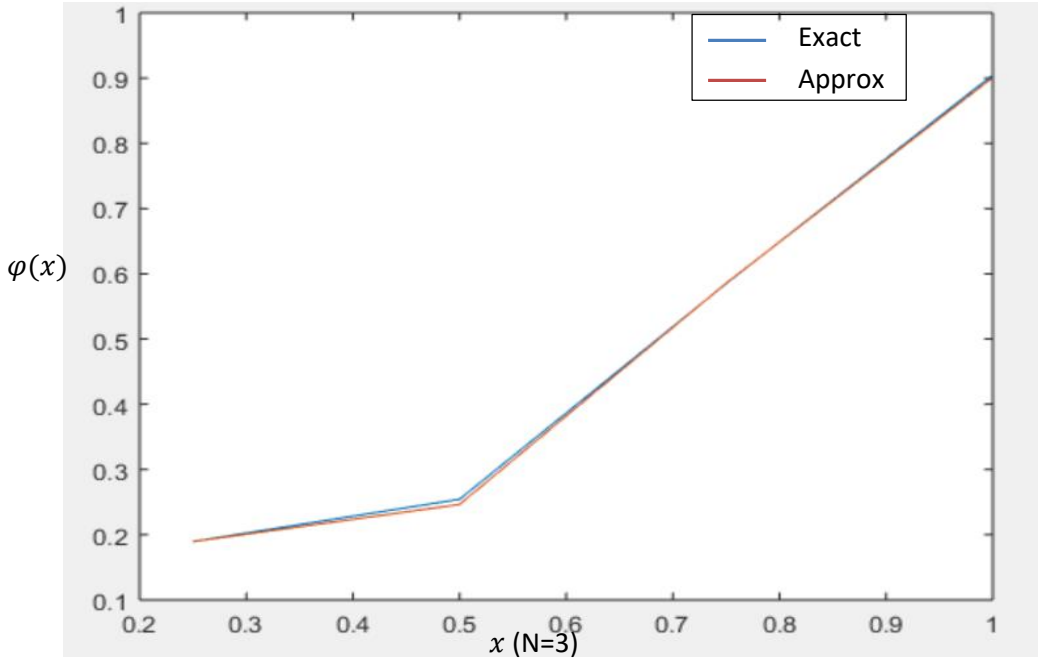


Fig 4.4 (a): A comparison between the exact and approximate solution in example 4.2.

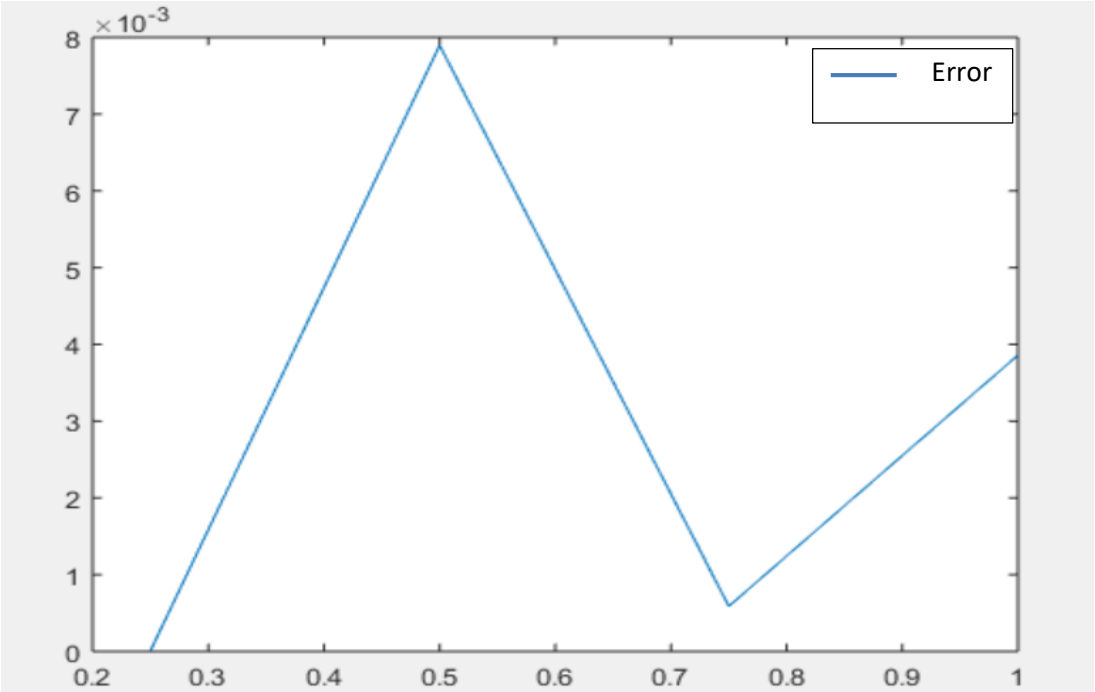


Fig. 4.4 (b): Absolute error between exact and numerical solution in example 4.2.

Table (4.5) contains the exact and the numerical results for the energy in example (4.2).

Table (4.5): The exact and the numerical results for the energy in example (4.2).

N	E_{exact}	$E_{numerical}$	Absolute error $\lvert E_{exact}\text{-}E_{num}\rvert$
1	5.72000000	3.77780000	1.94220000
2	20.00000000	10.65000000	9.35000000
3	45.40000000	39.45000000	5.95000000
4	49.84000000	47.76900000	2.07100000

It can be observed that the maximum absolute error is 9.35000000.

The exact and approximate results of E_n are shown in Fig. 4.5 (a) and the resulted error is shown in Fig. 4.5 (b).

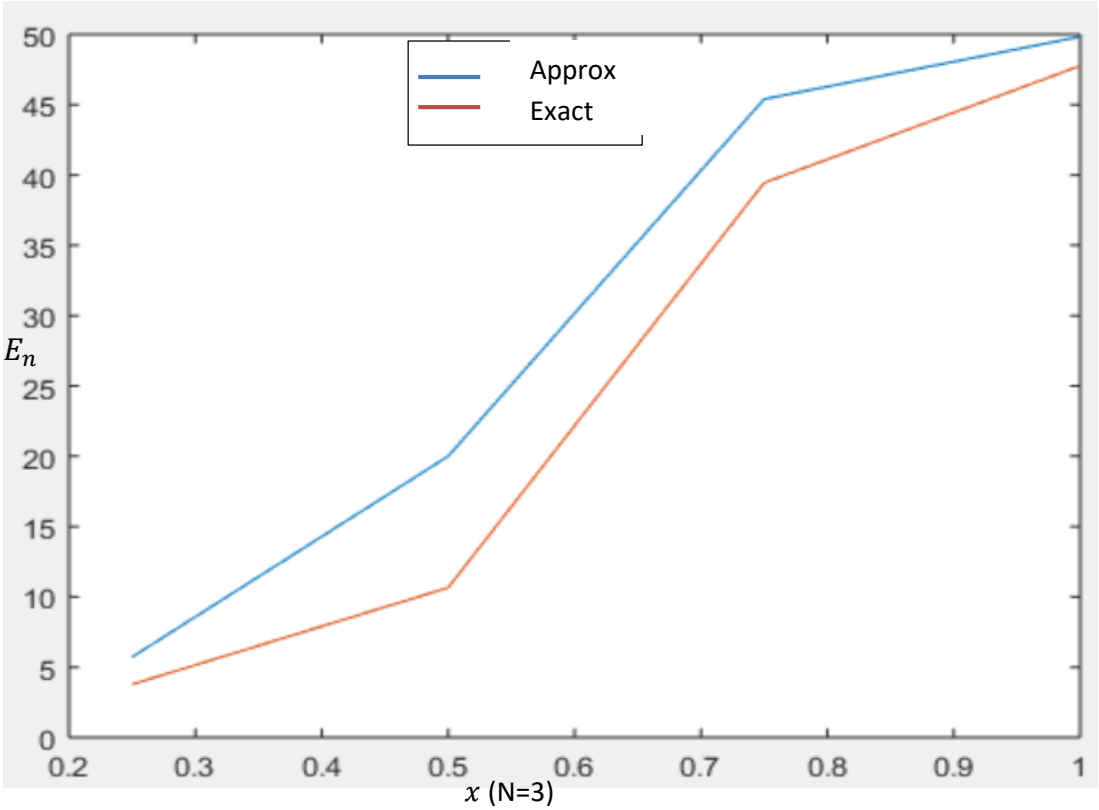


Fig 4.5 (a):A comparison between The exact and approximate results of $\boldsymbol{E_n}$.

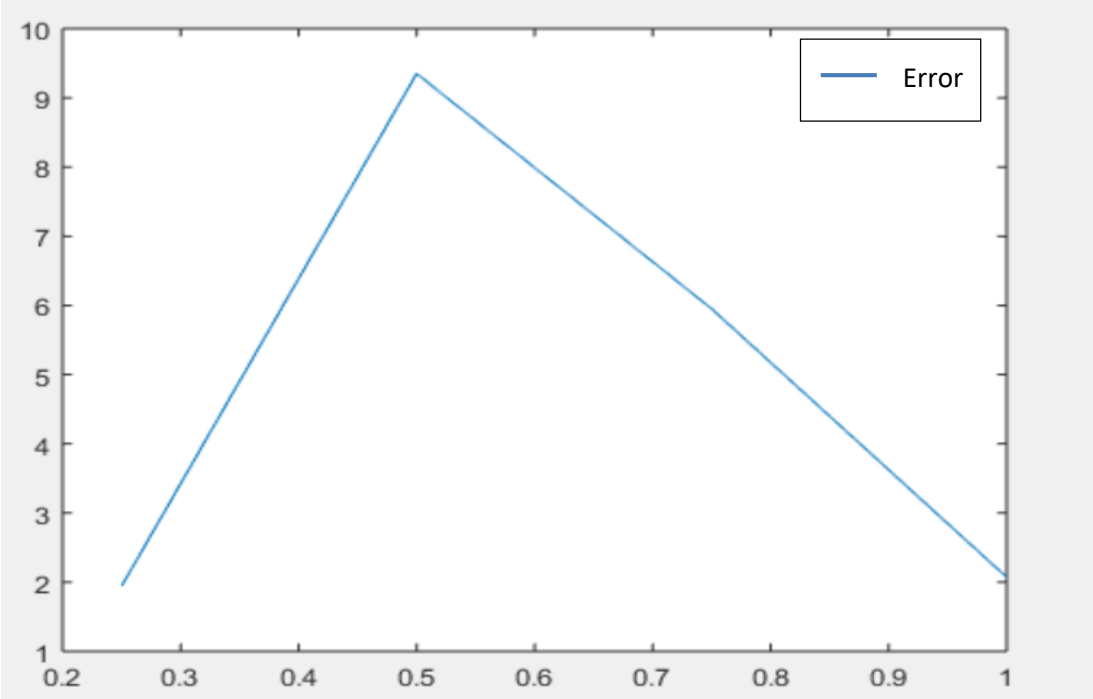


Fig 4.5 (b): Absolute error between exact and numerical energy in example 4.2.

Example $(\mathbf{4.3})$:

An electron in a finite square well 3 nm and 25 eV deep, consider the free time independent Schrödinger equation:

$$\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\,\psi(x) \tag{4.7}$$

with the boundary conditions

$$\psi(x) \to 0 \;\; as\; |x| \to \infty \tag{4.8}$$

the exact solution of (4.7) [1,23] is:

$$\varphi(x) = c\; e^{-\alpha x}$$

the following algorithm is applied to obtain the solution of the equation (4.7) using the finite difference method.

Algorithm $(\mathbf{4.3})$**: Finite Difference Method**

1- Find the general solution for the equation
$\frac{\partial^2}{\partial x^2}\psi(x) - \alpha^2\psi(x) = 0$

2- Define $L = 3\; nm,\; \hbar^2 = 2m, V_0 = 25$, interval=[0,3].

3- Define $\alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$

4- Find the energy E

where $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$

5- Choose positive integers $N = 5$.

6- Clarify $h = \frac{L_2 - L_1}{N+1} = \frac{3}{6} = 0.5$, this act separates the interval [0,3] into 6 equal parts of width 0.5.

7- Define the mesh point x_i as $x_i = ih,\; i = 0,1,2,3$.

The mesh points are

x_0	x_1	x_2	x_3	x_4	x_5	x_6
0	0.5	1	1.5	2	2.5	3

8- Use second-order centered difference formula for $\acute{\varphi}(x_i)$,

$i = 1,2,3$ and drop the error term, we get

$$\frac{\varphi_{i+1}-2\varphi_i+\varphi_{i-1}}{h^2} = -E\varphi_i.$$

Each linear combination will have a form

$$-\left(\frac{1}{h^2}\right)\left(\varphi(x_{i+1}) - 2\varphi(x_i) + \varphi(x_{i-1})\right) = E\varphi(x_i)$$

$$-\left(\tfrac{1}{h^2}\right)\varphi(x_{i-1}) + \tfrac{2}{h^2}\varphi(x_i) - \left(\tfrac{1}{h^2}\right)\varphi(x_{i+1}) = E\varphi(x_i) \quad (4.8)$$

where $\varphi(x_i) = 0, \forall\, x_i \notin [0,3]$.

For $i = 1$, equation (4.8) becomes

$$-\left(\frac{1}{h^2}\right)\varphi(x_0) + \frac{2}{h^2}\varphi(x_1) - \left(\frac{1}{h^2}\right)\varphi(x_2) = E\varphi(x_1)$$

for $i = 2$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_1) + \frac{2}{h^2}\varphi(x_2) - \left(\frac{1}{h^2}\right)\varphi(x_3) = E\varphi(x_2)$$

for $i = 3$,

$$-\left(\frac{1}{h^2}\right)\varphi(x_2) + \frac{2}{h^2}\varphi(x_3) - \left(\frac{1}{h^2}\right)\varphi(x_4) = E\varphi(x_3)$$

9- Use second-order centered difference formula for $\acute{\varphi}(x_i)$,

for $i = 4,5,6$ and drop the error term, we get

$$\frac{\varphi_{i+1} - 2\varphi_i + \varphi_{i-1}}{h^2} = \alpha^2\varphi_i.$$

Each linear combination will have a form

$$\left(\frac{1}{h^2}\right)\left(\varphi(x_{i+1}) - 2\varphi(x_i) + \varphi(x_{i-1})\right) = \alpha^2\varphi(x_i)$$

for $i = 4$,

$$\left(\frac{1}{h^2}\right)\varphi(x_3) - \frac{2}{h^2}\varphi(x_4) + \left(\frac{1}{h^2}\right)\varphi(x_5) = \alpha^2\varphi(x_4)$$

for $i = 5$,

$$\left(\frac{1}{h^2}\right)\varphi(x_4) - \frac{2}{h^2}\varphi(x_5) + \left(\frac{1}{h^2}\right)\varphi(x_6) = \alpha^2\varphi(x_5)$$

for $i = 6$,

$$\left(\frac{1}{h^2}\right)\varphi(x_5) - \frac{2}{h^2}\varphi(x_6) + \left(\frac{1}{h^2}\right)\varphi(x_7) = \alpha^2\varphi(x_6)$$

Thus, for $i = 1,2,3$ the matrix H will take form

$$\begin{pmatrix} \frac{2}{h^2} & -\frac{1}{h^2} & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2} & -\frac{1}{h^2} \\ 0 & -\frac{1}{h^2} & \frac{2}{h^2} \end{pmatrix}$$

and for $i = 4,5,6$ the matrix H will take form

$$\begin{pmatrix} -\frac{2}{h^2} & \frac{1}{h^2} & 0 \\ \frac{1}{h^2} & -\frac{2}{h^2} & \frac{1}{h^2} \\ 0 & \frac{1}{h^2} & -\frac{2}{h^2} \end{pmatrix}$$

Applying algorithm (4.3) for example (4.3). Table (4.6) contains both the exact and the numerical results using the finite difference method for example (4.3)

Table (4.6): The exact and the numerical solutions using finite difference method algorithm where N=5.

N	$\varphi_e = \varphi_{exact}$	$\varphi_i = \varphi_{numerical}$	Absolute error $\lvert\varphi_e - \varphi_i\rvert$
1	0.08688196	0.084587199	0.00229476
2	0.10372639	0.10373944	0.00001305
3	0.14332877	0.14432878	0.00100001
4	0.24664101	0.24742102	0.00078001
5	0.79179532	0.74039755	0.05139777

It can be observed that the maximum absolute error is 0.05139777.

The exact and approximate results of $\varphi(x)$ are shown in Fig. 4.6 (a) and the resulted error is shown in Fig. 4.6 (b).

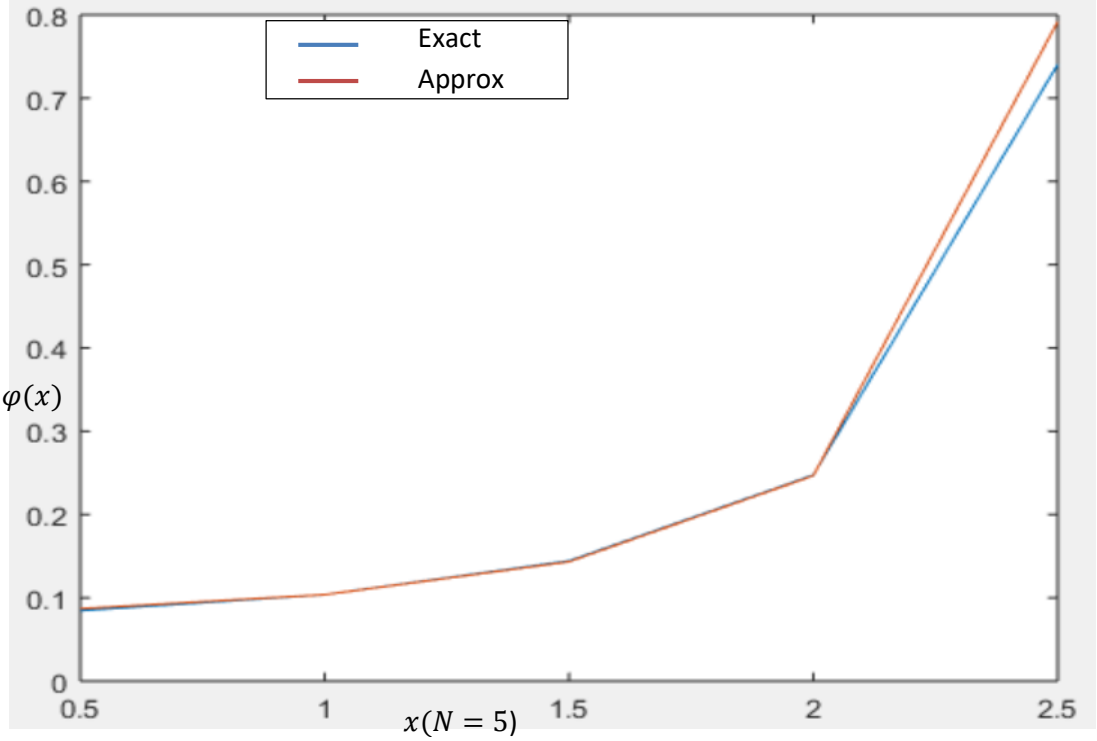


Fig 4.6 (a): A comparison between the exact and approximate solution in example 4.3.

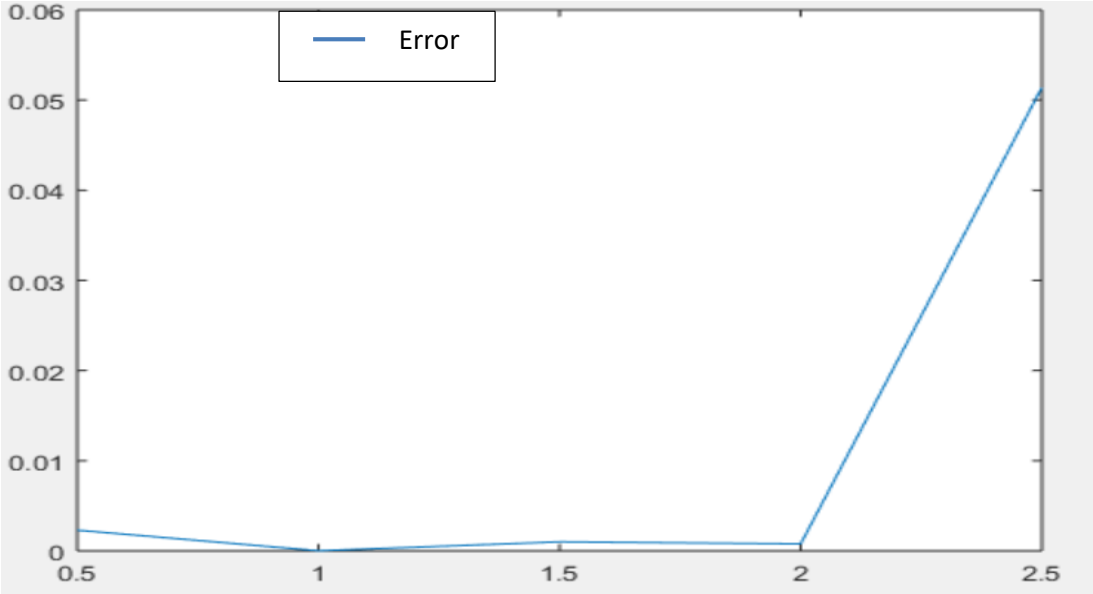


Fig. 4.6 (b): Absolute error between exact and numerical solution in example 4.3.

Table (4.7) contains the exact and the numerical results for the energy in example (4.3).

Table (4.7): numerical The exact and the results for the energy in example (4.3).

N	E_{exact}	$E_{numerical}$	Absolute error $\lvert E_{exact}\text{-}E_{num}\rvert$
1	1.12300000	1.09551111	0.02748889
2	4.46100000	4.38649084	0.07450916
3	9.90500000	9.86960440	0.03539560
4	17.16200000	17.545963379	0.383963379
5	24.78200000	27.4155677808	2.63356778

It can be observed that the maximum error is 2.63356778.

The exact and approximate results of E_n are shown in Fig. 4.7 (a) and the resulted error is shown in Fig. 4.7 (b).

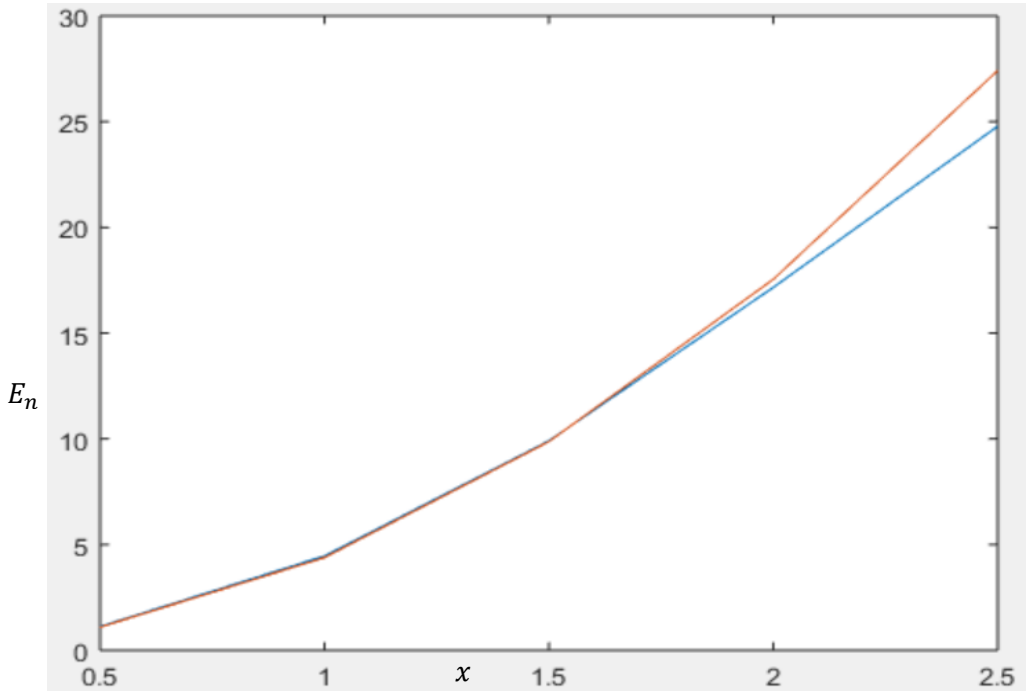


Fig 4.7 (a):A comparison between The exact and approximate results of $\boldsymbol{E_n}$.

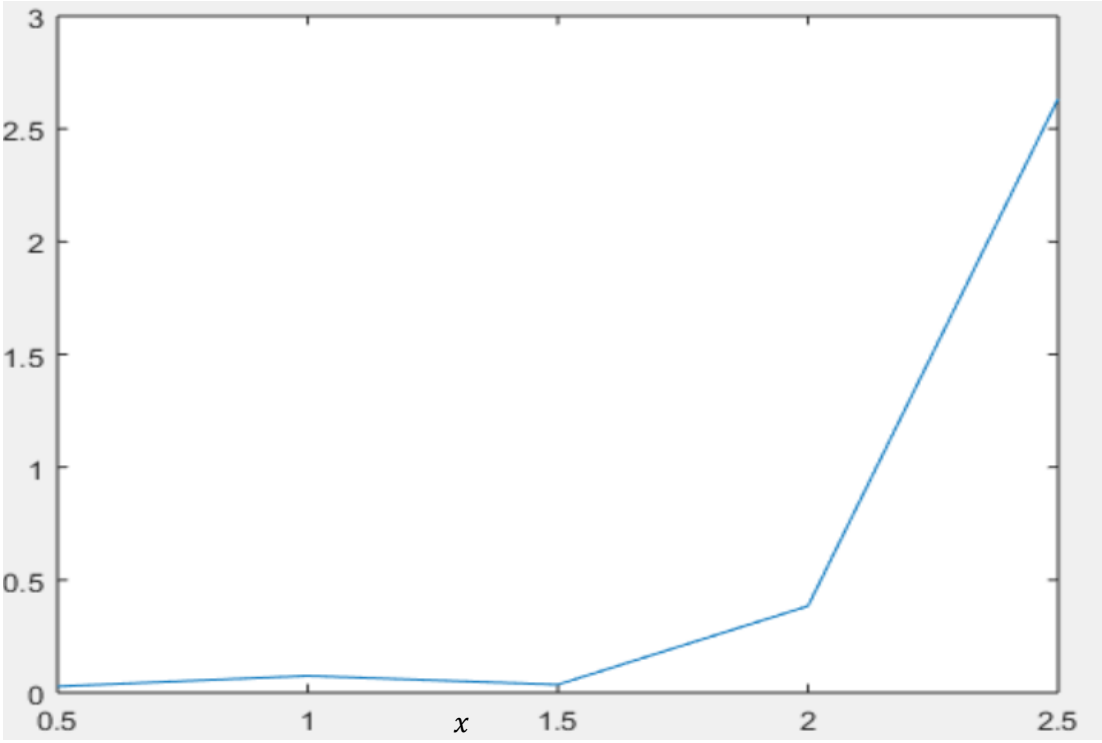


Fig 4.7 (b): Absolute error between exact and numerical energy in example 4.3.

Conclusion

In this work we have used some analytical methods, namely, the separation of variables method and the method of characteristics to solve the Schrödinger equation. However, our main focus was on implementing two numerical methods, these are: the finite difference and pseudo-spectral methods, for solving the Schrödinger equation.

Numerical results show clearly that the pseudo-spectral method (collocation) gives more efficient results than the finite difference method. One major advantage of the pseudo-spectral method is that it does not require a tedious steps of evaluating the unknown coefficients of the approximating function. It is also seen to be suitable for any class of linear differential equations with or without analytical solutions. Another advantage of pseudo-spectral method is that the time independent Schrödinger equation reduces to a system of algebraic equations which can be solved by many iterative methods. This provides an accurate approximation for a smooth solution with relatively few degree of freedom. Finally, less grid points are needed with the pseudo-spectral method than with finite difference methods to achieve the same accuracy.

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Appendix

Appendix (A)

Matlab code for finite difference method for time-independent Schrödinger equation (infinite square well).

```
Clear all
  L= input('\n Please enter the value of L');
  n= input('\n Please enter the value of n');
   m= input('\n Please enter the value of m');
  N= input('\n Please enter the value of N');
 (% since h=2m=1 )
h= (2*m)^(1/2) ;
(% find the values of the energy )
En=zeros(1,N);
for i=1:N+1
En(i)=(i*i*(22/7)*(22/7)*2*m)/(2*m*L*L)
end
En=[En1 En2 En3 En4 En5 En6 En7 En8 En9 En10 ];
  k=((2*m*En)/(h*h))^(1/2)
(%enter the values of the matrix Hamiltonian Ĥ)
 h1=(2/h*h)
 h2=-1/(h*h)
H=[h1 h2 0 0 0 0 0 0 0 0; h2 h1 h2 0 0 0 0 0 0 0;0 h2 h1 h2 0 0 0 0 0 0;0 0 h2
h1 h2 0 0 0 0 0;0 0 0 h2 h1 h2 0 0 0 0;0 0 0 0 h2 h1 h2 0 0 0;0 0 0 0 0 h2 h1 h2
0 0;0 0 0 0 0 0 h2 h1 h2 0;0 0 0 0 0 0 0 h2 h1 h2;0 0 0 0 0 0 0 0 h1 h2]
(% find the eigenvector and eigenvalue of  Ĥ)
```

```
[V,D] = eig(H)
(% the values of the diagonal of the eigenvalue)
app=[0 D(1,1) D(2,2) D(3,3) D(4,4) D(5,5) D(6,6) D(7,7) D(8,8) D(9, 9)
0];
 (% the exact value of the wavefunction)
ress=zeros(1,N);
for j=1:N
ress(j)=(2)^(.05) *(sin((22/7)*j/10))
end
real= [0 ress 0]
 (% enter the values of x)
x=[0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1]
 (%plot the exact solution and approximation of wavefunction)
plot(x,real)
hold on
plot(x,app)
(%the error between exact and approximation solutions)
diff=real-d1;
plot(x,diff);
(%the absolute error)
AbDiff= abs(diff);
plot(x,AbDiff);
```

Appendix (B)

Matlab code for finite difference method for time-independent Schrödinger equation (finite square well).

```
L= input('\n Please enter the value of L');

 v= input('\n Please enter the value of v');

  m= input('\n Please enter the value of m');

 N= input('\n Please enter the value of N');
if mod(N,2)==1
else N= input('\n Please renter the value of N, you entered even number')
end

f1= input('\n Please enter the value of start of interval');

f2= input('\n Please enter the value of end of interval');

h=(f2-f1)/(N+1);

; h1=(2/h*h)
 ;h2=-1/(h*h)
```

```
number_of_X= N+1;

H=zeros(number_of_X/2);
for(i=1:number_of_X/2)
for(j=1:number_of_X/2)
if (i==j)
H(i,j)=h2;
else if (abs(i-j)==1)
H(i,j)=h1;
else
H(i,j)=0;
end
end
end
end

H1=-H;


[V,D] = eig(H)
[V1,D1] = eig(H1)

En=zeros(1,N);
 for i=1:N
```

```
En(i)=(-1* alpha(1,i) *alpha(1,i)*(h)*(h)*2*m)+v
end
for(i=1:number_of_X/2)
for(j=1:number_of_X/2)
c(i,j)=D(i,i)
end

for(i=1:number_of_X/2)
for(j=1:number_of_X/2)
alpha1(i,j)=D1(0,0);
end

alpha=[c, alpha1];

plot(c,V)

plot(alpha,En);

a1=alpha(1,5:8)

plot(a1,V1)

En1=En(1:4)
En2=En(5:8)
```

Appendix (c)

Matlab code for Pseudo-spectral method for time-independent Schrödinger equation.

```
n= input('\n Please enter the max value of n');
N= input('\n Please enter the value of N');
theta= zeros(1,n);
 for ii=1:n
theta(ii)=((2*n-1)*(22/7))/(N-1);
tt=[0.5 0 0 0 0 0 0 0 0; 0.5 theta(1)  theta(1)^2 theta(1)^3 theta(1)^4
theta(1)^5 theta(1)^6 theta(1)^7 theta(1)^8;0.5 theta(2)  theta(2)^2
theta(2)^3 theta(2)^4 theta(2)^5 theta(2)^6 theta(2)^7 theta(2)^8;0.5
theta(3)  theta(3)^2 theta(3)^3 theta(3)^4 theta(3)^5 theta(3)^6 theta(3)^7
theta(3)^8;0.5 theta(4)  theta(4)^2 theta(4)^3 theta(4)^4 theta(4)^5
theta(4)^6 theta(4)^7 theta(4)^8;0.5 theta(5)  theta(5)^2 theta(5)^3
theta(5)^4 theta(5)^5 theta(5)^6 theta(5)^7 theta(5)^8;0.5 theta(6)
theta(6)^2 theta(6)^3 theta(6)^4 theta(6)^5 theta(6)^6 theta(6)^7
theta(6)^8;0.5 theta(7)  theta(7)^2 theta(7)^3 theta(7)^4 theta(7)^5
theta(7)^6 theta(7)^7 theta(7)^8;0.5 theta(8)  theta(8)^2 theta(8)^3
theta(8)^4 theta(8)^5 theta(8)^6 theta(8)^7 theta(8)^8].
```

جامعة النجاح الوطنية
كلية الدراسات العليا

الحلول العددية لمعادلة شرودينجر

اعداد
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قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الرياضيات المحوسبة في كلية الدراسات العليا، نابلس، فلسطين.

2019

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الملخص

تعتبر معادلة شرودنغر ومتغيراتها من المعادلات المحورية مجال البحث في مجال المعادلات التفاضلية الجزئية ولها تطبيقاتها المختلفة في هندسة الرياضيات ونظرية الضوء والطيف والانظمة المتكاملة. تهدف هذه الدراسة الى عرض المفاهيم الاساسية لميكانيكا الكم ومنها معادلة شرودنغر بشكليها: معادلة شرودنغر المرتبطة بالزمن وتلك غير المرتبطة بالزمن. اضافة الى ذلك, ستركز الباحثة وبشكل رئيسي على بعض الطرق التحليلية والعددية لحل معادلة شرودنغر ومتغيراتها. فبالنسبة الى الحل التحليلي لمعادلة شرودنغر، فان الباحثة ستعمل على مبدا فصل المتغيرات ومبدا الخصائص. اما بالنسبة للمعالجة العددية للمعادلة،فان الباحثة ستستخدم مبدا الفروق المنتهية ومبدا الطيف الزائف لحالتين من ميكانيكا الكم: الحالة المحدودة وغير المحدودة. ولكي يتم اختبار فاعلية هذه الطرق، تم الاخذ بعين الاعتبار بعض حالات الاختبار العددية. وقد اظهرت النتائج العددية بوضوح ان مبدا الطيف الزائف هو الطريقة الاقوى لحل معادلة شرودنغر غير المرتبطة بالزمن بالمقارنة مع التفاضل المحدود.