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A Matrix Method of Solving the Schrödinger Equation

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Abstract

Quantum mechanics, is an important branch in physics, that is used to describe physical behaviours at typical (quantum) scales. It is believed that many every day physical systems, at this scale behave in a manner that cannot be correctly described by classical mechanics. Unlike classical mechanics, which relies on Newtonian mechanics to describe the behaviour of physical systems, quantum mechanics relies on wave mechanics/ Schrödinger equation to describe their behaviour. The description of physical systems revolves around solving the Schrödinger equation, since the solutions can be used to describe the behaviour of atomic/subatomic, molecular systems. These calculations are usually approximate methods, since we can solve exactly for few physical systems. This has lead to the need of having a simpler, less numerically demanding way of solving this equation.

In this report, we investigate one such technique of solving the Schrödinger equation. This involves matrix formulation of the partial differential Schrödinger equation, approximation of wave functions using a set of orthonormal basis function of the harmonic oscillator. We also use analytic method, that is ladder operators, to solve for the partial differential Schrödinger equation. After developing this technique, we then apply it to some real world calculations, such as, quantum tunnelling, to study a particle moving in a region of more than one constant potential or studies of the molecular vibration of a diatomic molecule. In addition, this techniques is also applied on the theoretical basis, which typically involves modelling of the harmonic oscillations.

KEYWORDS: Schrödinger equation, Harmonic oscillator, Ladder operators, Matrix formulation.

Declaration

I, the undersigned, hereby declare that the work contained in this research project is my original work, and that any work done by others or by myself previously has been acknowledged and referenced accordingly.



Polycarp Omondi Okock, 12th July 2015

"That every definite mathematical problem must necessarily be susceptible of an exact settlement, either in the form of an actual answer to the question asked, or by the proof of the impossibility of its solution and therefore the necessary failure of all attempts."

David Hilbert, Paris, Wednesday 8th August, 1900.

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1. Introduction

1.1 Introduction.

The Schrödinger equation can be described as a partial differential equation(pde), formulated to explain how the quantum state of a physically realizable system evolves through time. It is an important equation in quantum mechanics, since it forms the basis of describing any quantum mechanical behaviour. This equation was formulated by Erwin [Schrödinger \(1926\)](#), who showed that it is the equivalent of the Newtonian laws but for quantum systems. Generally it is a linear pde, that explains the time-evolution of a system's wave function, [Griffith \(2005\)](#). *In quantum mechanics, the wave function, also referred to as the state function, is taken to be the most complete description that can be assigned to a physical system.* The Schrödinger equations solutions are applicable to describing the behaviour of atomic/subatomic, molecular, macroscopic systems and probably the whole universe, [Laloe \(2012\)](#).

The time independent Schrödinger equation,

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right) \phi_n(x) = E_n \phi_n(x).$$

Which in terms of the Hamiltonian is written as,

$$H\phi_n(x) = E_n\phi_n(x). \quad (1.1.1)$$

Where H is the Hamiltonian/Hermitian operator, $\phi_n(x)$ are the wave functions representing the state, m is the mass, x is the position and E_n are the eigenvalues/energy for the Hermitian operator. Solving the Schrödinger equation is one of the most basic problems in quantum mechanics. Analytical methods have been used to solve cases of the Harmonic oscillator and the Hydrogen atom, [Griffith \(2005\)](#), but in most cases, numerical methods have been employed to solve the eigenvalues E_n and the corresponding eigenfunctions as discussed in the paper [Sandvik \(Fall 2013\)](#).

Apart from the Schrödinger equation, there are other formulations that can be used to make predictions in quantum mechanics. These are Werner [Heisenberg \(1925\)](#) matrix mechanics and Richard [Feynman \(1948\)](#) path integral formulations. In matrix mechanics, the Schrödinger equation is recasted as a matrix problem, which is then solved using matrix solving methods.

This research focuses on the extension of the matrix mechanics but instead of just deriving a matrix method that can be used to solve the harmonic or an-harmonic oscillator, we come up with a general matrix expression that can be applied to solve any power series potential. To do this, we take the Schrödinger equation, and rewrite it in terms of another set of orthonormal basis wave functions. In this form, we derive eigenvalue equation for the Schrödinger equation. From here we find the matrix equation for the Hamiltonian operator. Our goal now becomes to solve for this matrix equation, so as to get energy/eigenstates and eigenfunctions. To make the whole process easy, the Hamiltonian is rewritten in terms of ladder operators, then we solve for the matrix elements.

To solve for the Hamiltonian matrix elements, we use a computer software, SAGE, to solve the eigenvalues and eigenfunction regardless of whether the matrix is diagonal or not (this is where the method derives it's strength).

1.2 Mathematical Formalism

Quantum mechanics is based on two constructs, that is wave functions and operators.

1.2.1 Wave functions.

These are usually denoted by $\phi_n(x)$, which are representative of the state of the system. We make the assumption that they belong to Hilbert space.

1.2.2 Operators.

An operator is an instruction to do something to the function that follows it, [Griffith \(2005\)](#), and is a representative of an observation. The relationship that exists between the operators and the wave functions is that of the form of a linear transformation where the operators act as a linear transformation.

The condition for representing any physical state is that the wave function must be normalizable. This is very critical, more so if the matrix method we are formulating is to work. As a result of this, we will restrict ourselves to potentials that give a **discrete spectra**. We now define hermitian operators and stationary states, which are fundamental for the eigenvalue equation.

1.2.3 Hermitian Operators.

In classical mechanics, these are represented by position and momentum measurements/observables. Crossing over to quantum mechanics, they are now referred to as position, x , and momentum, $p = \frac{\hbar}{i} \frac{d}{dx}$, operators respectively.

They are hermitian operators, of which the proofs can be found in [Griffith \(2005\)](#) or any quantum mechanic books, and they possess the following properties; they are real, linear and symmetric. The Schrödinger equation [1.1.1](#) can be written in terms of the position and momentum operator, which now becomes,

$$\left(\frac{P^2}{2m} + V(x) \right) \phi_n(x) = E_n \phi_n(x).$$

1.2.4 Stationary States.

Now that we have the Schrödinger equation in terms of the hermitian operators, the wave functions are now referred to as the determinate states of H . In other words, the stationary states are the determinate states of the Hamiltonian, [Griffith \(2005\)](#).

1.2.5 Eigenvalue Equation for the Hermitian operator H .

From equation [1.1.1](#), the determinate states, $\phi_n(x)$, of the energies, E_n , are referred to as the eigenfunction of Hamiltonian H . Therefore, [1.1.1](#) is also referred to as the **eigenvalue equation**. We are certain that measurement of H is going to yield the eigenvalue E_n . This is where the idea that the Schrödinger equation can be solved using a matrix method arises. The solutions of the eigenvalue equation are the spectrum and eigenfunctions.

1.2.6 Spectrum.

The collection of eigenvalues of an operator is called its spectrum, [Griffith \(2005\)](#). Cases where two or more eigenfunctions share the same eigenvalue is called a degenerate. There are two types of spectra, discrete and continuous. This research focuses on potentials that give discrete spectra, which means that the eigenvalues are separated. This is because of the conditions we placed on the states (**refer to section [1.2.2](#)**). The condition for representing a physical state is that the wave function [1.2.1](#) must be normalizable and the eigenvalues to be real.

1.2.7 Report structure.

Having set-up all the formalism needed to to formulate the matrix method, we briefly introduce each chapter. Chapter 2 introduces the matrix method and discusses its formulation and Dirac notations.

Chapter 3 deals with the case study of the simple harmonic oscillator, showing how the matrix method can be applied to solve the eigenvalues/energy for the simple harmonic oscillator. It is here that we define the ladder operators which forms a useful tool for deriving the general expression for the matrix method.

Chapter 4 focuses on deriving a general matrix expression for the Hamiltonian for power series type of potentials. This is achieved by taking the Hamiltonian and writing it in terms of ladder operators. Then using the matrix definitions for the ladder operators, we get the general matrix expression for the Hamiltonian.

Chapter 5 discusses the computer routine that involves the use of a computer program, SAGE, to solve the Hamiltonian matrix for the two case studies; Harmonic oscillator and the power series potentials. At the end, we develop an algorithm that can be used to solve a Taylor or power series potential.

Chapter 6 mainly focuses on the discussion of the results derived from chapter 5 and the possibility of further research. Finally, we have Appendix 7, which contains SAGE codes used in computer routine and the links to the blog containing the rest of the computer codes.

2. The Matrix Method

In this chapter we derive a general matrix for the 1D Schrödinger equation (**defined in 1.1.1**). To do this, we expand the eigenfunctions in terms of another orthonormal set of basis function, then after applying some algebra, we come up with a formula that gives us the matrix entries. We then use this formula to fill out the matrix for the Schrödinger equation.

2.1 The Matrix method

The eigenfunctions are normalized and orthogonal. Therefore, the eigenfunctions are orthonormal,

$$\int_{\mathbb{R}} \phi_m^*(x) \phi_n(x) dx = \delta_{mn}. \quad (2.1.1)$$

These result from the fact that we are dealing with potentials that give discrete spectra and the condition we imposed on the eigenfunctions. The idea is to expand the eigenfunction in terms of another orthonormal set of basis functions $\Psi_i(x)$. That is,

$$\phi_n(x) = \sum_{i=0}^{\infty} c_i^{(n)} \Psi_i(x), \quad (2.1.2)$$

where $\Psi_i(x)$ is another orthonormal set of basis, i.e.

$$\int_{\mathbb{R}} \Psi_j^*(x) \Psi_i(x) dx = \delta_{ji}. \quad (2.1.3)$$

Note that c_i is a complex coefficient. Multiplying equation 2.1.2 by $\Psi_j^*(x)$ and integrating with respect to x over the \mathbb{R} line, we get,

$$\begin{aligned} \int_{\mathbb{R}} \Psi_j^*(x) \phi_n(x) dx &= \sum_{i=0}^{\infty} c_i^{(n)} \int_{\mathbb{R}} \Psi_j^*(x) \Psi_i(x) dx, \\ \int_{\mathbb{R}} \Psi_j^*(x) \phi_n(x) dx &= \sum_{i=0}^{\infty} c_i^{(n)} \delta_{ji}, \\ \int_{\mathbb{R}} \Psi_j^*(x) \phi_n(x) dx &= c_j^{(n)}. \end{aligned} \quad (2.1.4)$$

So the expression for $c_i^{(n)}$ inferring from 2.1.4 is,

$$c_i^{(n)} = \int_{\mathbb{R}} \Psi_i^*(x) \phi_n(x) dx. \quad (2.1.5)$$

Then using equation 2.1.2 in equation 1.1.1 we get,

$$\sum_{i=0}^{\infty} c_i^{(n)} H \Psi_i(x) = E_n \phi_n(x), \quad (2.1.6)$$

multiplying both sides by $\Psi_j^*(x)$ we have,

$$\sum_{i=0}^{\infty} c_i^{(n)} \Psi_j^*(x) H \Psi_i(x) = E_n \Psi_j^*(x) \phi_n(x), \quad (2.1.7)$$

and integrating with respect to x over the \mathbb{R} line,

$$\sum_{i=0}^{\infty} c_i^{(n)} \int_{\mathbb{R}} \Psi_j^*(x) H \Psi_i(x) dx = E_n c_j^{(n)}. \quad (2.1.8)$$

Lets define H_{ji} as,

$$H_{ji} = \int_{\mathbb{R}} \Psi_j^*(x) H \Psi_i(x) dx, \quad (2.1.9)$$

then equation 2.1.8 becomes,

$$\sum_{i=0}^{\infty} c_i^{(n)} H_{ji} = E_n c_j^{(n)}. \quad (2.1.10)$$

Examining closely equation 2.1.10, it is noticeable that it is a set of equations for each j , i.e.

$$\begin{array}{ccccccc} c_0^{(n)} H_{00} & + & c_1^{(n)} H_{01} & + & \cdots & = & E_n c_0^{(n)} \\ c_0^{(n)} H_{10} & + & c_1^{(n)} H_{11} & + & \cdots & = & E_n c_1^{(n)} \\ \vdots & & \vdots & & \vdots & & \vdots \end{array}$$

Which can be written as a matrix equation,

$$\begin{pmatrix} H_{00} & H_{01} & \cdots \\ H_{10} & H_{11} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} c_0^{(n)} \\ c_1^{(n)} \\ \vdots \end{pmatrix} = E_n \begin{pmatrix} c_0^{(n)} \\ c_1^{(n)} \\ \vdots \end{pmatrix}. \quad (2.1.11)$$

Equation 2.1.10 is an exact equation but the matrix equation 2.1.11 is not, since we need a matrix of a finite size which is the same as truncating the sum in 2.1.10. Thus, matrix equation 2.1.11 is no longer exact. We write it as,

$$H x^{(n)} = E_n x^{(n)}. \quad (2.1.12)$$

Therefore, for a given potential, we construct the matrix H by filling out it's entries using equation 2.1.9. We would then use a software package to find the eigenvalues E_n and the corresponding eigenvectors $x^{(n)}$ of H . If we choose H to be an $N \times N$ matrix, then we will have N eigenvalues and eigenvectors. Namely n will run from 1 to N .

We are most interested in the eigenvalues, but also the eigenvectors are interesting because they are the column vector of coefficients,

$$x^{(n)} = \begin{pmatrix} c_0^{(n)} \\ c_1^{(n)} \\ \vdots \end{pmatrix}, \quad (2.1.13)$$

so they are equivalent to the eigenfunctions due to equation 2.1.2. If we increase the dimension of the matrix (N) we get more accurate results. This is because we are using a non exact equation (after truncating equation 2.1.10) to approximate the eigenvalues and eigenfunctions and the accuracy improves as we increase the finite size. Also, we anticipate that the matrix method will work best at small n and big N , when approximating eigenvalues and eigenfunctions.

2.2 Dirac Notations

We now want to express all the previous equations in Dirac notations, that is kets, $|a\rangle$, and bra, $\langle a|$. This is because the kets can be taken to represent column vectors and bras to represent row vectors. It is known that the linear operators of Dirac brackets are simply square matrices. Therefore, the 'kets' and 'bras' represent the state vectors. It was mentioned earlier that the relationship that exist between the operators and wave functions is that of a linear transformation. Use of 'bras' and 'kets' would seem appropriate to represent wave function. We then view the relationship as a linear operation on 'bras' or 'kets'.

To start off lets define the eigenfunctions using the following bra-ket notations,

$$\begin{aligned}\langle x|n\rangle &= \phi_n(x), \\ \langle x|i\rangle &= \Psi_i(x).\end{aligned}$$

Then the dirac notations will be as follows,

$$\begin{aligned}H|n\rangle &= E_n|n\rangle \quad \text{for eq. 1.1.1,} \\ \langle m|n\rangle &= \delta_{mn} \quad \text{for eq. 2.1.1,} \\ |n\rangle &= \sum_{i=0}^{\infty} |i\rangle \langle i|n\rangle \quad \text{for eq. 2.1.2,} \\ \langle j|i\rangle &= \delta_{ji} \quad \text{for eq. 2.1.3,} \\ \langle i|n\rangle &= \int_{\mathbb{R}} \langle i|x\rangle \langle x|n\rangle dx \quad \text{for eq. 2.1.5,} \\ \langle j|H|i\rangle &= \int_{\mathbb{R}} \langle j|x\rangle H \langle x|i\rangle dx \quad \text{for eq. 2.1.9,} \\ \sum_{i=0}^{\infty} \langle j|H|i\rangle \langle i|n\rangle &= E_n \langle j|n\rangle \quad \text{for eq. 2.1.10,} \\ \begin{pmatrix} \langle 0|H|0\rangle & \langle 0|H|1\rangle & \cdots \\ \langle 1|H|0\rangle & \langle 1|H|1\rangle & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \langle 0|n\rangle \\ \langle 1|n\rangle \\ \vdots \end{pmatrix} &= E_n \begin{pmatrix} \langle 0|n\rangle \\ \langle 1|n\rangle \\ \vdots \end{pmatrix} \quad \text{for eq. 2.1.11,} \\ x^{(n)} &= \begin{pmatrix} \langle 0|n\rangle \\ \langle 1|n\rangle \\ \vdots \end{pmatrix} \quad \text{for eq. 2.1.13.}\end{aligned}$$

The above definitions would prove useful when writing the matrix representations. We proceed to examine case studies using this matrix method, that is,

1. Harmonic oscillator, chapter 3.
2. An-harmonic, oscillator chapter 5 section 5.3.
3. Double-well potential, chapter 5 section 5.4.
4. Morse oscillator. chapter 5 section 5.5.

3. The Quantum Harmonic Oscillator

In classical mechanics, a harmonic oscillator, is taken to be a system that, when displaced from its assumed equilibrium position, experiences a restoring force, F , proportional to the displacement, x . The quantum harmonic oscillator is the quantum-mechanical equivalent of the classical harmonic oscillator. Since an arbitrary potential can normally be approximated as a harmonic potential, in the presence of a stable equilibrium point, it is one of the most essential model systems in quantum mechanics. Furthermore, it is among the few quantum-mechanical systems, of which an exact solution is known. See [Hayek \(2003\)](#).

In this chapter, we find the quantum harmonic Hamiltonian matrix, then solve it using matrix techniques. We do this by defining ladder operators, and then writing the Hamiltonian in terms of the ladder operators. We then solve the matrix elements. In addition, we also find the matrix definitions for the ladder operators. This, later will form an important basis for deriving the general matrix expression for the Hamiltonian matrix.

Harmonic Hamiltonian.

The Hamiltonian for the harmonic oscillator, defined in [Griffith \(2005\)](#) book, is,

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}. \quad (3.0.1)$$

Where $\frac{p^2}{2m}$ is the kinetic energy and $\frac{m\omega^2 x^2}{2}$ is the potential energy.

3.1 1D Schrödinger equation

For the harmonic oscillator, the 1D time independent Schrödinger Equation will be given by,

$$\frac{1}{2m} (p^2 + (m\omega x)^2) \phi_n(x) = E_n \phi_n(x). \quad (3.1.1)$$

Before solving the Schrödinger Equation, it is convenient to make everything dimensionless by making the following assumptions; $m=\hbar=\omega = 1$. With these units, the Schrödinger equation becomes easy to solve and also the solutions look neater.

It has been shown in [Griffith \(2005\)](#) or any other quantum mechanic book, using the ladder operators or analytic methods, that the unperturbed energy levels for harmonic oscillator are given by,

$$E_n = \left(n + \frac{1}{2} \right). \quad (3.1.2)$$

And the wave functions are given by,

$$\phi_n(x) = \frac{1}{\sqrt{2^n \cdot n!}} \cdot H_n(x) \cdot \frac{1}{\sqrt[4]{\pi}} e^{-\frac{x^2}{2}}. \quad (3.1.3)$$

For all $n = 0, 1, 2, \dots$. Where $H_n(x)$ is a Hermite polynomial, see [Griffith \(2005\)](#) or [Lecture notes](#). Ladder operator methods allow us to directly solve the energy values without solving the differential equation [1.1.1](#), whereas analytic methods solve the differential equation directly to extract the energy values.

3.2 Ladder operators

Define a_+, a_- to be $a_+ = \frac{1}{\sqrt{2}}(-ip + x)$, $a_- = \frac{1}{\sqrt{2}}(ip + x)$. And

$$a_- a_+ = \frac{1}{2}(p^2 + x^2) - \frac{i}{2}(xp - px). \quad (3.2.1)$$

Dirac Bracket, $[,]$.

Let E and F be two observables, we want to define a bracket $[E, F]$ of two observables. We would like that,

1. That $[E, F]$ be an observable (linear and symmetric operator).
2. That $[E, F] = i\hbar$. (see Born and Jordan (1925))
3. For observable E, F we must have the following $[F, F] = 0 = [E, E]$.

Therefore $xp - px = i\hbar$. Setting $\hbar = 1$ and then substituting back into equation (3.2.1) we get;

$$a_- a_+ = \frac{1}{2}[p^2 + x^2] + \frac{1}{2}. \quad (3.2.2)$$

Analog to the process, for $a_- a_+$ we have that

$$a_+ a_- = \frac{1}{2}[p^2 + x^2] - \frac{1}{2}, \quad (3.2.3)$$

The pair are known as ladder operators with a_+ defined as the raising operator and a_- defined as the lowering operator. We also define a number operator, N , which has the following property,

$$N = a_+ a_-. \quad (3.2.4)$$

With the above definitions we easily obtain the following commutators (see Born and Jordan (1925)).

1. $[a_-, a_+] = 1$,
2. $[N, a_+] = a_+$,
3. $[N, a_-] = -a_-$.

The 1D Schrödinger equation 3.1.1 in terms of the ladder operators is,

$$\left(a_- a_+ - \frac{1}{2}\right) \phi_n(x) = E_n \phi_n(x) \quad \text{or} \quad (3.2.5)$$

$$\left(a_+ a_- + \frac{1}{2}\right) \phi_n(x) = E_n \phi_n(x). \quad (3.2.6)$$

From the above two definitions for the Schrödinger equation, we are bound to have the states $a_{\pm} \phi_n(x)$. The states $a_{\pm} \phi_n(x)$ are not yet normalized and they are proportional to $\phi_n \pm 1$. Lets define the following equations,

$$a_+ \phi_n(x) = c_n \phi_{n+1}(x), \quad (3.2.7)$$

$$a_- \phi_n(x) = d_n \phi_{n-1}(x). \quad (3.2.8)$$

Where c_n, d_n are unknown proportionality constants, which make the states $a_{\pm}\phi_n(x)$ to be normalized.

Determination of Proportionality constants c_n, d_n

Using equations 3.2.5 and 3.1.2 it is easy to check that,

$$\begin{aligned} \left(a_- a_+ - \frac{1}{2}\right) \phi_n(x) &= \left(n + \frac{1}{2}\right) \phi_n(x), \\ a_- a_+ - \frac{1}{2} &= \left(n + \frac{1}{2}\right), \\ a_- a_+ &= n + 1. \end{aligned} \quad (3.2.9)$$

And also,

$$\begin{aligned} \left(a_+ a_- + \frac{1}{2}\right) \phi_n(x) &= \left(n + \frac{1}{2}\right) \phi_n(x), \\ a_+ a_- + \frac{1}{2} &= \left(n + \frac{1}{2}\right), \\ a_+ a_- &= n. \end{aligned} \quad (3.2.10)$$

3.2.1 Lemma.

$$\int_{\mathbb{R}} f^* (a_{\pm} g) dx = \int_{\mathbb{R}} (a_{\mp} f)^* g dx. \quad (3.2.11)$$

The proof can be found in (see Griffith (2005)) book.

So from equation 3.2.7 and using the lemma 3.2.1,

$$\begin{aligned} \int_{\mathbb{R}} (a_+ \phi_n(x))^* (a_+ \phi_n(x)) &= |c_n|^2 \int_{\mathbb{R}} \|\phi_{n+1}(x)\|^2 dx, \\ \int_{\mathbb{R}} (a_+ \phi_n(x))^* (a_+ \phi_n(x)) &= n + 1 \int_{\mathbb{R}} \|\phi_{n+1}(x)\| dx. \end{aligned}$$

Comparing above two equations it's clear that $|c_n|^2 = n + 1$. Similarly for 3.2.8,

$$\begin{aligned} \int_{\mathbb{R}} (a_- \phi_n(x))^* (a_- \phi_n(x)) &= |d_n|^2 \int_{\mathbb{R}} \|\phi_{n-1}(x)\|^2 dx, \\ \int_{\mathbb{R}} (a_- \phi_n(x))^* (a_- \phi_n(x)) &= n \int_{\mathbb{R}} \|\phi_{n-1}(x)\| dx. \end{aligned}$$

Comparing above two equations it's clear that $|d_n|^2 = n$. Substituting this values for c_n and d_n back to equations 3.2.7 and 3.2.8 respectively. Therefore we have,

$$a_+ \phi_n(x) = \sqrt{n+1} \phi_{n+1}(x), \quad (3.2.12)$$

$$a_- \phi_n(x) = \sqrt{n} \phi_{n-1}(x). \quad (3.2.13)$$

3.3 Dirac notations

A quantum state in the Fock space is called a Fock State (see Bargmann (1961)). It is an element of the occupancy number basis (the trailing zeros can be dropped without changing the number of particles

in that state). In our case, the operators are the raising and lowering operators which upon acting on a Fock state, add/remove a particle in that quantum state, $\phi_n(x)$. To see this in action, we define our Fock space for the states, $\phi_n(x)$ using n as an index to have the following vectors,

$$\phi_0 \rightarrow \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} = |0\rangle, \phi_1 \rightarrow \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} = |1\rangle, \dots, \phi_n \rightarrow \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ \vdots \end{pmatrix} \swarrow_{n^{th} row} = |n\rangle.$$

We therefore express the arbitrary eigenstates 3.1.3 as $|n\rangle$. And apply the equations 3.2.12 and 3.2.13 to get following,

$$a_+|n\rangle = \sqrt{n+1}|n+1\rangle, \quad (3.3.1)$$

$$a_-|n\rangle = \sqrt{n}|n-1\rangle, \quad (3.3.2)$$

and the number operator N ,

$$N|n\rangle = n|n\rangle. \quad (3.3.3)$$

The proofs can be found in Griffith (2005) or Computational Physics. The above three properties reaffirm that a_+ is a creation operator, a_- is annihilation and the number operator returns the quantum number n , for particles of the corresponding energy level. Hence it follows that the Schrödinger equations 3.2.5 and 3.2.6, in terms of Dirac notations are,

$$\begin{aligned} \left(a_-a_+ - \frac{1}{2}\right)|n\rangle &= E_n|n\rangle \quad \text{or} \\ \left(a_+a_- + \frac{1}{2}\right)|n\rangle &= E_n|n\rangle. \end{aligned}$$

3.4 Matrix representation

Lets define a notation that will prove useful in generating the matrix expression. Using Dirac delta, $\delta_{m,n}$, where $\delta_{m,n} = \begin{cases} 1 & m = n \\ 0 & m \neq n \end{cases}$.. We use this definition to express the Delta as a matrix, where if row number equals column number, we assign 1, else 0 i.e.

$$\langle m|n\rangle = \delta_{m,n} \Rightarrow \mathbb{I} = \begin{pmatrix} 1 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \vdots & \vdots & 0 & \ddots \end{pmatrix} = \mathbb{I} \Leftarrow \delta_{j,i} = \langle j|i\rangle.$$

The rest of the notations can be found in chapter two 2.2. The matrix elements for H are given by,

$$H = \begin{pmatrix} \langle 0|H|0\rangle & \langle 0|H|1\rangle & \langle 0|H|2\rangle & \dots \\ \langle 1|H|0\rangle & \langle 1|H|1\rangle & \langle 1|H|2\rangle & \dots \\ \langle 2|H|0\rangle & \langle 2|H|1\rangle & \langle 2|H|2\rangle & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (3.4.1)$$

But $\langle j|H|i\rangle$ the matrix elements are equivalent to,

$$\langle j|H|i\rangle = \langle j|a_+a_- + \frac{1}{2}|i\rangle, \quad (3.4.2)$$

$$\langle j|H|i\rangle = \left(i + \frac{1}{2}\right) \delta_{ji}. \quad (3.4.3)$$

The matrix elements for the ladder operators, starting with the raising operator a_+ (refer to equation 3.3.1) is given by,

$$\langle j|a_+|n\rangle = \sqrt{n+1} \delta_{j,n+1} \quad \text{which is} \quad a_+ = \begin{pmatrix} 0 & 0 & 0 & \dots \\ 1 & 0 & 0 & \dots \\ 0 & \sqrt{2} & 0 & \dots \\ 0 & 0 & \sqrt{3} & 0 \\ \vdots & \vdots & 0 & \ddots \end{pmatrix}. \quad (3.4.4)$$

For the lowering operator (refer to equation 3.3.2) we have,

$$\langle j|a_-|n\rangle = \sqrt{n} \delta_{j,n-1} \quad \text{which is} \quad a_- = \begin{pmatrix} 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & \sqrt{2} & 0 & \dots \\ 0 & 0 & 0 & \sqrt{3} & \dots \\ 0 & 0 & 0 & 0 & \ddots \\ \vdots & \vdots & 0 & \dots & \end{pmatrix}. \quad (3.4.5)$$

For the number operator (refer to equation 3.3.3), we have,

$$\langle j|N|n\rangle = n\delta_{j,n} \quad \text{which is} \quad N = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 2 & 0 & \dots \\ 0 & 0 & 0 & 3 & \dots \\ \vdots & \vdots & 0 & \dots & \ddots \end{pmatrix}. \quad (3.4.6)$$

It is easy to check that $H = \left(a_+a_- + \frac{1}{2}\right)$ is defined by the following matrix, where the elements along the diagonal are the eigenvalues,

$$H = \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 & \dots \\ 0 & \frac{3}{2} & 0 & 0 & \dots \\ 0 & 0 & \frac{5}{2} & 0 & \dots \\ 0 & 0 & 0 & \frac{7}{2} & \dots \\ \vdots & \vdots & 0 & \dots & \ddots \end{pmatrix}. \quad (3.4.7)$$

Later, we will use a computer program, SAGE, to generate these results and work out the eigenvalues, eigenvectors and use the eigenvectors to determine the wave functions 2.1.2.

4. The Power Series Potential

These are potentials that can be expressed as an infinite series, usually are of the form,

$$f(x) = \sum_{n=0}^{\infty} a_n (x - k)^n,$$

where a_n is the n^{th} coefficient, k is a constant and variable x varies around the constant (being centred at k). It usually arises as the Taylor series of some known function.

In this section, we consider the Hamiltonian for power series potential and recast it in matrix form. Thereby setting up a general matrix expression for solving the power series potentials.

4.1 Introduction

Consider a Hamiltonian where everything is dimensionless, so,

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + V(x). \quad (4.1.1)$$

Where $V(x)$ is some power series,

$$V(x) = a_0 + a_1x + a_2x^2 + \dots = \sum_{k=0}^{K_{max}} a_k x^k. \quad (4.1.2)$$

The goal is to find a general solution for the Schrödinger equation for such potentials. Some of the potentials which can be expressed as power series includes the following;

- Harmonic potential,
- Anharmonic potentials,
- Double well potential,
- Morse potentials.

Therefore, having a general method for solving the Schrödinger equation for such potentials would not only prove useful but it would also make the process of solving the energy values less time consuming.

Moreover, we can take the potential and do a Taylor series expansion,

$$V(x) = V(x_0) + (x - x_0)V'(x_0) + \frac{(x - x_0)^2}{2}V''(x_0) + \frac{(x - x_0)^3}{6}V'''(x_0) + \dots \quad (4.1.3)$$

Often we will expand about the minimum, so the first derivative will be equated to zero, $V'(x_0) = 0$ and we choose the minimum point to be $x_0 = 0$ i.e.

$$V(x) = V(0) + \sum_{k=2}^{K_{max}} V^{(k)}(0) \frac{x^k}{k!}.$$

4.1.1 Remark. The potentials that can be expressed as power series are of two types; finite and infinite polynomials. For instance, harmonic and double-well potential are finite polynomial, whereas Morse potential, when expanded as Taylor series is an infinite series. But generally, these potential are discrete in nature, and will therefore give a discrete energy spectra (eigenvalues). We develop a general Hamiltonian matrix for the power/Taylor series potential but later, when solving the different potentials, we adjust it to a finite expansion.

The method for finding the general solution of equation 4.1.1 will deviate from the traditional methods of using numerical methods, (Sandvik, Fall 2013). These usually consumes a lot of time.

We proceed to find the general expression for equation 4.1.1 in terms of matrices.

4.2 General Expression

The goal is to find a general expression for equation 4.1.1 which is now written as,

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \sum_{k=0}^{K_{max}} a_k x^k. \quad (4.2.1)$$

We need ladder operators, which as had been defined in equation 3.2, are $a_{\pm} = \frac{1}{\sqrt{2}} \left(\mp \frac{d}{dx} + x \right)$. Then rewrite x and $\frac{d}{dx}$ in terms of a_+ and a_- . That is,

$$x = \frac{1}{\sqrt{2}} (a_+ + a_-), \quad \frac{d}{dx} = \frac{1}{\sqrt{2}} (a_- - a_+).$$

The next step is to substitute these expression for x and $\frac{d}{dx}$ into equation 4.2.1 so that it now becomes,

$$H = -\frac{1}{2} \left(\frac{1}{\sqrt{2}} (a_- - a_+) \right)^2 + \sum_{k=0}^{K_{max}} a_k \left(\frac{1}{\sqrt{2}} (a_+ + a_-) \right)^k. \quad (4.2.2)$$

Normally we try to find the matrix elements $\langle j|H|i \rangle$ for H , so as to determine the matrix, but this would be a long process deriving all the matrix elements. Instead, we use a short cut that gives the matrix directly without deriving the matrix elements then forming the matrix itself. This is possible when using the matrix definitions for the raising 3.4.4 and lowering 3.4.5 operators that we derived.

We proceed to determine $(a_- - a_+)$ and $(a_+ + a_-)$ since they are included in equation 4.2.2. Therefore, for $(a_- - a_+)$ we get,

$$(a_- - a_+) = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ -\sqrt{1} & 0 & \sqrt{2} & 0 & \dots \\ 0 & -\sqrt{2} & 0 & \sqrt{3} & \dots \\ 0 & 0 & -\sqrt{3} & 0 & \ddots \\ \vdots & \vdots & 0 & \dots & \end{pmatrix}. \quad (4.2.3)$$

And for $(a_+ + a_-)$ we get,

$$(a_+ + a_-) = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \dots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \dots \\ 0 & 0 & \sqrt{3} & 0 & \ddots \\ \vdots & \vdots & 0 & \dots & \end{pmatrix}. \quad (4.2.4)$$

With the above matrices, it is easy to directly find the matrix representation for 4.2.2. Note that,

$$\left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2} \quad \text{and} \quad \left(\frac{1}{\sqrt{2}}\right)^k = \left(\frac{1}{2}\right)^{\frac{k}{2}}.$$

The matrix H will be defined as follows,

$$H = -\frac{1}{4} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ -\sqrt{1} & 0 & \sqrt{2} & 0 & \dots \\ 0 & -\sqrt{2} & 0 & \sqrt{3} & \dots \\ 0 & 0 & -\sqrt{3} & 0 & \ddots \\ \vdots & \vdots & 0 & \dots & \end{pmatrix}^2 + \sum_{k=0}^{K_{max}} a_k \left(\frac{1}{2}\right)^{\frac{k}{2}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \dots \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \dots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \dots \\ 0 & 0 & \sqrt{3} & 0 & \ddots \\ \vdots & \vdots & 0 & \dots & \end{pmatrix}^k. \quad (4.2.5)$$

Using the short cut, we did not have to go through all the processes of deriving the matrix elements $\langle j|H|i\rangle$, then forming the matrix H . But by rewriting 4.2.1 in terms of ladder operators and using the matrix definition for the ladder operators, we got the matrix directly. In the next chapter, we perform computer routines for known examples of Taylor/power series potential.

5. Computer Simulations

In this chapter, we demonstrate the simulations of the matrix method using the SAGE program, whose codes can be found in appendix 7.1. Some of the solutions we will simulate includes the harmonic oscillator we solved in chapter 3 and an-harmonic oscillators.

5.1 Code Structure

Given that we are dealing with matrices, the first thing we have to do is to specify the dimensions of the matrix that we want to achieve. Let N represent the dimension. Note that we are only dealing with square matrices, $N \times N$. But since we have matrices for the lowering, raising, and Hamiltonian matrix, it is best we start with defining the ladder operators first. For instance, lowering operator matrix is defined by l_{op} ,

```
l_op=matrix(RDF,(N)) #creates an N by N matrix of zeros
#we then fill the initial matrix with the correct entries
for i in range(l_op.nrows()):
    for j in range(l_op.ncols()):
        if i <> j-1:
            l_op[i, j] = 0
        else:
            l_op[i, j] = sqrt(j)
```

The square matrix dimension is defined by the code `matrix(RDF,(N))`. The same applies to the raising operator matrix, which is defined as r_{op} . We then define two new variables, A and B , which will contain the following operations, see equations 4.2.3 and 4.2.4,

```
A=r_op+l_op;B=l_op-r_op
```

The Hamiltonian matrix 4.2.5, is defined by the following code function,

```
def H(A,B,list): #input values A, B and list of coefficients.
    k = len(list)
    a=-0.25*B**(2) #evaluates the first part of the summation of H
    def bb(k): #generates the summations for the second part
        b = 0 #initialise the starting value
        for i in range(k): #added one to include the end value
            b = b + list[i]*(0.5)**(i/2)*A**(i)
        return b
    HH=a + bb(k) #H as defined
    return HH #return the results to the function call
```

To use this function, we call $H(A,B,list)$, where A , B are as defined earlier. The *list* contains the coefficients a_k for that specific potential. The same applies to the function for getting the eigenvalues and eigenvectors, which are defined by the following code functions.

```
def eva(A,B,list):# eigenfunction
    mat = H(A,B,list)#Hamiltonian matrix
    ls=mat.eigenvalues()#list of eigenvalues
```

```
ls.sort()#sorts in ascending order
return ls
```

And

```
def evec(A,B,list):#eigenvector function
    mat = H(A,B,list)#Hamiltonian matrix
    ls=mat.eigenvectors_left()#list of eigenvector
    ls.sort()#sorts in ascending order
    return ls
```

The rest of the code, that is, for plotting and Hermite polynomial can be found in the appendix. The next step is to check the eigenvalues and wave functions for the following,

- harmonic Oscillator,
- anharmonic Oscillators,
- double well potential and
- Morse potential.

Since their Schrödinger solutions are well known, but this isn't exactly true of the double well (although some properties of its solution, eg the pairing up of energy levels, is well-known). With them, we can confirm if the matrix method actually works in solving the Schrödinger equation.

5.2 Quantum Harmonic Oscillator

The potential for the Harmonic oscillator given by 3.0.1, when expressed as a power series 4.1.2 has the following coefficients,

$$a_k = \begin{cases} \frac{1}{2} & k = 2 \\ 0 & k \neq 2 \end{cases}.$$

Before solving the potential, we plot it to have an idea of how the graph looks.

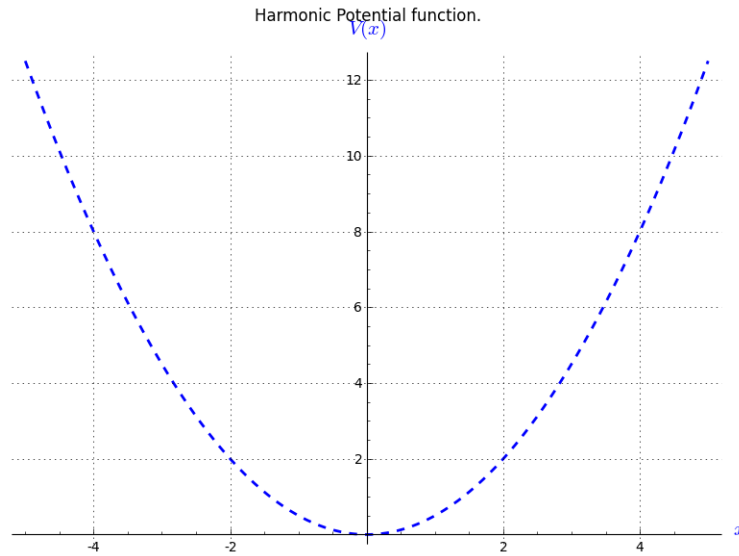


Figure 5.1: Harmonic potential function plot.

We then plug it to the general matrix expression 4.2.5. With these definitions we then apply the matrix function code,

```
H(A,B,[0,0,0.5]).
```

where $[0,0,0.5]$ is the list containing the coefficients. We get the same matrix as defined in 3.4.7. The elements along the main diagonal are the eigenvalues and we get them by running the following code,

```
eva(A,B,[0,0,0.5]).
```

We get the following $[0.5, 1.5, 2.5, 3.5, 4.5, 5.5, 6.5, 7.5, \dots]$, which is the correct list containing the eigenvalues. For this case, the eigenfunctions are easy to determine, since it is a diagonal matrix. They are just the vectors we defined in the definition for a Fock space for the states $\phi_n(x)$ in section 3.3. They are found by running the following code,

```
evvec(A,B,[0,0,0.5]).
```

The wave functions for the simple harmonic oscillator using equation 2.1.2, are represented by the following graphs, showing the first four energy levels.

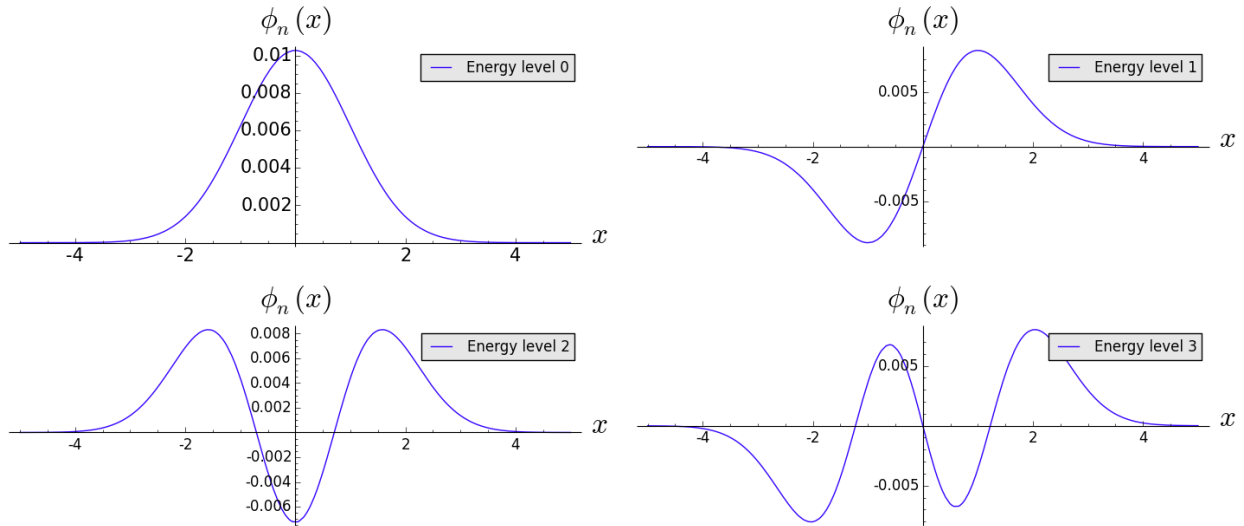


Figure 5.2: Wave function, $\phi_n(x)$, for the harmonic oscillator.

Which are the correct wave functions, see [Griffith \(2005\)](#).

5.3 Anharmonic Oscillators

By definition, this is the deviation of a system from being a harmonic oscillator. An oscillator that is not oscillating in an harmonic motion is known as being anharmonic oscillator and can be approximated using the harmonic oscillator (recall equation 2.1.2 where we expand the wave function in terms of another orthonormal set). The other orthonormal set will be chosen to be the harmonic oscillator wave functions. Also, instead of having the unperturbed energy levels as defined in equation 3.1.2, we have perturbed energy levels which can be calculated using the Perturbation theory, see [Monserrat et al. \(2013\)](#). This is because the energy levels for harmonic oscillation are taken to be unperturbed and deviation from this oscillation, the energy levels are considered perturbed.

Well-known examples of anharmonic potentials include shifted harmonic and double well. Also we have the Morse potential, whose oscillation is anharmonic. Just like the harmonic oscillator, these potentials are known to give discrete spectra and we use the matrix method to solve these potentials and check that the results confirm with their known solutions. Moreover, these potentials belong to the family of power series potentials 4.1.2. It should therefore be easy to solve them using the general matrix expression 4.2.5 we defined earlier.

We begin by solving the shifted harmonic potential, then the rest follows.

5.3.1 Shifted Harmonic Potential.

The potential for the shifted harmonic is defined as,

$$V(x) = \frac{1}{2}x^2 + x. \quad (5.3.1)$$

The plot for the shifted harmonic potential is shown below.

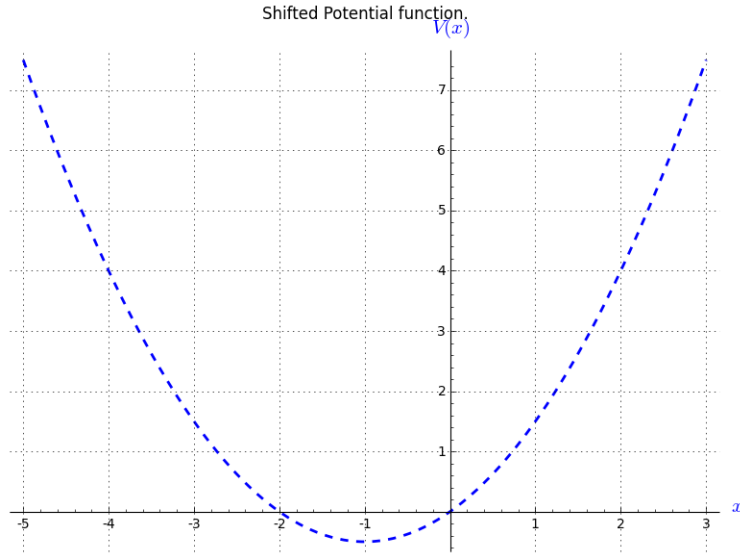


Figure 5.3: Shifted potential function plot.

From the above figure 5.3, it is clear that the potential has shifted compared to the harmonic potential function, 5.1. Note that we are still under the assumption of unit mass, Planck's constant and angular frequency, $m=\hbar=\omega = 1$. The Hamiltonian for this potential 5.3.1 is,

$$H = \frac{1}{2} \left(-\frac{d^2}{dx^2} + x^2 \right) + x.$$

The above Hamiltonian is rewritten in the following way,

$$H = \frac{1}{2} \left(-\frac{d^2}{dx^2} + (x+1)^2 \right) - \frac{1}{2}. \quad (5.3.2)$$

We make the following change of variable, $\tilde{x} = x + 1$, and substitute it back into equation 5.3.2, to get the new Hamiltonian, now denoted by \tilde{H} ,

$$\tilde{H} = \frac{1}{2} \left(-\frac{d^2}{d\tilde{x}^2} + \tilde{x}^2 \right) - \frac{1}{2}.$$

Comparing this Hamiltonian to the Hamiltonian for the harmonic oscillator defined in 3.0.1, we can rewrite \tilde{H} as,

$$\tilde{H} = H(\tilde{x}) - \frac{1}{2},$$

where $H(\tilde{x})$ is the harmonic Hamiltonian.

The 1D Schrödinger equation is written as,

$$\tilde{H}\phi_n(\tilde{x}) = \tilde{E}_n\phi_n(\tilde{x}).$$

The eigenvalues, \tilde{E}_n in this case (shifted) when expressed in terms of the unperturbed energy levels for the harmonic oscillator 3.1.2 are,

$$\tilde{E}_n = E_n - \frac{1}{2}.$$

Given that we already know the eigenvalues for the harmonic oscillator, we anticipate that the eigenvalues for the shifted harmonic will be less by 0.5 for the corresponding eigenvalue in the harmonic oscillator, i.e.

$$\tilde{E}_n = n.$$

For all $n = 0, 1, 2, 3, \dots$.

We now run the simulations for the shifted Harmonic oscillator. Clearly the coefficient for the potential are $a_0 = 0, a_1 = 1, a_2 = 0.5$ The code for finding the shifted Hamiltonian matrix is given by,

```
H(A,B,[0,1,0.5])
```

where $[0, 1, 0.5]$ is the list containing the coefficients.

5.3.2 Remark. For this kind of Hamiltonian, it is not diagonal, so we calculate the eigenvalues using SAGE. This is where, the advantages of using the matrix method, begins to show. Usually, calculating the energy levels for a non diagonal Hamiltonian, can prove to be very difficult. Especially if one is using numerical methods, but in this case, solving energy levels using a computer program becomes easier.

The eigenvalues are given by the following code function,

```
eva(A,B,[0,1,0.5])
```

The energy at different levels and matrix dimension are shown in the table below.

Table 5.1: Table of eigenvalues at different levels n and different matrix dimension size N

level n	N = 10	N = 15	N = 20
0	0.0	0.0	0.0
1	1.00000343411	1.0	1.0
2	2.00015843959	2.0	2.0
3	3.00335602621	3.0	3.0
4	4.03375809008	4.000001	4.0
5	5.17207710068	5.00003	5.0
6	6.53359289158	6.00057	6.0
7	8.23698137747	7.00657	7.00000009
\vdots	\vdots	\vdots	\vdots

The eigenvalues are less by 0.5 compared to the corresponding Harmonic oscillator eigenvalues.

5.3.3 Remark.

The accuracy of the eigenvalues for a given level n improves as we increase the dimension of the matrix and as we increase the level n for a given N the accuracy worsens. This can be seen in table 5.1.

The eigenvectors are given by the following code function,

```
evec(A,B,[0,1,0.5])
```

We now plot the wave functions for the shifted Harmonic oscillator. Comparing the plot for the harmonic potential in figure 5.1 and the shifted harmonic potential in figure 5.3, we anticipate that the wave functions for the shifted harmonic should also be shifted to the left by a factor of 1 just as the potential was shifted to the left by that same factor.

We plot the first four wave functions corresponding to the four lowest energy states for the shifted harmonic oscillator.

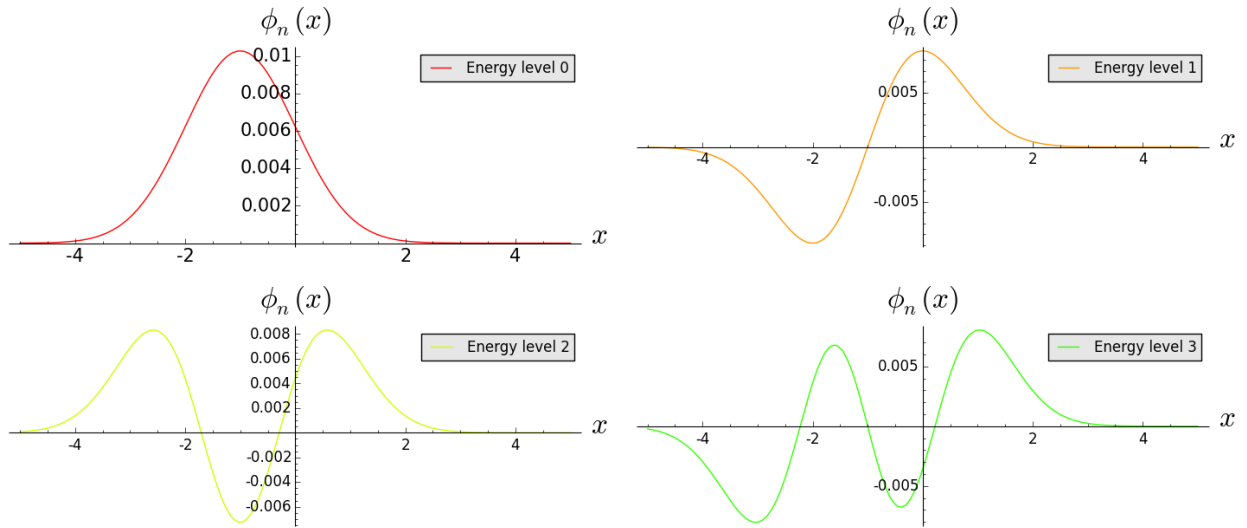


Figure 5.4: Wave function, $\phi_n(\tilde{x})$, for the shifted harmonic oscillator.

It is clear that the wave functions have shifted to the left by one from figure 5.4.

As n the energy level tends towards the N , the matrix method fails to generate accurate wave functions. To counter this, we increase the dimensions N of the matrix. This effect and how to counter it is demonstrated by the following.

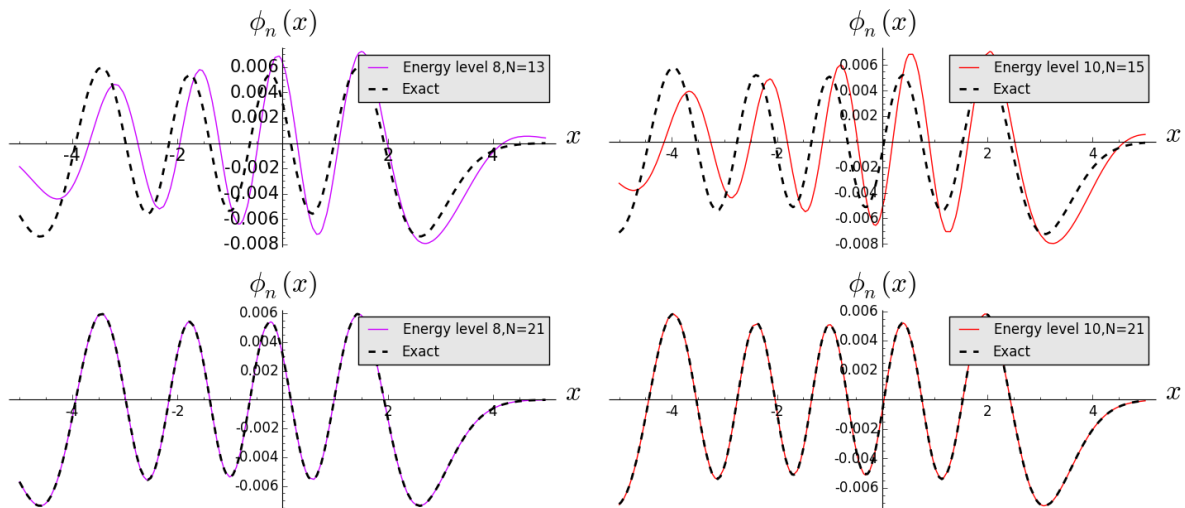


Figure 5.5: Wave function, $\phi_n(\tilde{x})$, for the shifted harmonic oscillator

From figure 5.5, the two examples given, clearly show that as we increase N for a fixed level n the approximated wave function become more and more accurate.

5.4 The Double-Well Potential

The double well potential has a number of applications; it is applied in the modelling of the ammonia potential [Peacock-Lopez \(2006\)](#) in studies involving ionization energy, quantum tunnelling to study a particle moving in a region of more than one constant potential [Veguilla-Berdecia \(1993\)](#) and ring puckering potential function, [Laane and Lord \(1967\)](#), where in chemistry a ring molecule is a molecule made up of several series of atoms bonded together to form a ring or cycle. Therefore ring puckering/gathering is the study that analyses the anharmonic energies that results from ring puckering/gathering vibrations.

The double-well potential, though there are several functional forms, is usually in the form of,

$$V(x) = \alpha x^2 + \beta x^4.$$

With $\alpha < 0$, the barrier height and $\beta > 0$, the steepness parameter. Despite the different functional forms of the double-well, the potential always has the following basic shape.

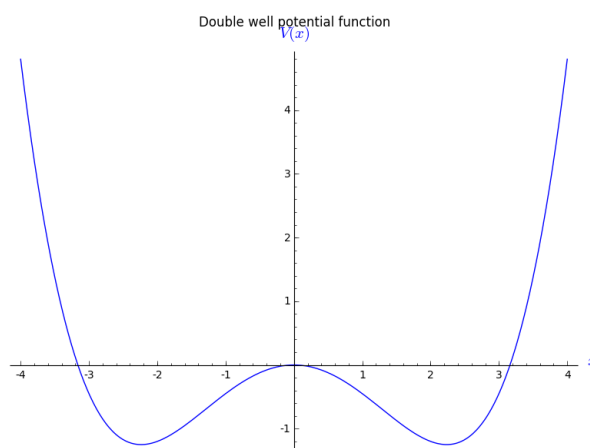


Figure 5.6: Double-well potential

One notices that near the two local minima, the potential looks similarly to the harmonic potential. The height of the potential barrier at the center is represented by α but it is also affected by β , taken as the steepness parameter. As $\alpha \rightarrow \infty$ the barrier height becomes infinite and the system decomposes into two independent components (almost harmonic potential but not, due to the quartic term), separated from each other. Harmoniously, the wave function of the system should tend to two split up sets of wave functions. If α is no longer infinite, a particle in either of the left or right hand region, has a non-zero tunnelling probability, that is tunnelling through the barrier to the other well. And therefore the wave functions for the left and right hand region are mixed with each other. Since the action will be symmetric, $x \rightarrow -x$, the solutions for the Schrödinger equation can be broken up into symmetric and antisymmetric wave functions. Usually the symmetric states have a lower energy compared to the antisymmetric states (since fewer number of nodes implies less kinetic energy for the particle). But this difference in lower energies is usually very small (slightly non-degenerate) and it gets more smaller and smaller as we increase α . See [Muñoz-Vega et al. \(2013\)](#).

For instance, we take the example of Ammonia inversion. It is used to explain the inversion of the ammonia molecules, nitrogen and two hydrogen molecules. The hydrogen atoms forms a plane and at any given time, the nitrogen can be above or below the plane (quantum tunnelling). The position x ,

represent the position above or below this plane and the potential barrier is represented by the energy gap between the states of the positions of the nitrogen (above or below), see Pareek (2013).

With the above arguments, we are bound to encounter interesting results, that there will be two slightly ordered pair non-degenerate energy levels for the system. This means that the wave functions for ordered pairs of eigenvalues will be symmetric and asymmetric of each other and this effect will be more pronounced at a larger barrier height. Using this well known argument, we use the matrix method to confirm them.

Consider the following functional form double well potential,

$$V(x) = -\alpha x^2 + \beta x^4 \quad (5.4.1)$$

The following code function generates the eigenvalues for a specific α and fixed $\beta = 0.05$,

```
eva(A,B,[0,0,-1*alpha,0,0.05])
```

We proceed to investigate if increasing the barrier height will result to having two slightly non-degenerate paired energy levels for system. The results are shown in the table below. Note that the routines were all done at $N = 25$.

Table 5.2: Table of eigenvalues, E_n , at different barrier heights α

Level n	$E_n, \alpha = 0$	$E_n, \alpha = 0.4$	$E_n, \alpha = 0.8$	$E_n, \alpha = 1.0$	$E_n, \alpha = 1.4$	$E_n, \alpha = 1.9$
0	0.246088	-0.310467	-2.340349	-4.026639	-8.635363	-16.685933
1	0.881825	-0.173383	-2.339374	-4.026606	-8.635317	-16.685278
2	1.730314	0.541689	-0.823374	-2.204148	-6.387041	-14.045773
3	2.702506	1.200373	-0.763823	-2.20079	-6.385771	-14.016476
4	3.774035	2.031553	0.208164	-0.684479	-4.274351	-11.522706
5	4.928989	2.958714	0.704142	-0.578455	-4.270654	-11.402079
6	6.156710	3.973062	1.516793	0.382904	-2.337512	-10.289035
7	7.449426	5.06316	2.380957	0.974825	-2.324037	-8.912339
8	8.801158	6.221048	3.336842	1.830769	-1.320793	-8.697902
9	10.207122	7.440943	4.366883	2.741802	-0.600494	-7.008072
10	11.659480	8.716319	5.461443	3.646259	-0.460279	-5.590924
11	13.165896	10.044426	6.613236	4.785807	0.792689	-4.551003

From table 5.2, the effect as we increase $\alpha = a$, we get two slightly non-degenerate paired energy levels i.e. the splitting between ordered pairs becomes smaller and smaller as we increase the barrier height. In addition, looking at the table the effect of two slightly non-degenerate paired energy levels is more pronounced for the lower energy levels 0, 1, 2, 3, 4, 5 compared to the other levels 6, 7, 8, \dots .

We now investigate the corresponding eigenfunctions/wave functions. As mentioned earlier, the wave functions for ordered pairs of eigenvalues will be symmetric and asymmetric of each other and this effect will be more pronounced at a larger barrier height. Below are the results of paired wave functions for the first 7 energy levels.

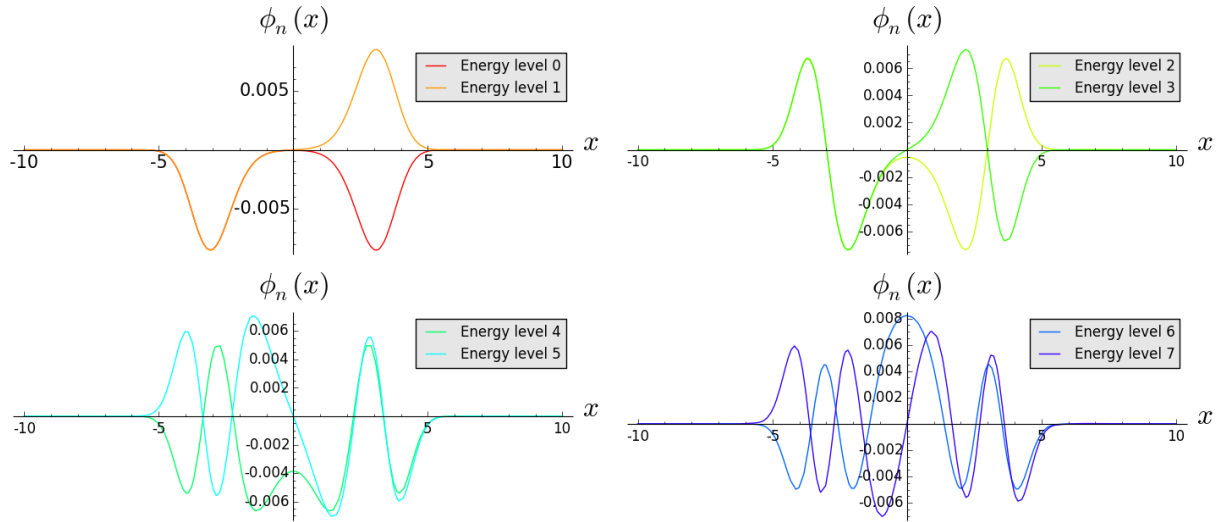


Figure 5.7: Paired wave functions, $\phi_n(x)$, for the double-well.

Figure 5.7 agrees with what is already known about the wave function. That as we increase the barrier height, the wave functions for ordered pairs of eigenvalues will be symmetric and asymmetric of each other.

5.5 Morse Potential

The Morse potential, which arose in studies of diatomic molecules (Morse (1929)), is defined in terms of the internuclear distance in the form,

$$V(r) = D_e \left(1 - e^{-\alpha \left(\frac{r-r_0}{r_0} \right)} \right)^2,$$

where r_0 is the equilibrium internuclear distance, r the internuclear distance, D_e is the dissociation energy and α is the range parameter (steepness of the potential) and therefore affects the vibrational frequencies. The Morse potential realistically leads to disassociations making it more useful than the harmonic potential when studying molecular vibration since a diatomic molecule which is actually bounded by harmonic potential will never dissociate. It can therefore be taken as the simplest representation of the potential between two nuclei in which dissociation is possible.

We make a change of variables, where $x = \frac{r-r_0}{r_0}$, then substitute in the Morse potential so that now it becomes a function of x i.e.

$$V(x) = D_e (1 - e^{-\alpha x})^2.$$

With the change of variable, we write the Hamiltonian for the 1D Morse oscillator as follows,

$$H = \frac{p^2}{2} + D_e (1 - e^{-\alpha x})^2. \quad (5.5.1)$$

Before trying to solve for the Hamiltonian, we do a Taylor expansion of potential in equation 5.5.1 to the first four terms so that it becomes,

$$H = \frac{p^2}{2} + D_e \left(\alpha^2 x^2 - \alpha^3 x^3 + \frac{7}{12} \alpha^4 x^4 \right). \quad (5.5.2)$$

The Morse energy levels are defined using the following equation, [Simons \(2003\)](#),

$$E_n = hV_0 \left(n + \frac{1}{2} \right) - \frac{(hV_0)^2}{4D_e} \left(n + \frac{1}{2} \right)^2. \quad (5.5.3)$$

With $V_0 = \frac{\alpha}{2\pi} \sqrt{\frac{2D_e}{m}}$. We then translate it into "natural units" by making the following transformation,

$$\begin{aligned} hV_0 &= \frac{h\alpha}{2\pi} \sqrt{\frac{2D_e}{m}}, \\ hV_0 &= \hbar\alpha \sqrt{\frac{2D_e}{m}}, \text{ where } \hbar = \frac{h}{2\pi}, \\ hV_0 &= \alpha\sqrt{2D_e}, \text{ as } \hbar = m = 1. \end{aligned}$$

Then substitute these $hV_0 = \alpha\sqrt{2D_e}$ back in to equation 5.5.3 to get the following,

$$E_n = \alpha\sqrt{2D_e} \left(n + \frac{1}{2} \right) - \frac{\alpha^2}{2} \left(n + \frac{1}{2} \right)^2. \quad (5.5.4)$$

This potential supports both bound states (below the disassociation threshold, for which vibration is confined by an outer turning point) and continuum states lying above the disassociation threshold. The degree of anharmonicity is regulated by the ratio $\hbar\frac{\alpha}{2\pi}\sqrt{2D_e/m}$ to D_e . The energy spacings between the vibrational levels is defined by, see [Simons \(2003\)](#),

$$E_{n+1} - E_n = \hbar\frac{\alpha}{2\pi}\sqrt{2D_e/m} \left(1 - \frac{(n+1)\hbar\frac{\alpha}{2\pi}\sqrt{2D_e/m}}{2D_e} \right). \quad (5.5.5)$$

By energy spacing, we mean the difference energy value at that level and the preceding or previous level energy value. The spacing will decrease upto a $V_{max} = \frac{2D_e - \hbar\frac{\alpha}{2\pi}\sqrt{2D_e/m}}{\hbar\frac{\alpha}{2\pi}\sqrt{2D_e/m}}$, such that,

$$1 - \frac{(V_{max+1})\hbar\frac{\alpha}{2\pi}\sqrt{2D_e/m}}{2D_e} = 0. \quad (5.5.6)$$

At this point, the series of bound Morse levels stop to exist. This implies that the Morse potential has only a finite number of bound states. In other words, the equation 5.5.4 for energy levels becomes invalid and can not be used to calculate the energies for continuum states (above the disassociation threshold).

Unlike the equation for the Morse energy levels, which fails when $E_n > V_m$, the matrix method does not and can be used to approximate the eigenvalues for both bound and continuum states. To tell that the Morse energy levels equation is failing, the energies generated are either zero or negative or decreasing.

With the above arguments set up, the next step is to verify them. This will be inclusive of the following,

- the matrix method, is a good estimator of the energies. We compare the results with the ones calculated using the Morse energy levels equation 5.5.4.
- the wave functions and energies deviate further and further from the harmonic oscillator's as we increase α .
- at $E_n > V_m$, where the Morse energy levels equation 5.5.4 fails to calculate the energies above the disassociation threshold, the matrix methods is still able to approximate the energies even for continuum states.

We shall use the following parameters values,

Table 5.3: Set of different parameter values for D_e and α .

D_e	α
200	0.05
8	0.25
1	0.7071

We choose the above combinations so that the coefficient of x^2 is always $\frac{1}{2}$, i.e. $D_e\alpha^2 = \frac{1}{2}$, which is very similar to the harmonic oscillator. As α increases, the cubic and quartic terms become more and more significant, and the Morse potential will deviate further from the harmonic potential. These combinations will help us verify the arguments we stated.

5.5.1 The matrix method is a good estimator of the Morse energy levels.

We are using the parameter values $D_e = 200$ and $\alpha = 0.05$. The eigenvalue function will be defined as,

$$\text{eva}(A, B, [0, 0, D, -D, D * (7/12)], 200, 0.05)$$

The list of coefficients is $[0, 0, D, -D, D * (7/12)]$. The table below summarises the results obtained,

Table 5.4: Summary of energy values extracted using matrix method with the exact values(both Morse and Harmonic potentials).

	E_n at $n = 0$	E_n at $n = 1$	E_n at $n = 2$	E_n at $n = 3$
$N = 10$	0.4996874999266825	1.497187500536916	2.4921872051977467	3.4846484775131215
$N = 20$	0.4996875000000003	1.4971875000000017	2.4921875000000013	3.4846874999999815
$N = 30$	0.4996874999999975	1.4971875000000074	2.4921874999999999	3.4846874999999904
$N = 40$	0.4996875000000038	1.4971874999999961	2.4921874999999973	3.4846875000000006
Exact	0.4996875	1.4971875	2.4921875	3.4846875
HO	0.5	1.5	2.5	3.5

From the table 5.4, the first argument, of the matrix method being a good estimator of the energy levels, works as argued. Moreover, the energies are very close to those for the harmonic potential(HO). This was expected. In the next part, we verify that as α increases, the Morse energies deviate further and further from those of harmonic potential(HO).

5.5.2 The wave functions and energies deviate further and further from the harmonic oscillator's(HO) as we increase α .

Still using the parameter definition from table 5.3, we extract the eigenvalues and summarise in the below table. Note that, these results were calculated using matrix dimension, $N = 40$.

Table 5.5: Summary of set of eigenvalues at different α, D_e values compared with those for Harmonic potentials.

Level n	E_n at $\alpha = 0.05.D_e = 200$	E_n at $\alpha = 0.25.D_e = 8$	E_n at $\alpha = 0.7071.D_e = 1$	HO E_n
0	0.4996875000000038	0.49218750000001377	0.4375000855965472	0.5
1	1.4971874999999961	1.4296875000000333	0.9407253535006053	1.5
2	2.4921874999999973	2.3046875000002913	1.1439852496723713	2.5
3	3.4846875000000006	3.117187500127351	1.4280652618133887	3.5

The exact values for parameters $\alpha = 0.05.D_e = 200$, can be found in the previous table 5.4 at $N = 40$, for $\alpha = 0.25.D_e = 8$, they are $[0.4921875, 1.4296875, 2.3046875, 3.1171875]$ The exact values were not included for $\alpha = 0.7071.D_e = 1$, because the equation 5.5.4 becomes invalid for calculating values above D_e . This will be discussed in the next section. From the table 5.5, it is easy to check that as α , the energy values become further deviated from those of the Harmonic oscillator (HO). The same principle also applies to the wave functions, as shown in the figure below,

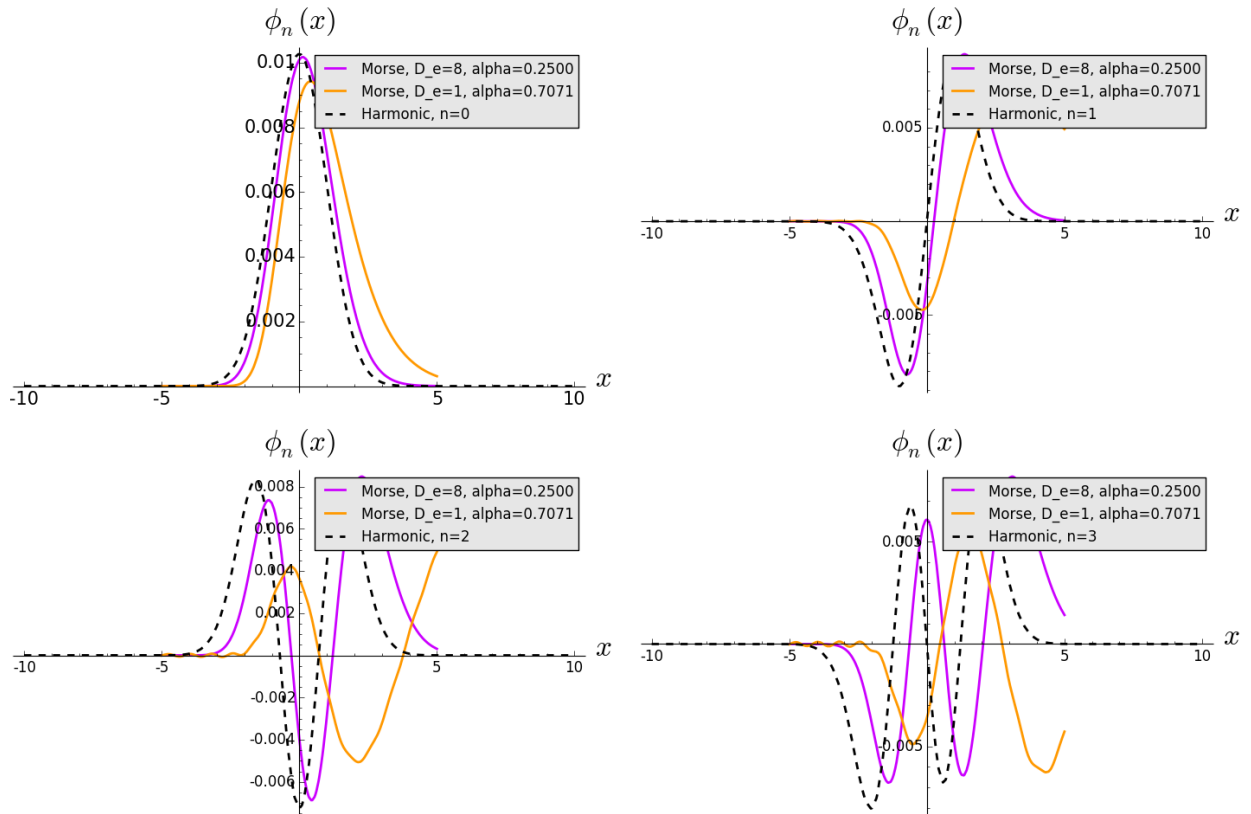


Figure 5.8: Wave functions, $\phi_n(x)$, for the Morse and Harmonic oscillator compared at different α, D_e values.

Finally, we verify that at $E_n > V_m$, where the Morse energy levels equation becomes invalid, the matrix methods is still able to approximate the energies. In other words, equation 5.5.4 cannot be used to calculate values above the disassociation energy, D_e .

5.5.3 At $E_n > V_m$, where the Morse energy levels equation becomes invalid for continuum states, the matrix methods is still able to approximate the energies.

The results are summarised in the below table(at $N = 150$).

Table 5.6: Eigenvalues generated using the equation 5.5.4 versus the matrix method.

n	Equation 5.5.4	Matrix method
0	0.4375	0.4374999985109682
1	0.9375	0.9375089499836712
2	0.9375	1.0281450516221002
3	0.4375	1.1022488214056039
4	-0.5625	1.2126913168034152
5	-2.0625	1.355543168552944
6	-4.0625	1.5287616255830494
7	-6.5625	1.7310739537457982
8	-9.5625	1.9616083302355336
9	-13.0625	2.219730261844933
10	-17.0625	2.504959499539324
11	-21.5625	2.8169213197060796
12	-26.5625	3.155318613639822
13	-32.0625	3.5199126856593703
14	-38.0625	3.9105116031147533
15	-44.5625	4.3269613371915545
16	-51.5625	4.769140102014493
17	-59.0625	5.236953682203706

(a) Eigenvalues, given by $\alpha = 0.7071.D_e = 1$.

	Equation 5.5.4	Matrix method
	0.4921875	0.4921874999993362
	1.4296875	1.4296874999974376
	2.3046875	2.304687500000195
	3.1171875	3.1171875000000138
	3.8671875	3.867187499999751
	4.5546875	4.554687499999648
	5.1796875	5.179687499999779
	5.7421875	5.742187499999672
	6.2421875	6.242187500001464
	6.6796875	6.679687501299343
	7.0546875	7.054688014505219
	7.3671875	7.367267483693835
	7.6171875	7.620876125549745
	7.8046875	7.846563400718177
	7.9296875	8.09876243276436
	7.9921875	8.392596084625126
	7.9921875	8.723152277901612
	7.9296875	9.08613097126883

(b) Eigenvalues, given by $\alpha = 0.25.D_e = 8$.

From the above table 5.6, the difference start showing at level 2 for table 5.6a and level 16 for table 5.6b. The explanation for this, is that at that level the energy spacing is zero, from which onwards it becomes negative. That is why the values for that column start decreasing, because with every level the spacing becomes negatively bigger. The argument that the Morse energies equation 5.5.4 become invalid for calculating the eigenvalues above the disassociation threshold, is clearly shown by the above table. At its failure, it is advisable to use the values from the matrix method, to approximate energies above the disassociation threshold. In summary, Morse energies equation 5.5.4 is valid for finite bound levels, energies below the disassociation threshold. This result, will be discussed more in the last section about further research.

6. Discussion of Results and Further Research

6.1 Results

The goal from the beginning was to formulate a matrix method for solving the Schrödinger equation. We started by deriving the matrix method, which at initial derivation, revolved around filling out the matrix entries. Fortunately, in chapter 3, after defining ladder operators and defining their matrix representations, we were able to derive the Hamiltonian matrix directly as done for the harmonic Hamiltonian equation. Though we were able to derive the matrix entries as done in equation, it is apparent that the two methods are akin. But for preference sake, went ahead and used the method of rewriting the Hamiltonian entirely in terms of ladder operators and then substituting these values with their matrix representation to get the matrix for the Hamiltonian. This was clearly illustrated in chapter 4, where we came up with the general matrix expression. It became much easier to solve for the Hamiltonian matrix this way.

In chapter 5, computer simulations for the matrix method were done to check if the method works. Simulations were done for well-known discrete potentials i.e. harmonic, shifted harmonic, double-well and Morse potential. The method, successfully modelled the harmonic and shifted harmonic potential, since we were able to reproduce the correct eigenvalues and the corresponding wave functions. For the simulation of the double-well and Morse potential, we set up the arguments using well known real world examples. That is ammonia inversion potential and molecular vibration of a diatomic molecule. The effects, for these two case, were clearly reproduced using the method. Throughout this process, we used the harmonic wave functions as the standard set of the orthonormal basis. This is because an arbitrary potential can normally be approximated as a harmonic potential, in the presence of a stable equilibrium point, it is one of the most essential model systems in quantum mechanics. Furthermore, it is among the few quantum-mechanical systems, of which an exact solution is known. See Hayek (2003).

At the end of chapter 5, we had had sufficient results to make a concrete conclusion that the matrix method actually solves the Schrödinger equation, and it has a wide range of applications where it can be applied i.e. quantum tunnelling to study a particle moving in a region of more than one constant potential, Veguilla-Berdecia (1993) or helping quantum mechanics students find solutions for anharmonic oscillators e.t.c. The real challenge comes when we want to study potentials that do not necessarily have discrete nor real spectra. This leads us to the next section about further research.

6.2 Further Research

In chapter five, when performing computer routines for the Morse potential, an interesting analysis was made. This analysis regards the direct comparison between the eigenvalues given by matrix method versus the Morse energy levels equation. The Morse energy levels equation is valid only for bound states, and is invalid for calculating energies above the disassociation threshold(continuum states). In the direct comparison, the matrix method was able to generate energy values for both bound and continuum states. Before making any winning remarks for the matrix method, further research should be conducted, to confirm that the values are indeed for the continuum states. Just because, the matrix method calculates energies, even above the disassociation energy, D_e , is not enough to conclude that it is the better for approximating Morse potential eigenvalues.

Throughout the report we remained, fixated on the assumption that we are dealing with potentials that give a discrete spectra, which is akin to the assumption that the wave function belongs to the Hilbert space, see [Griffith \(2005\)](#). But what happens, when we consider potentials that give, a mixture of real and complex spectra? This is when the matrix method we have formulated starts to experience shortcomings. One thing is sure, using the method we are bound to derive the set of eigenvalues regardless of whether they are real or complex. But when it comes to eigenfunctions, it is not always the case. This is so because the corresponding eigenvectors have a mixture of real and complex parts. The computer program fails to generate the wave functions for eigenvectors that have complex values. So we are not able to generate the wave functions at certain energy levels (complex energy states.)

This opens the door for further research, as to how the method can be adopted for such cases. Moreover, the question of how can we adapt the method for multidimensional cases also arises. It is assumed the energy is always real for physically realizable states, see [Griffith \(2005\)](#).

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7. Appendices

7.1 Computer Routines

This section contains the SAGE codes that were used for the computer simulation. The code to simulate the Harmonic potential.

```
def harmonic(N,n):
    l_op=matrix(RDF,(N)) #creates an N by N matrix of zeros
    for i in range(l_op.nrows()):
        for j in range(l_op.ncols()):
            if i <> j-1:
                l_op[i, j] = 0
            else:
                l_op[i, j] = sqrt(j)
#####
r_op=matrix(RDF,(N)) #creates an N by N matrix of zeros
for i in xrange(r_op.nrows()):
    for j in xrange(r_op.ncols()):
        if i <> j+1:
            r_op[i, j] = 0
        else:
            r_op[i, j] = sqrt(j+1)
#####
A=r_op+l_op
B=l_op-r_op
#####
def H(A,B,list):
    k = len(list)
    a=-0.25*B**(2) #evaluates the first part of the summation of H
    def bb(k): #generates the summations for the second part
        b = 0 #initialise the starting value
        for i in range(k): #added one to include the end value
            b = b + list[i]*(0.5)**(i/2)*A**(i)
        return b
    HH=a + bb(k) #H as defined
    #return HH[0:N-1,0:N-1] #return the results to the call
    return HH
#####
#calculates and returns the eigen values
def evec(A,B,list):
    matrix = H(A,B,list)
    return matrix.eigenvectors_left()
#####
def coefficients(A,B,list,n):
    eigenvectors = evec(A,B,list)
    List = eigenvectors[n][1][0].list()
```

```

    return List
#####
def hermite(n):
    var('x')
    if n==0:
        return 1
    else:
        return (-1)**(n)*np.exp(x**(2))*derivative(np.exp(-1*(x**(2))),x,n)
#####
def wave_function(n):
    pn = 1/(np.pi**(4))*(1/np.sqrt(2**(n)*m.factorial(n)))
    *hermite(n)*np.exp(-(x)**(2))/2)
    return pn
#####
def wave_function_new(A,B,list,n):
    x = var('x') #variable x
    CI = coefficients(A,B,list,n)
    pn = 0 #iniatialis the wavefunctin, equation 1.3
    for i in range(len(CI)):
        pn = pn + CI[i]*wave_function(i)#equation 3.1 using the coefficients Ci
    return pn #the wavefunction for a given level n
#####For plotting use the code below
#for case II
y = wave_function_new(A,B,[0,0,0.5],n)
pp= plot(y,(x,-5,5),color=hue(0.1*N),
    legend_label="Energy level %d" %(n),axes_labels=['$x$', '$\phi_n(x)$'])
pp.axes_label_color=((0,0,1))
return pp
#####For eigenvalues use the code below
return eva((A,B,[0,0,0.5])

```

For the Morse potential, we have the following code,

```

#modules that we will use for plotting the wave functions
import numpy as np
import math as m
####Thr morse function
def morse2(N,n,D,p):
    l_op=matrix(RDF,(N)) #creates an N by N matrix of zeros
    for i in range(l_op.nrows()):
        for j in range(l_op.ncols()):
            if i <> j-1:
                l_op[i, j] = 0
            else:
                l_op[i, j] = sqrt(j)
#####
r_op=matrix(RDF,(N)) #creates an N by N matrix of zeros
for i in xrange(r_op.nrows()):
    for j in xrange(r_op.ncols()):

```

```

        if i <> j+1:
            r_op[i, j] = 0
        else:
            r_op[i, j] = sqrt(j+1)
#####
A=r_op+l_op;B=l_op-r_op
#####
def H(A,B,list):
    k = len(list)
    a=-0.25*B**(2.0) #evaluates the first part of the summation of H
    def bb(k): #generates the summations for the second part
        b = 0 #initialise the starting value
        for i in range(k): #added one to include the end value
            b = b + list[i]*(0.5)**(i/2)*(A*p)**(i)
        return b
    HH=a + bb(k) #H as defined
    return HH
#####
def eva(A,B,list):
    mat = H(A,B,list)
    ls=mat.eigenvalues()
    ls.sort()
    return ls
#####
def evec(A,B,list):
    mat = H(A,B,list)
    ls=mat.eigenvectors_left()
    ls.sort()
    return ls
#####
def coefficients(A,B,list,n):
    eigenvectors = evec(A,B,list)
    List = eigenvectors[n][1][0].list()
    return List
#####
def hermite(n):
    var('x')
    if n==0:
        return 1
    else:
        return (-1)**(n)*np.exp(x**(2))*derivative(np.exp(-1*(x**(2))),x,n)
#####
def wave_function(n):
    pn = 1/(np.pi**(4))*(1/np.sqrt(2**(n)*m.factorial(n)))
    *hermite(n)*np.exp(-(x)**(2))/2
    return pn
#####
def wave_function_new(A,B,list,n):

```



```

x = var('x') #variable x
CI = coefficients(A,B,list,n)
pn = 0 #iniatialis the wavefunctin, equation 1.3
for i in range(len(CI)):
    pn = pn + CI[i]*wave_function(i)#equation 3.1 using the coefficients Ci
return pn
#####
y = wave_function_new(A,B,[0,0,D,-D,D*7/12.0],n)
#return plot(y,(x,-10,10),color = hue(0.1*n),
    legend_label="Energy level %d, N=%d" %(n,N),thickness=2)
return eva(A,B,[0,0,D,-D,D*7/12.0])
#return H(A,B,[0,0,D,-D,D*7/12.0])

```

To save on space, the codes for the rest of the potentials simulated can be found at the following on-line blog,

- harmonic oscillator, <https://cloud.sagemath.com/projects/d232bd85-3974-4052-8cd8-6a237b9e10e8/files/Harmonicpotential/>,
- shifted harmonic oscillator, <https://cloud.sagemath.com/projects/d232bd85-3974-4052-8cd8-6a237b9e10e8/files/ShiftedHarmonicpotential/>,
- double-well potentail <https://cloud.sagemath.com/projects/d232bd85-3974-4052-8cd8-6a237b9e10e8/files/Doublewellpotential/>,
- Morse potential, <https://cloud.sagemath.com/projects/d232bd85-3974-4052-8cd8-6a237b9e10e8/files/Morsepotential/>.

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