

Finite Difference Method to Solve the Schrodinger Equation & Perturbation Theory Investigation

Conor Sheehan

May 20, 2024

1 Introduction

The Schrödinger equation lies at the heart of quantum mechanics, governing the behavior of quantum systems. Its solutions provide invaluable insights into the behavior of particles at the atomic and subatomic levels, offering a profound understanding of the fundamental principles of nature.

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (1)$$

In this project, we embark on a journey to explore the solutions of the Schrödinger equation for various well-known potential energies in physics. Our approach firstly relies on the Finite Difference Method (FDM), a powerful numerical technique widely used for solving differential equations, including partial differential equations like the Schrödinger equation. Secondly, we will investigate the Schrodinger Solution using Perturbation theory, which is a method that investigates the Hamiltonian of a system that differs from an amlytical solution by a small amount.

2 The Finite Difference Method

The FDM discretizes the differential equation by replacing derivatives with finite differences, transforming the continuous problem into a discrete one that can be solved computationally. This method offers a flexible and efficient way to approximate the solutions of complex differential equations, allowing us to explore quantum phenomena across a range of scenarios.

Our primary objective is to implement and apply the Finite Difference Method to solve the time-independent Schrödinger equation for different potential energy functions. By discretizing space and representing wavefunctions as vectors, we aim to numerically calculate the eigenstates and eigenenergies corresponding to these potentials.

2.1 Implementation

So, assuming that we're using the 1-dimensional Schrodinger equation, with time independence, we have:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle = (\hat{T} + \hat{V})|\Psi\rangle = E|\Psi\rangle \quad (2)$$

Or more explicitly the RHS of 2, ignoring Dirac notation for now:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi = E\Psi \quad (3)$$

The kinetic second order differential equation is where we implement the FDM here. We can approximate this differential as:

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{\Psi_{j+1} - 2\Psi_j + \Psi_{j-1}}{\Delta x^2} \quad (4)$$

where Δx is the interval width. Firstly, we're going to take a quick look at where (4) comes from.

2.1.1 Derivation

Given the Taylor Series Expansion:

$$f(x) = \sum_{n=0}^{\infty} \frac{f^n(a)(x-a)^n}{n!} \quad (5)$$

Say, we coincidentally have some function called Ψ , and we want to determine the function value either side of x by an amount Δx . We can use the Taylor expansion to do so. This gives us:

$$\Psi(x + \Delta x) = \Psi(x) + \Delta x \Psi'(x) + \frac{\Delta x^2}{2!} \Psi''(x) + \frac{\Delta x^3}{3!} \Psi'''(x) + \dots \quad (6)$$

$$\Psi(x - \Delta x) = \Psi(x) - \Delta x \Psi'(x) + \frac{\Delta x^2}{2!} \Psi''(x) - \frac{\Delta x^3}{3!} \Psi'''(x) + \dots \quad (7)$$

By adding (6) and (7), we get some handy cancellations. We're also only considering $n = 2$ terms and lower here.

$$\Psi(x + \Delta x) + \Psi(x - \Delta x) = 2\Psi(x) + \Delta x^2 \Psi''(x) + O(\Delta x^4) \quad (8)$$

We can rearrange (8), to obtain (4), ignoring fourth order terms and above.

$$\Psi''(x) = \frac{\Psi(x + \Delta x) + \Psi(x - \Delta x) - 2\Psi(x)}{\Delta x^2} \quad (9)$$

2.2 Application to the Schrodinger Equation

So, after our brief detour we're back at (4). This equation allows us to discretize the Schrodinger Equation from its given continuous form. Say we want to solve the equation in the interval $\in [a, b]$. We know that the particle is to be confined to this interval, therefore the wavefunctions probability amplitude, and wavenfunction value at these points must be 0. Or more succinctly $\Psi_{a,b} = 0$.

As we know these values are 0, if we've discretized our axis into N , points, this means we need only calculate $N-1$ values. Say we chose $N = 5$ for arguments sake. We can rewrite the kinetic segment of (3) using the FDM approximation (9) as:

$$-\frac{\hbar^2}{2m} \begin{pmatrix} 2 & -1 & 0 & 0 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ 0 & 0 & -1 & 2 \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} \quad (10)$$

We can also write the potential as a purely diagonal matrix. This is as the potential (at least in our cases) is only a function of position. Where each point on the x -grid has its own potential independent of any other points. V below is for $N = 5$.

$$\begin{pmatrix} V_1 & 0 & 0 & 0 \\ 0 & V_2 & 0 & 0 \\ 0 & 0 & V_3 & 0 \\ 0 & 0 & 0 & V_4 \end{pmatrix} \quad (11)$$

Combining the two, we get our Hamiltonian, and subsequent matrix to solve for Eigenvectors & Values:

$$\left(-\frac{\hbar^2}{2m} \begin{pmatrix} 2 & -1 & 0 & 0 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ 0 & 0 & -1 & 2 \end{pmatrix} + \begin{pmatrix} V_1 & 0 & 0 & 0 \\ 0 & V_2 & 0 & 0 \\ 0 & 0 & V_3 & 0 \\ 0 & 0 & 0 & V_4 \end{pmatrix} \right) \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = E \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} \quad (12)$$

Finally, by subtracting the potential matrix from the Kinetic, we are left with the matrix we must gain eigenvectors for. Simples.

2.3 Potential Energies to be investigated

As we already looked at the particle in a box in another project, in this one we'll start by looking at the following two potentials:

$$V(x) = \frac{m\omega^2 x^2}{2} \quad (13)$$

$$V(x) = ax^4 - bx^2 \quad (14)$$

These equations being the potentials for the Quantum Harmonic Oscillator, and the Double Well Potential respectively. For ease, in the C++ program we'll default physical constants to 1, however you can easily modify these in the function calls if need be!

2.4 Results and Discussion

In this section we'll show graphs containing the first four Eigenvectors from each section, as well as the potential itself as this will make the analysis of the results more intuitive.

2.5 Double Well Potential $x^4 - 3x^2$

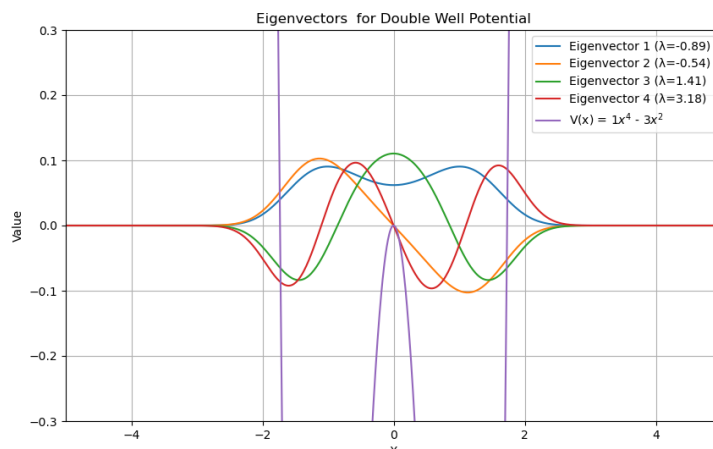


Figure 1: Double Well Potential compared to first 4 Eigenstates & Eigenvalues

This section investigated the above Potential. This can be graphically seen superimposed over the first 4 Eigenvectors of the subsequent Hamiltonian obtained using the FDM approach.

It can be seen that as $V(x)$ approaches what we can effectively consider ∞ in this case, the wavefunction amplitude tends to 0 for all Eigenstates, implying that this massive potential acts as a barrier for any particle within this range, almost like the particle in a box situation.

We can see in the above, our first few Eigenvalues are negative. In the context of QM, this means that these eigenstates are bound within the Double-Well, with insufficient energy to escape. Once you reach $n=3$ however we start trending upwards from 0.

The shapes of the Eigenvectors are interesting here also. For the ground state, we can see two maxima, within each well, with no node inbetween. This indicates that the particle is most likely to be found in either centre of both wells. The non-negative value at the barrier also indicates Quantum Mechanical tunnelling occurs between both wells. Ψ is also symmetric in this case with respect to 0, similar to $V(x)$.

Both of the Odd wavefunction solutions contain a node at $x = 0$. This is interesting, as it means the particle cannot exist in this location. Therefore for the odd eigenstate solutions, the particle must oscillate between both wells. This increased oscillation increases position uncertainty Δp therefore reducing Δx by the Heisenberg Uncertainty Principle.

2.6 Quantum Harmonic Oscillator

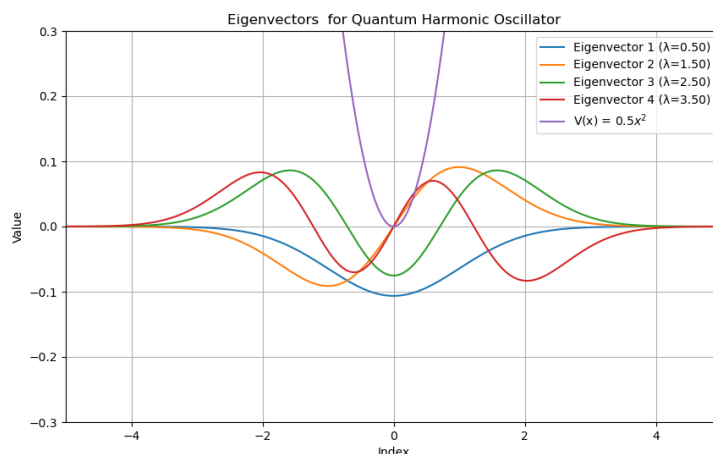


Figure 2: Monte Carlo prediction for expectation value of position operator $\langle \hat{x} \rangle$

Again we have a similar story with the Quantum Harmonic Oscillator, with odd solutions containing a node, and even being without. Also, the Eigenvalues match the known literature values: $E_N = \frac{n+1}{2} \hbar \omega$, where we have \hbar & ω defaulted to 1.

3 Perturbation Theory

Perturbation theory in quantum mechanics is a method used to find an approximate solution to a problem that cannot be solved exactly. It is particularly useful when the problem at hand can be seen as a small deviation from a problem that has an exact, known solution. The idea is to start with a simple system for which the solution is known and then add a "perturbing" Hamiltonian to account for the complexity. This perturbation is typically small, allowing the use of a series expansion to approximate the solution.

In Quantum MEchanics, the Hamiltonian can also be expressed as:

$$H = H_0 + \lambda V \quad (15)$$

The Eigenstates of H_0 are assumed to be known:

$$H_0|\Psi_n^0\rangle = E_n^0|\Psi_n^0\rangle \quad (16)$$

The corrections to this known Hamiltonian can be expressed as a Power Series in λ . For this project, we will only work with first-order perturbation corrections, but just for awareness second order corrections are very commonly used.

We're now going to quickly derive the first order corrections to both the energy and wavefunction.

3.0.1 First Order Energy Correction

As we previously stated, both the Energy and Wavefunction corrections can be expanded as a power series, as seen below:

$$E_N = E_N^0 + \lambda E_N^1 + O(\lambda^2) \quad (17)$$

We want to find λE_N^1 .

$$|\Psi^N\rangle = |\Psi^0\rangle + \lambda|\Psi^1\rangle + O(\lambda^2) \quad (18)$$

Here we ignore second order terms and above. We substitute (15), (17) & (18) into the Schrodinger equation.

$$(H_0 + \lambda V)(|\Psi^0\rangle + \lambda|\Psi^1\rangle) = (E_N^0 + \lambda E_N^1)(|\Psi^0\rangle + \lambda|\Psi^1\rangle) \quad (19)$$

If we expand (19), and keep only first order terms of λ , and then divide across by λ we are left with:

$$H_0|\lambda^1\rangle + V|\Psi^0\rangle = E_N^0|\Psi^1\rangle + E_N^1|\Psi^0\rangle \quad (20)$$

Now by multiplying across by the ket of the non perturbed wavefunction $\langle\Psi^0|$, and using the both orthogonality: $\langle\Psi^i|\Psi^j\rangle = 0$ for $i \neq j$ and the normalised state condition: $\langle\Psi^i|\Psi^j\rangle = 1$ for $i = j$, we get the desired output:

$$E_N^1 = \langle\Psi^1|V|\Psi^1\rangle \quad (21)$$

3.0.2 First Order Wavefunction Correction

We're gonna start here with (20) above. If we rearrange, to solve for the first order wavefunction we get:

$$(H_0 - E_N^0)|\Psi^1\rangle = (E_N^1 - V)|\Psi^0\rangle \quad (22)$$

If we then project onto an orthogonal state $\langle\phi^0|$ with $\phi \neq \Psi$ and sub in (21):

$$\langle\phi^0|(H_0 - E_N^0)|\Psi^1\rangle = \langle\phi^0|(\langle\Psi^1|V|\Psi^1\rangle - V)|\Psi^0\rangle \quad (23)$$

The first term on the right disappears due to orthogonality. We can then rearrange to get:

$$(E_M^0 - E_N^0)\langle\phi^0|\Psi^1\rangle = -\langle\phi^0|V|\Psi^0\rangle \quad (24)$$

And so to be formal we can state:

$$|\Psi^1\rangle = \sum_{m \neq n} \frac{\langle\phi^0|V|\Psi^0\rangle}{(E_N^0 - E_M^0)}|\phi^0\rangle \quad (25)$$

3.1 Problem

So, what problem are we now trying to solve?

Say we apply a small perturbation $V(x) = \lambda x^4$ to our Quantum Harmonic Oscillator system, which we've already solved the eigenvalues & eigenstates for. Using Perturbation theory, how will the ground state Eigen-value and first excited state eigen value be affected with increasing lambda? Let's check. Also, lets take a look at the resultant eigenstate and see how it looks with some perturbation applied.

3.2 Results & Discussion

Lets take a look initially at how Perturbation affects the first two Eigenvalues: In the

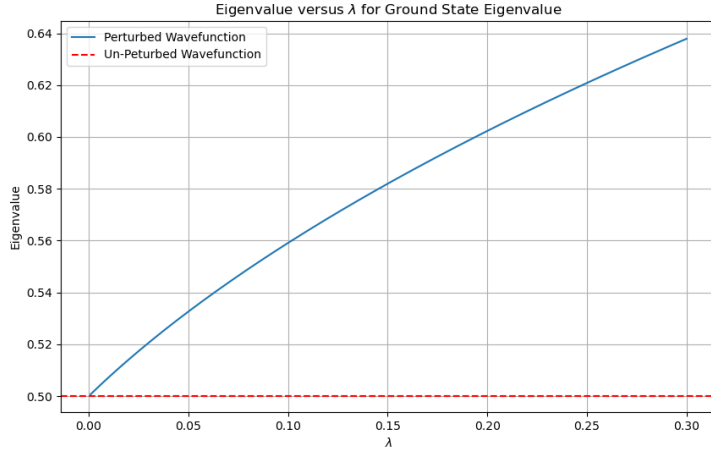


Figure 3: Ground State Eigenvalue Comparison

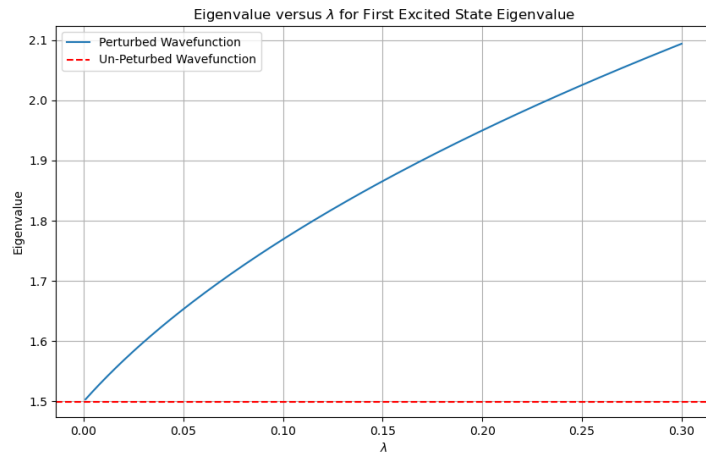


Figure 4: First Excited State Eigenvalue Comparison

above, we can see that as λ increases, the solution for these Eigenvalues diverges from the known analytical solution. This intuitively makes sense, (at least in my mind).

As the lambda term increases, this causes the potential to change from the known analytical potential also, which subsequently alters the Hamiltonian. Therefore the Eigenvalues will subsequently be changed.

Using the perturbation theory formulas for a first order non degenerate system as the Harmonic Oscillator is non degenerate:

$$E_n^1 = n^0 |V| n^0 \quad (26)$$

Where $V = x^4$. Now using the Ladder Operators and their properties, which are as following:

$$\hat{x} = \left(\frac{\hbar}{2M\omega}\right)^{\frac{1}{2}} (\hat{a} + \hat{a}^\dagger) : n^0 = \frac{\hat{a}^\dagger}{n!} 0^0 \quad (27)$$

So, by using the above information:

$$E_n^0 = n^0 \left| \left(\frac{\hbar}{2M\omega}\right)^2 (\hat{a} + \hat{a}^\dagger)^4 \right| n^0 \quad (28)$$

The only terms that are non-zero are (after a good bit of maths I won't bother putting here):

$$E_N^0 = \langle n^0 | \hat{a}^2 \hat{a}^{\dagger 2} + \hat{a}^{\dagger 2} \hat{a} + 4 \hat{a}^\dagger \hat{a} \hat{a} \hat{a}^\dagger + 4 \hat{a}^\dagger \hat{a} + 1 | n_0 \rangle = 6n^2 + 6n + 3 \quad (29)$$

Therefore we get that the first order correction to the n^{th} energy level will be:

$$E_n^1 = \left(\frac{\hbar}{2M\omega}\right)^2 \lambda (6n^2 + 6n + 3) \quad (30)$$

Now for the ground state, $n=0$, so this term simplifies to :

$$E_0^1 = 3\lambda \left(\frac{\hbar}{2M\omega}\right)^2 \quad (31)$$

And for the first excited state this simplifies to:

$$E_1^1 = 15\lambda \left(\frac{\hbar}{2M\omega}\right)^2 \quad (32)$$

If we look at figures 3 & 4, we can see that the first excited state increases much more (≈ 0.6) compared to the ground state (≈ 0.14) for the same interval. Based on figures (31) and (32) this makes sense, consider λ get scaled by 15 as opposed to 3. However, one thing is that the increase is only about 4.28 times larger than the ground state, considering that pre- λ term is 5 times larger. This isn't a major issue, but interesting to note nonetheless. We can

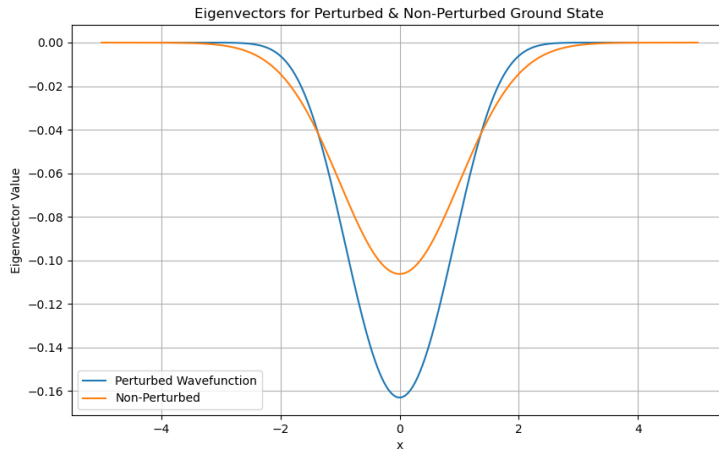


Figure 5: Ground State Eigenvector Comparison

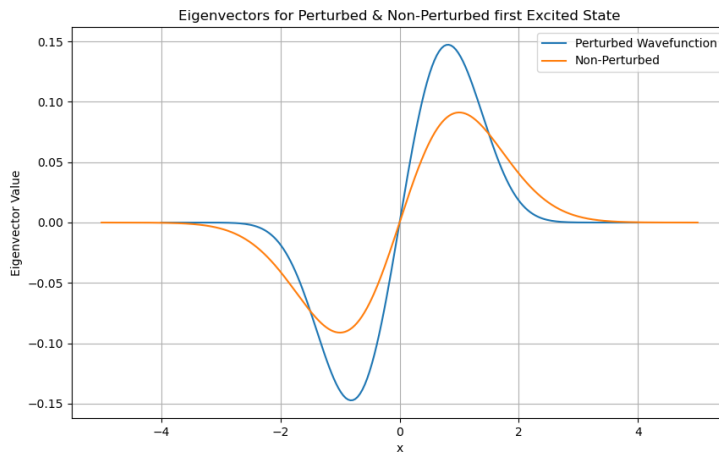


Figure 6: First Excited State Eigenvector Comparison

see the same trend in both cases. The Wavefunction Solution gets narrower, with a larger peak. This implies two things respectively. The narrowing of Ψ means the corresponding probability distribution will also be narrower, meaning whatever particle is existing within the QHO at the time will exist in a smaller x -axis interval with an increased perturbation.

Also, the larger peak, indicates a larger energy. Which would make sense, remember in the initial Power Series expansion of the Hamiltonian and corresponding Energies in the First order derivation, we added positive terms to the analytical non perturbed Energies/Hamiltonians. This would explain the increased wavefunction.