

Investigation on One-Dimensional Schrödinger's Equation

R. Van Laer

Department of Physics & Engineering Physics, Fordham University, Bronx, NY 10458

In this work, we will use Givens Rotation matrices as well as the Finite Difference method in an attempt to reproduce the expected patterns the Schrödinger Equation shows for the wavefunctions at various energy states. These simulations allow us to confirm the predictions made by the equation as well as show its distribution and probability natures.

I. INTRODUCTION

In 1926, Erwin Schrödinger, a Austrian physicist, reinterpreted the Quantum Mechanical concept of “Quantization” with a mathematical equation of his own, based on the work of Louis de Broglie. Indeed, while in Zurich, Schrödinger got interested in the atomic model that Niels Bohr modified in 1913, stating the electron were sitting at stationary orbits. The Austrian scientist then saw in the 1924 French scholar's thesis on the relationship between waves and particles, the opening he could use to transform the model.

In this context, Schrödinger published a paper on the famous wave equation, marking the first step in what will be known as “Wave Mechanics.” Later on, the scientist used it in order to re-express the atomic model in terms of those new mechanics, instead of particles leaps.

The central idea behind the wave equation is that, contrarily to Bohr's approach, it was not determining the path followed by an electron but rather, the probability of an electron to be present at a specific location around the nucleus. The ideas of probability densities and electron clouds were born. This would become the Quantum Mechanical Model of the atom. [1]

In Sec. II we will introduce the Schrödinger's Equation, make its operator form apparent and showing it as Schrödinger demonstrated it, as an eigenvalue problem. Following that, in Sec. III we will state, explore and explain the different methods we came to use in our simulations. In Sec. IV we will dive into the different particular cases for which we decided to solve the Schrödinger's equation. We will explain the theoretical, mathematical part of the expected results as well as showing and commenting on our numerical results. We will conclude in Sec. V.

II. SCHRÖDINGER'S EQUATION

A. Quantum Mechanics and Operators

In Quantum Mechanics, there exist operators which can act on wavefunctions in order to generate other wavefunctions.

$$\hat{O}\psi = \psi' \quad (1)$$

We can go one step further and say that for a certain operator \hat{O} , there exist a wavefunction $\psi(x)$ such that

$$\hat{O}\psi(x) = \lambda\psi(x) \quad (2)$$

where λ is a constant independent of x , often being the value measured in an experiment.

Heisenberg's Uncertainty Principle states that, for small particles, it is impossible to exactly measure both the position and velocity of the said particles. For this reason, the position, \hat{r} , and momentum, \hat{p} , operators will be non commutative linear operators, used as the basic operators.

$$\hat{r}\psi = \vec{r} \times \psi \quad (3)$$

$$\hat{p}\psi = -i\hbar\nabla\psi \quad (4)$$

Using our knowledge of mechanics, one can rewrite the kinetic energy, \hat{T} , and potential energy, \hat{V} , operators in terms of those two basic operators. In one dimension,

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \quad (5)$$

$$\hat{V} = V(x) \times \quad (6)$$

If we then refer to our Classical Mechanics, we can recall what the Hamiltonian Operator is and translate that in Quantum Mechanics, [2]

$$\hat{H} = \hat{T} + \hat{V} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (7)$$

B. Equation of Motion

Undertaking the role of Newton's Laws of Motion and the Law of Conservation of Energy, Schrödinger's equation is a Linear Partial Differential Equation which predicts the probability of an event to occur.

It is in terms of the Hamiltonian Operator [Eq. (7)] that Schrödinger will express his wave equation. In fact, a time-dependent wavefunction will be found thanks to the Time Dependent Schrödinger Equation

$$\hat{H}\psi = i\hbar \frac{\partial\psi}{\partial t} \quad (8)$$

In here, the time evolution is described by the Hamiltonian because the operator is itself express as depending on time.

However, if it is not the case, Schrödinger's equation will have a solution separating the spatial and temporal variables into different functions,

$$\psi = \psi(x)T(t) = \psi(x)e^{iEt/\hbar} \quad (9)$$

As the wavefunction only changes phase and not amplitude, the energy does not change with time. We call those energy state "Stationary States."

This concept allows us to focus on the spatial component of Schrödinger's equation, the Time-Independent Schrödinger Equation,

$$\hat{H}\psi = E\psi \quad (10)$$

with E being the energy state of the wavefunction.

Looking back at [Eq. (2)], we can make the relation between the energy state being an eigenvalue and the wavefunction being an eigenvector in order to interpret Schrödinger's equation as an eigenvalue problem. [3] [4]

III. METHODS TO SOLVE SCHRÖDINGER'S EQUATION

In order to determine these eigenvalues and eigenvectors, energy states and wavefunctions, we need a way to express the Hamiltonian operator as a matrix and to solve for its eigenvalues and eigenvectors.

A. Finite Difference Method - Equation in Matrix Form

The first thing we have to realize is that with this eigenvalue problem, we have to discretize our space. In one dimension, this means that we do not have a line as our possible values for x but rather a fixed set of points.

Secondly, we have to separate the kinetic energy operator from the potential energy one. That way, we can express the Hamiltonian operator as the sum of two ($n \times n$) matrices, with n being the number of data points.

For the potential, V , we simply write the potential at each of our x points along the diagonal,

$$\hat{V} = \begin{bmatrix} V(x_0) & \dots & 0 \\ \vdots & \ddots & \\ 0 & & V(x_n) \end{bmatrix} \quad (11)$$

For the kinetic, \hat{T} , expressing it in terms of the second derivation, we use the finite difference method to determine the centered second derivative. To do so, we Taylor expand $y(x+h)$ and $y(x-h)$, and add them together,

$$\frac{d^2y}{dx^2} = \frac{y_{i-1} - 2y_i + y_{i+1}}{h^2} + O(h^2) \quad (12)$$

Those three coefficient will become the entries of each row for those particular indexes. For this work, we will consider the boundary conditions to be zero at all time, filling the rest of the kinetic energy operator matrix with zero coefficient, although we acknowledge the possibly for those boundaries to be different. We can note that this method will give us a second order accuracy. However, as we will later on explain, we will focus on qualitative results.

We rewrite the kinetic energy operator as,

$$\hat{T} = -\frac{\hbar^2}{2m} \begin{bmatrix} -2 & 1 & 0 & \dots & 0 \\ 1 & -2 & 1 & & \\ 0 & 1 & -2 & & \\ \vdots & & & \ddots & \\ 0 & & & 1 & -2 \end{bmatrix} \quad (13)$$

This result shows that [Eq. (13)] is constant. Therefore, the Hamiltonian operator will only depend on the form of our potential energy function.

B. Givens Rotation Matrices - Solving Eigenvalue Problems

Givens Rotational matrices are orthogonal matrices which transform a real matrix into an equivalent one and annihilate off-diagonal elements of the original matrix.

Those matrices will allow us to create a triangular matrix out of an original one for which the main diagonal elements will be the eigenvalues of the said matrix. [5] [6]

In order to define a Givens rotation matrix, we set two real numbers c and s such that $c^2 + s^2 = 1$ and two integer m and n such that $0 < m < n < K$ for some K representing the size of the square matrix.

We then write the Givens rotation matrix $G(K, m, n, c)$ to be the $(K \times K)$ identity matrix with the entries,

$$\begin{aligned} G_{m,m} &= c \\ G_{m,n} &= s \\ G_{n,m} &= -s \\ G_{n,n} &= c \end{aligned}$$

Two important aspects which will help us in our simulations are, first, their orthogonality, $G^{-1} = G^T$ - in order to use the Givens rotations, we do not have to compute any inverses. It is faster and less memory costly to find a transpose than an inverse - , second, their equivalent transformations - we approximate the original matrix to be the product of itself with the Givens matrix as the Givens matrix is approximately the identity matrix, except at four entries.

Nevertheless, despite those elements making these somewhat important, the Givens Rotation Matrices'

true usefulness for us appears in their faculty to annihilate non-diagonal entries and so approximating a diagonalization of a matrix.

To annihilate the nm^{th} entry of the matrix A , A_{nm} , assuming $A_{mm} \neq 0$, we set c and s to be,

$$c = \frac{A_{mm}}{\sqrt{A_{mm}^2 + A_{nm}^2}}$$

$$s = \frac{A_{nm}}{\sqrt{A_{mm}^2 + A_{nm}^2}}$$

In the new GA matrix,

$$(GA)_{nm} = -sA_{mm} + cA_{nm}$$

$$= 0$$

By setting up such a system in an iterative manner, which would stop after the error would reach a certain tolerance, we can determine a triangular matrix which will contain the eigenvalues of the matrix.

We can find a matrix, for which the columns represent each eigenvector in the order of the corresponding eigenvalues, by multiplying the identity matrix by the Givens matrix at each iteration. [5] [7] [6]

C. The Shooting Methods - Boundary Value Problems

An interesting but challenging part of solving Schrödinger's equation resides in its nature. It is a boundary value problem. This means that the differential equation must also satisfy some constraints, the boundary conditions. In our case, we specified our endpoints for the wavefunction to be zero.

However, due to its probabilistic essence, the success of our result depends on the number of points in our data set: too few and we could not observe the expected patterns of a certain system; too many could disrupt the pattern as well.

In order to determine the right number of points we use the shooting method which transform our boundary value problem into an initial value problem for which we keep changing the initial conditions until we find the ones that make our results agree with the boundary conditions. In our case, this means we manually plug in different values for that number of data points.

An interesting phenomenon we observed is that viability of a number of data points is not necessarily absolute. For a same number, depending on the energy eigenstate, the wavefunction was sometimes agreeing with boundary conditions, sometimes not. [8]

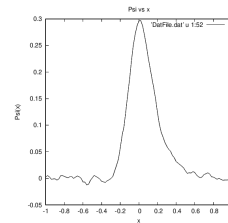


FIG. 1: Quantum Harmonic Oscillator at $n = 1$

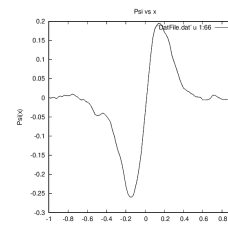


FIG. 2: Quantum Harmonic Oscillator at $n = 2$

IV. SPECIFIC CASES OF SCHRÖDINGER'S EQUATION

A. Quantum Harmonic Oscillator

A common situation to be analyzed by the Schrödinger's equation is the one-dimensional simple harmonic oscillator.

In Classical Mechanics, we can think of it as a spring of coefficient k exerting a restoring force $\vec{F} = -kx$ on an object of mass m . We could then find its frequency $\omega_0 = \sqrt{k/m}$, its period $T = 2\pi\sqrt{m/k}$, and most importantly, its potential energy $V = \frac{1}{2}kx^2$.

Schrödinger's equation is thus of the form,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \quad (14)$$

At Ground State, the general form of the solution to the equation will be,

$$\psi(x) = Ae^{-ax^2} \quad (15)$$

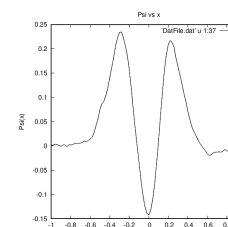
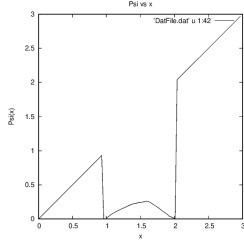
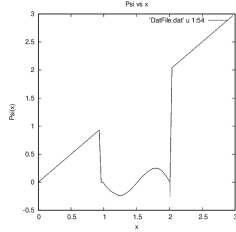


FIG. 3: Quantum Harmonic Oscillator at $n = 3$

FIG. 4: Finite Potential Well at $n = 1$ FIG. 5: Finite Potential Well at $n = 2$

Now, we can evaluate $d\psi/dx$ and $d^2\psi/dx^2$ and we observe them to be proportional to $\psi(x)$ by multiplying it by a polynomial of first and second degree respectively.

If we thus substitute them back into [Eq. (15)] and cancel the wavefunctions, we obtain

$$\frac{\hbar^2 a}{m} - \frac{2a^2 \hbar^2}{m} x^2 + \frac{1}{2} k x^2 = E \quad (16)$$

This yields

$$a = \frac{\sqrt{km}}{2\hbar} \quad (17)$$

$$E = \frac{1}{2} \hbar \sqrt{k/m} = \frac{1}{2} \hbar \omega_0 \quad (18)$$

Through normalization, we can find for the ground state,

$$\psi(x) = \left(\frac{m\omega_0}{\hbar\pi} \right)^{1/4} e^{-(\sqrt{km}/2\hbar)x^2} \quad (19)$$

In the Fig. 1, 2 and 3, we can see the result of our simulation for the few first energy eigenstates. While noticing some discrepancies due to our approximations in our methods, we observe the expected patterns.

Interestingly, for higher energy states, on the contrary, we can observe disagreements with the boundary conditions we set up, proving the importance of the shooting method (specific number of data points for specific eigenstates). [3] [4] [9]

B. Infinite and Finite Potential Well

In the Infinite Potential Well, or “Particle in a Box,” the potential energy function can be defined as,

$$\begin{aligned} V(x) &= 0 \\ V(x) &= \infty \end{aligned} \quad (20)$$

when $0 \leq x \leq L$ and when $x < 0$ and $x > L$ respectively, with 0 and L being the boundaries of a region.

Within the region, the wavefunction will be of the form

$$\psi(x) = A \sin kx + B \cos kx \quad (21)$$

By solving the differential equation and using the normalization condition, we can find,

$$\begin{aligned} B &= 0 \\ k &= \frac{n\pi}{L} \\ A &= \sqrt{\frac{2}{L}} \end{aligned} \quad (22)$$

with n being a positive integer.

This allows us to express the wavefunction as

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (23)$$

For the Finite Potential Well, in the closed region, the solution, the wavefunction, will be of the same form, meaning a linear combination of a sine and cosine function.

However, due to the potential energy to be finite outside the region, there will be some probability that the particle enter those “forbidden” regions in the infinite potential case as the wavefunction must be “smooth.”

When $x < 0$, the wavefunction should be of the form,

$$\psi(x) = C e^{k'x} \quad (24)$$

When $x > L$, the wavefunction should be of the form,

$$\psi(x) = C e^{-k'x} \quad (25)$$

In the data that we collected from our simulations, Fig. 4 and 5, we can see the oscillatory behavior of the wavefunction within the bounded region, confirming the expected form of the solution to Schrödinger’s equation.

Nonetheless, for the region outside the bounds, it seems that the simulation was not able to properly normalize the wavefunction, which thus appears to be linearly increasing. [3] [4] [9]

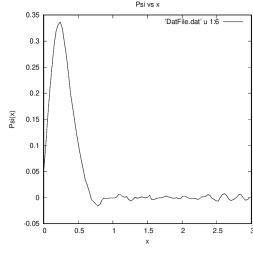
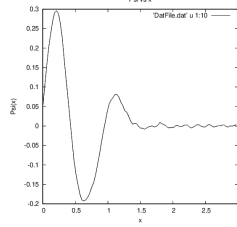
FIG. 6: Constant Potential at $n = 1$ 

FIG. 7: Free Particle with larger amplitude on the left

C. Free Particle and Constant Potential Energy

For a Constant Potential Energy system, Fig. 6, Schrödinger's equation will be of the form,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi = E\psi \quad (26)$$

and the solution, the wavefunction will assume two different forms depending on the energy states.

If $E > V_0$, as the derivatives are periodic,

$$\psi(x) = A \sin kx + B \cos kx \quad (27)$$

$$\text{with } k = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}.$$

If $E < V_0$,

$$\psi(x) = Ae^{k'x} + Be^{k'x} \quad (28)$$

$$\text{with } k' = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}.$$

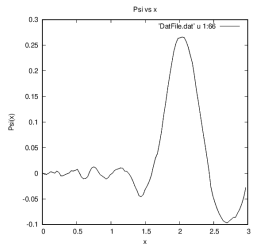
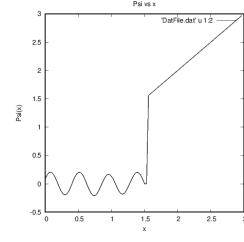
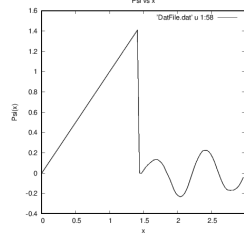


FIG. 8: Free Particle with larger amplitude on the right

FIG. 9: Potential Step, from zero to V_0 FIG. 10: Potential Step from V_0 to zero

For the Free Particle, the force is zero. Therefore, we assumed that the potential energy was also zero, partially so that we have a different expression than for Constant Potential.

In this case, the wavefunction will also be expressed by [Eq. (27)] and have an oscillatory behavior. However, the energy of the particle,

$$E = \frac{\hbar^2 k^2}{2m} \quad (29)$$

will not be quantized as the wavefunction creates no restriction on k . This means that the energy can have any values, making it harder to determine the solution analytically.

In our simulations, Fig. 6, 7 and 8, we observe the predicted oscillatory behavior for smaller energy eigenstates. Nonetheless, due to the nature of our work, we focused on qualitative patterns rather than accurate results, the difference between the Free Particle and the Constant Potential systems is very light. [3] [4] [9]

D. Potential Step

A Potential Step is a system in which a region is divided into two smaller ones. In each of those two, the potential is constant. However, there is a significant difference between those constants.

In our case, we will take the lower potential to be zero.

This gives us a potential energy function,

$$\begin{aligned} V(x) &= 0 \\ V(x) &= V_0 \end{aligned} \quad (30)$$

when $x < L$ and when $x > L$ respectively.

Now, if $E > V_0$, Schrödinger's equation will have two solutions and they will be of the form,

$$\psi_0 = A \sin k_0 x + B \cos k_0 x \quad (31)$$

with $k_0 = \sqrt{\frac{2mE}{\hbar^2}}$ when $x < L$ and

$$\psi_1 = C \sin k_1 x + D \cos k_1 x \quad (32)$$

with $k_1 = \sqrt{\frac{2m}{\hbar^2} (E - V_0)}$ when $x > L$

These wavefunctions should give an oscillatory behavior on one side followed by a constant behavior on the other. In our simulations, we can clearly observe the oscillatory patterns. However, we note that once again the normalization did not occur for every eigenstates in Fig. 9 and 10.

If $E < V_0$, Schrödinger's equation will also have two different solutions. The first one, before the step, will be of the same form, with the same k_0 . Nevertheless, the one corresponding to the region after the step, $x > L$, will be,

$$\psi_1 = C e^{k_1 x} + D e^{-k_1 x} \quad (33)$$

with $k_1 = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)}$

In this case, the wavefunction in the second region should have an exponential behavior. [3] [4] [9]

E. Tunneling

The phenomenon of Tunneling, also called Potential Energy Barrier, is the system in which a particle goes through one energy step which consists in an increase in potential energy and then through another step which

consists in the opposite, a decrease, resulting in the particle being in a third region of potential energy equal to the one in the first region.

In this scenario, the solution to the Schrödinger's equation will have three different solutions, corresponding to the three separated regions.

If $E < V_0$, outside of the barrier, the wavefunctions will not be equal to one another, but their forms will be the same. They will be a linear combination of sine and cosine functions. They should differ only in terms of amplitude, not wavelength. Additionally, similarly to the Potential Step, the pattern within the region should follow an exponential function.

If $E > V_0$, then the particle will simply "avoid" the barrier and the wavefunction should be the same as for the Potential Step when $E > V_0$. That is, it should be constant, given proper normalization, or linear for the misbehaving eigenstates.

Interestingly, this phenomenon shared patterns with the Potential Step, as expected, but also with the Finite Potential Well. This must be related to the way we define those potential energy functions.

V. CONCLUSION

In conclusion, we believe that through this work, we were able to fully explain the methods that we used in our code to not only set up but solve Schrödinger's equation as an eigenvalue problem.

Additionally, we were able to explain the Schrödinger's equation by expressing its overall nature and its behavior for specific cases.

Lastly, through our simulations, we believe we were able to reproduce numerous, expected patterns for those various cases, while, at the same time, portray the probability nature of the equation and the need for the shooting method to be applied.

-
- [1] P. Weinberger, *Revisiting louis de broglie's famous 1924 paper in the philosophical magazine* (2006), URL <https://www.tandfonline.com/doi/full/10.1080/09500830600876565>.
 - [2] M. Ranganathan, *Lecture 2: Operators, eigenfunctions and the schrödinger ...*, URL <https://home.iitk.ac.in/~madhavr/CHM102/Physical/Lec2.pdf>.
 - [3] K. S. Krane, *Modern physics* (Wiley, 2020), 3rd ed.
 - [4] *schrodinger equation*, URL <http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/schr.html>.
 - [5] S. Cole, *Simplifying 3-d migration operators using givens rotations* (1997), URL http://sepwww.stanford.edu/public/docs/sep70/steve2/paper_html/node2.html.
 - [6] M. Taboga, *Givens rotation matrix* (2021), URL <https://www.statlect.com/matrix-algebra/Givens-rotation>.
 - [7] M. Mehl, *A 'must' for engineers - m2/allgemeines*, URL https://www-m2.ma.tum.de/foswiki/pub/M2/Allgemeines/CSENumerikWS12/18_handout_eigenvalues_II.pdf.
 - [8] R. Johansson, *Python numerical methods* (2020), URL <https://pythonnumericalmethods.berkeley.edu/notebooks/chapter23.02-The-Shooting-Method.html>.
 - [9] M. Fowler, *Schrödinger's equation in 1-d: Some examples*, URL <https://galileo.phys.virginia.edu/classes/751.mf1i.fall02/OneDimSchr.htm>.