Numerical Analysis of the Time Independent Schrodinger Equation

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Abstract

Numerical solutions to the Time Independent Schrodinger Equation (TDSE) were analyzed using the open source programming language python and using various numerical schemes to compare accuracy of solutions in space, time, and energy. The methods involved were Euler, fourth order Runge-Kutta (RK4), second order Runge-Kutta (RK2), and leapfrog. Furthermore, the time independent solutions were then plotted using the principle of superposition to observe how these solutions evolved over time using separation of variables techniques in partial differential equations.

1 The Schrodinger Equation

The TDSE is given by

$$\iota\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

Using seperation of variables techniques, this can be reduced to two ordinary differential equations in both space and time which yields a time solution of

$$h(t) = e^{-\frac{\iota E t}{\hbar}}$$

And the time independent equation now looks like

$$\hat{H}\Psi = E\Psi$$

Where E is the energy of the particle in question, and $\hat{H}$ is the Hamiltonian operator which is the total energy of the system, with potential energy V and kinetic energy K, where V is typically dependent on position and K is dependent on the mass and momentum of the particle as

$$K = \frac{p^2}{2m}$$

Where p is the momentum and m is the mass of the particle. Expanding the Hamiltonian gives.

$$(K+V)\Psi = \frac{p^2}{2m}\Psi + V(x)\Psi = E\Psi$$

Essentially, this equation is simply demonstrating that the total energy of a particle is equal to its energy. We can all agree on this, and if this were as deep as the iceberg went, this would be a trivial problem in physics. What makes this a non-trivial problem is how we relate quantum mechanics to classical physical observables. In classical mechanics, if we are given the initial position and momentum of a classical particle, we know all there is to know about the particle. However, in quantum mechanics, position and momentum are no longer functions of time. They are instead operators, which operate on the wavefunction Ψ. By taking an ordinary plane wave, it can be demonstrated (Heuristically) that momentum operates on the wavefunction Ψ as

$$p\Psi = -\iota\hbar\frac{\partial}{\partial x}\Psi$$

Where ι is the imaginary unit and $\hbar$ is rationalized Planck's constant. For any operator with position dependence, like the Potential energy, it operates linearly on the wavefunction as

$$x\Psi = x\Psi$$

That is, the position operating on the wavefunction does not change the wavefunction. It is important here to note that the Hamiltonian is a linear operator. When substituting these operators back into the equation, we are left with

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

This is the equation with which we will be working. For reference, if one were to extend this to three dimensions, the equation would be

$$\iota\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi$$

2 Leapfrog: A simple example

If we look at the Schrodinger equation for a region in one dimension in which the potential is zero, it becomes an ordinary differential equation in space

$$-\frac{\hbar^2}{2m}\frac{d}{dx}\Psi(x) = E\Psi(x)$$

Without loss of generality, we can simplify this expression to be

$$\frac{d^2}{dx^2}\Psi(x) + \frac{2mE}{\hbar^2}\Psi(x) = 0$$

Which has solutions like the simple harmonic oscillator. With this idea in mind we consider the harmonic oscillator. The harmonic oscillator has an acceleration that is linear with position x in one dimension, a velocity that varies with time, and a position that varies in time. The equation for simple harmonic motion is

$$\frac{d^2x}{dt^2} + \omega^2 x = 0$$

This equation has well known solutions with which we can compare our numerical results. The equation is a result of being in a quadratic potential of the form $V(x) = \frac{1}{2}kx^2$ where k is the spring constant. We will use this, along with the kinetic energy to consider the total energy of the system at any given time. To solve this numerically, 3 different numerical schemes were used; leapfrog, second order Runge-Kutta, and forward Euler. Forward Euler is a linear approximation of the derivative given by

$$y_{n+1} = y_n + hf(t_n, y_n)$$

Where h is the step size used in discretizing time and space, f is the given function of y and t, and y_{n+1} is the value of y at the end of the time step. This method does have its limits, which are well illustrated in the problem of the simple harmonic oscillator. This can be observed in the figure below.

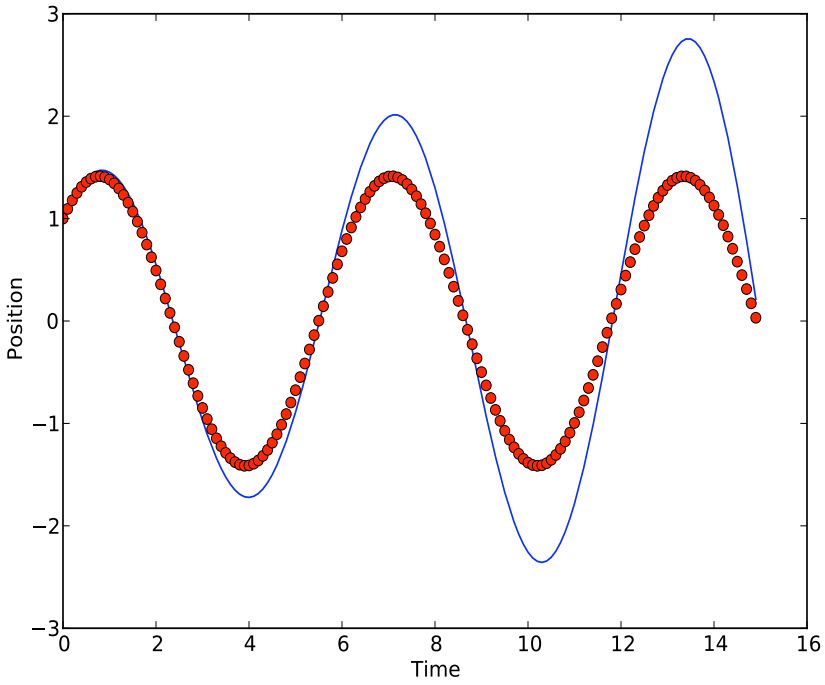


Figure 1: Position-Time solution using forward Euler. (Euler = Blue, True solution = Red)

It is clear from the above figure that the forward Euler method is severely inadequate at solving this simple ordinary differential equation. The next obvious choice would be second order Runge-Kutta, which approximates the derivative using quadratic approximations. The graph of the RK2 solution for both position and velocity is shown next.

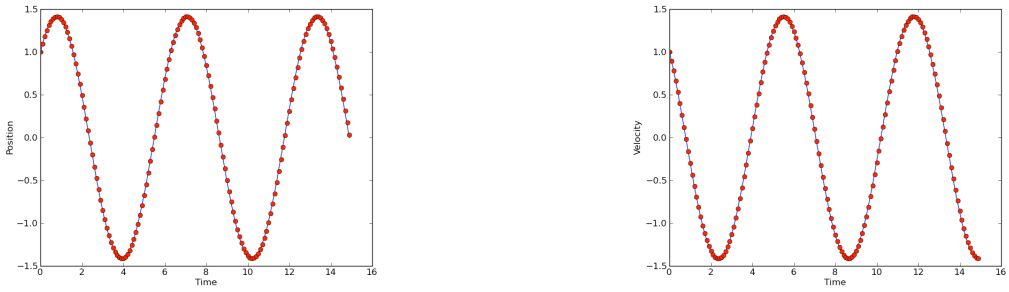
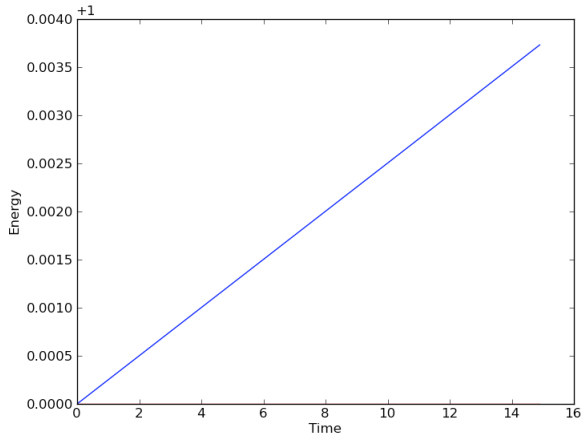


Figure 2: Position and Velocity solutions using RK2(RK2 = Blue, True Solution = Red)

Here we see that the RK2 solutions of position and velocity agree very well with known analytic solutions. The issue now comes in when we observe the way the energy changes over time. In Figure **??**, we can observe that the system is in fact gaining energy in linear proportion with time. This violates the law of conservation of energy. So again we must revisit our method. The solution to this problem lies in the leapfrog method for numerically evaluating



ordinary differential equations. The leapfrog method is useful for systems of ordinary differential equations in which acceleration is dependent on position, much like our simple harmonic oscillator. Instead of taking full steps forward in time and space, the method instead takes half steps, illustrated in the following equations.

$$x_{\frac{1}{2}} = x_0 + v * (\frac{h}{2})$$

$$v_1 = v_0 + a(x_{\frac{1}{2}}) * h$$

$$x_1 = x_{\frac{1}{2}} + v_1 * \frac{h}{2}$$

Where h is again the step size. Using this method of numerical integration on the simple harmonic oscillator, similar position and velocity solutions were obtained. The difference this time is in the energy of the system. In figure **??**, we see the numerical solutions graphed in red, and the known constant in blue. One can observe here that the energy of the system is still not constant. However, the energy is bounded with some upper and lower limit, and the average energy is somewhere close to the desired constant energy. This problem demonstrates both motivation for using the leapfrog numerical integration scheme, as well as its superiority over other better known basic numerical integration routines.

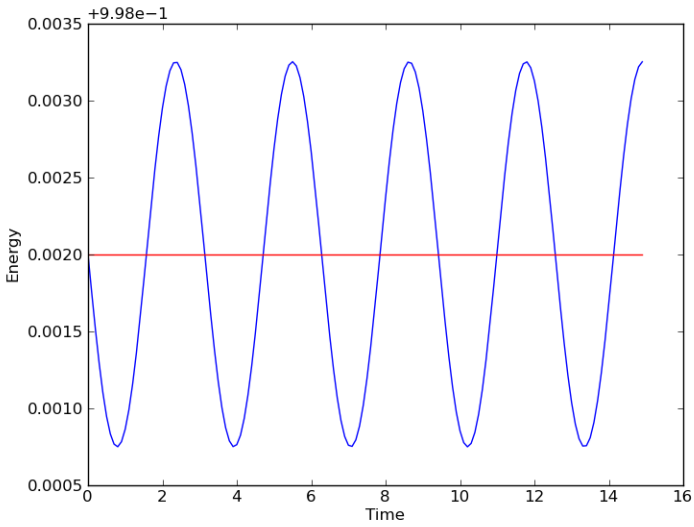


Figure 3: Leapfrog numerical solution of energy

3 Numerical Solutions and Time Propogations

By seperation of variables, the time solution to the Schrodinger equations is of the form

3.1 The Infinite Potential Well

$$h(t) = e^{-\frac{\iota E t}{\hbar}}$$

Where the spatial solution is dependent on the type of potential that the particle is in. In a region of zero potential, with vanishing endpoints, the spatial solution is identical in form to the simple harmonic oscillator. The spatial solutions in the problem are

$$u(x) = Asin(\frac{n\pi x}{L})$$

Where L is the length of the region in which the particle exists. This problem is known as the infinite potential well. It consists of a region of length L in which there is no potential inside the region, and an infinite potential outside the region causing the wavefunction Ψ do disappear. By the principle of superposition, the solutions to this problem should be of the form.

$$\Psi(x,t) = \sum_{n=1}^{\infty} A_n sin(\frac{n\pi x}{L}) e^{-\frac{\iota E t}{\hbar}}$$

Using the leapfrog method for integrating the spatial portion of this problem, and using the exponential, it was possible to graph this solution and observe its behavior over time. What was observed was that the wavefunction was actually periodic. What hasn't been mentioned up until this point is what the wavefunction is to actually be interpreted as. In essence, it represents the probability that a particle will be found at a particular point in the region. So what this actually means is that the particle's probability of being found in certain points in the region is periodic in time.

3.2 The Quantum Harmonic Oscillator

The Quantum harmonic oscillator describes a particle in a potential much like the one described in the simple harmonic oscillator case. However, the solution is nowhere near as trivial. The potential is quadratic again, so is proportional to the distance squared inside the region, much like in figure 4 In this potential, solutions are

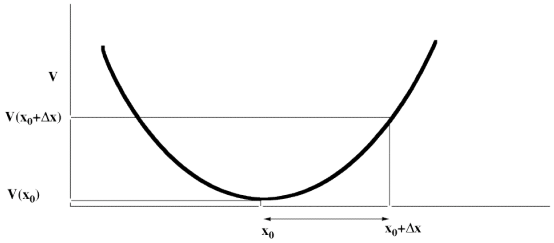


Figure 4: The harmonic potential function

$$H_n(x)e^{\frac{m\omega x^2}{2\hbar}}$$

Where H_n are Hermite polynomials, which are recursively defined, ω is the frequency of oscillations, and m is the mass. This particular potential had more interesting consequences. The wavefunction was still periodic as before, however this time there were extremely sharp peaks at certain points. So, at some time, the wavefunction actually acted as a Dirac Delta function centered somewhere to the right of the origin. There is no real reason why this should happen, which led me to believe that there was something wrong with my code. However, there is nothing wrong with the code being run. So what can be concluded is that at certain times in this potential, we can determine a particles position to a good degree of certainty. What this further implies is that the momentum of the particle is unable to be determined at certain times, due to the Heisenberg uncertainty principle.

4 Future work

Due to major problems in the beginning with my leapfrog program, it took longer than anticipated to begin to get numerical solutions to the simple harmonic oscillator. Ideally, if this were to be continued, we would evaluate problems in which there are no known analytical solutions using perturbative methods. Additionally, wavepackets, in which momentum varies in space would also be evaluated numerically. This would then lead to observing laser excitation of atoms and modeling 3 dimensional atoms such as hydrogen and helium.