Numerically Solving the Schrodinger Equation for the Quartic Potential

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(Dated: April 3, 2017)

A numerical method to solve the Schrodinger equation for an arbitrary potential was programmed in python. The program's functionality was verified by comparing the outputted solutions to the known solutions of the harmonic oscillator and the infinite square well. The python program was then used to solve the Schrodinger equation for the quartic well. The energy eigenvalues and the wave function eigenvectors, and expectation values for position and momentum for these potentials were calculated.

I. INTRODUCTION

The simple harmonic oscillator is one of the few potentials for which a solution to the Schrodinger equation can be solved analytically. However, there are many other potentials of theoretical and practical interest. A close cousin to the harmonic oscillator is the quartic well. The Schrodinger equation for this potential can not be solved analytically. We therefore must resort to numerical methods to solve the Schrodinger equation for such a potential. Using python, I programed a numerical method to solve the Schrodinger equation for the quartic potential.

II. BACKGROUND

The central equation in the Schrodinger picture of quantum mechanics is the Schrodinger equation:

$$\frac{\hbar^2}{2m}\nabla^2\Psi + V(\mathbf{r})\Psi = -i\hbar\frac{\partial\Psi}{\partial t}$$

The Schrodinger equation is second order linear partial differential equation. Dealing only with time-independent solutions in one dimension, the Schrodinger equation reduces

to:

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

The Schrodinger equation can be written more abstractly and succinctly by expressing the Hamiltonian as an operator acting on a wave-function vector in Hilbert space and returning the same wave function vector times a eigenvalue. This eigenvalue is the wave functions energy. This is the standard eigenvector equation form of the Schrodinger equation:

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

Solving the Schrodinger equation will yield a solution called the wave function. The wave function contains the quantum dynamical information of a particle in a given potential. By acting on the the wave function, that describes a quantum state, with quantum mechanical operators, information about energy, momentum and position can be retrieved. This information about energy, momentum and position extracted by operating on a wave function with the corresponding quantum operators can be viewed as an average of the values that would be found for an ensemble of quantum systems prepared in the same state. In general the expectation values for energy, position and momentum are:

$$\left\langle\Psi|\hat{H}|\Psi\right\rangle=\int_{-\infty}^{\infty}\Psi^*\hat{H}\Psi dx$$

$$\langle\Psi|\hat{x}|\Psi\rangle=\int_{-\infty}^{\infty}\Psi^*\hat{x}\Psi dx$$

$$\langle\Psi|\hat{p}|\Psi\rangle=\int_{-\infty}^{\infty}\Psi^*\hat{p}\Psi dx$$

Where the corresponding operators are defined by:

$$\hat{H}=H$$

$$\hat{x}=x$$

$$\hat{p}=\frac{\hbar}{i}\frac{\partial}{\partial x}$$

The Schrodinger equation can only be solved analytically for a small handful of problems. The quadratic potential(harmonic oscillator), infinite square well, and the Coulomb potential, are some of the potentials for which the Schrodinger equation can be solved analytically. For other and more sophisticated potentials, numerical techniques must be employed. Thus

to verify a numerical method, the results of the method should be compared to simple base case solutions such as the square well and the harmonic oscillator. The infinite square well solutions and energy values are given by:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$
$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

The harmonic oscillator well solutions and energy values are given by:

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{14} \frac{1}{\sqrt{2^n n!}} H_n(\xi)\, e^{\frac{-\xi^2}{2}}$$
$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

For the harmonic oscillator, the expectation values for position and momentum are:

$$\langle\hat{p}\rangle = 0$$

$$\langle\hat{x}\rangle = 0$$

These solutions will be used as a test basis to verify the numerical solutions of the code.

III. METHODS

One way to numerically solve the Schrodinger equation is to use a matrix diagonalization mehod. The second derivative in the Schrodinger equation can be replaced by a difference formula:

$$\frac{d^2u}{dr^2} = \frac{u(r+h) - 2u(r) + u(r-h)}{h^2} + \emptyset(h^2)$$

Knowing the boundary conditions , these equations can be indexed through to form a system of linear systems of equations which linearly relate the value of the solution to the difference between nearby points as described by the differential equation. This system of linear equations can be written as a matrix eigenvalue equation. This equation is:

$$\begin{pmatrix} \frac{2}{h^2}+V_1 & -\frac{1}{h^2} & 0 & \cdots & \cdots & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2}+V_2 & -\frac{1}{h^2} & & & \vdots \\ 0 & -\frac{1}{h^2} & \ddots & & & \vdots \\ \vdots & & & \ddots & & -\frac{1}{h^2} \\ 0 & \cdots & \cdots & & -\frac{1}{h^2} & \frac{2}{h^2}+V_{N-1} \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ \vdots \\ u_{N-1} \end{pmatrix} = E \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ \vdots \\ u_{N-1} \end{pmatrix}$$

This is essentially the eigenvalue equation of the Schrodinger equation, only this time with a finite wave function vectors and finite Hamiltonian operator matrix. The eigenvalue matrix equation describing the Schrodinger equation can be solved by diagonalizing the matrix to find the eigenvectors and eigenvalues. Diagonalization of matrices can easily and efficiently be preformed by a computer. Thus the core of the python code for this numerical method is setting up the Hamiltonian matrix and diagonalizing it. The Hamiltonian matrix was generated by first initializing a matrix of the correct dimensions using numpy.zeros then this matrix was indexed through using a double for loop to in-place the matrix elements. Once the matrix is created it can diagonalized using the standard numpy linear algebra eigenvalue solve function. The standard numpy diagonalization function outputs the eigenvectors and eigenvalues, which are the corresponding wave functions and energy values to the Hamiltonian matrix prescribed by a certain potential. Once the eigenvectors are obtained, calculating the expectation values for position momentum are straightforward in theory. The numerical validation cases were calculated using a 4000 point mesh. A 4000 point mesh corresponds to a 16000000 dimensional matrix. The boundaries conditions were set to be zero at the x values of -1 and -1 for the square well verification ,and -5 and 5 for the harmonic oscillator verification. For the quartic well calculation a 4000 point mesh was used with the boundary interval being -10 to 10. All constants in the equations were set equal to unity.

IV. VALIDATION

To validate the program, the program was performed on the harmonic oscillator well and the square well, so these results could be compared to the known analytical results.

The plots of the square well wave functions and corresponding probability density functions are shown in figure 12. The plot of the numerically calculated energy eigenvalues for the square well are shown in figure one. The plots of the numerically determined expectation values for the square well are shown in figure two.

The plots of the harmonic oscillator wave functions and corresponding probability density functions are shown in figure 11. The plot of the numerically calculated energy eigenvalues for the harmonic oscillator are shown in figure three. The plots of the numerically determined expectation values for the harmonic oscillator are shown in figure four.

The wave-function appearances of both the validation potential wells agreed with the known analytical results. The numerical results were determined to be acceptable also. Thus the program can be used with confidence to solve the Schrodinger equation for potentials only numerically solvable.

V. RESULTS

The program was used to solve the Schrodinger equation for the quartic well. The quartic potential has an appearance similar to the harmonic oscillator potential, but has a potential barrier island in the middle. A graph of a quartic potential with a high potential energy barrier "island" is shown in figure six. This potential is specified by

$$V(x) = x^4 - 10x^2$$

A graph of a quartic well potential with a low potential energy potential barrier "island" is shown in figure five. This potential is specified by the potential energy function:

$$V(x) = x^4 - x^2$$

In the case of a quartic well with a really high energy potential barrier island and a low energy wave function, it is reasonable to approximate the quartic well as two harmonic oscillator wells. Both could be approximated as harmonic oscillators with no tunneling probability/no interaction between the two. In the case of a quartic well with a low energy potential barrier island, there is a high probability of particle/s tunneling through the potential barrier. Thus in this regime the quartic well can not be treated as two separated harmonic oscillators. When the potential's potential energy barrier island is low and the energy of the wave functions are very high, the wave functions easily "flood" over the barrier. Thus in this regime the quartic well could be approximated as a harmonic oscillator with a small perturbation at the bottom of the well. The graphs of the first six wave function solutions for the high energy potential barrier "island" quartic well can be seen in figure seven. The graph of the energy eigenvalues for the high energy potential barrier "island" quartic well ground state is shown in figure nine. The graphs of the first six wave function solutions for the low energy potential barrier "island" quartic well are shown in figure eight. The graph of the energy eigenvalues for the low energy potential barrier "island" quartic well ground state is shown in figure ten.

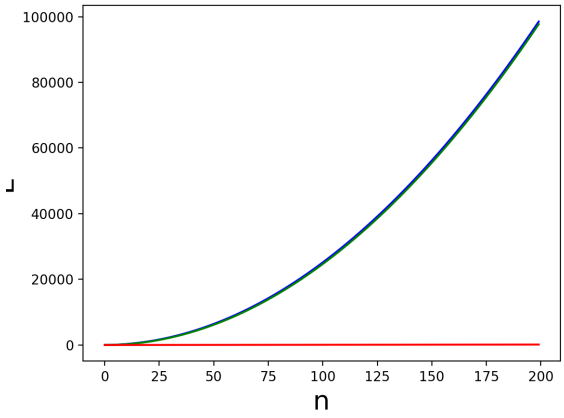

FIG. 1: This plot shows the numerically calculated energies and the analytical energies for the square well. The numerically calculated values are in blue and the analytical values are in green. The red curve represents the energies of a harmonic oscillator versus n. The harmonic oscillator energies are linearly related to n where as the square well is quadratically related to n. The numerical energies are thus seen to match the analytical energies very well.

VI. CONCLUSION

The Schrodinger equation was successfully solved numerically for the quartic well potential by a validated matrix diagonalization numerical routine. The basic physics of the shallow and deep quartic well were analyzed. The quartic well has both an appearance and properties similar to the harmonic oscillator. The notable differences are the occurrence of wave function tunneling in the center of the quartic well and the anharmonicity of the eigenvalue spectrum. It was inferred in the low energy states regime that the quartic well has an anharmoic eigenvalue spectrum in contrast to the harmonic eigenvalue spectrum of the harmonic oscillator.

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[1] Griffiths David, *Introduction to Quantum Mechanics* (Second Edition, 2005).

[2] Prof. Dick Furnstahl *Solving the Schrodinger equation numerically.*

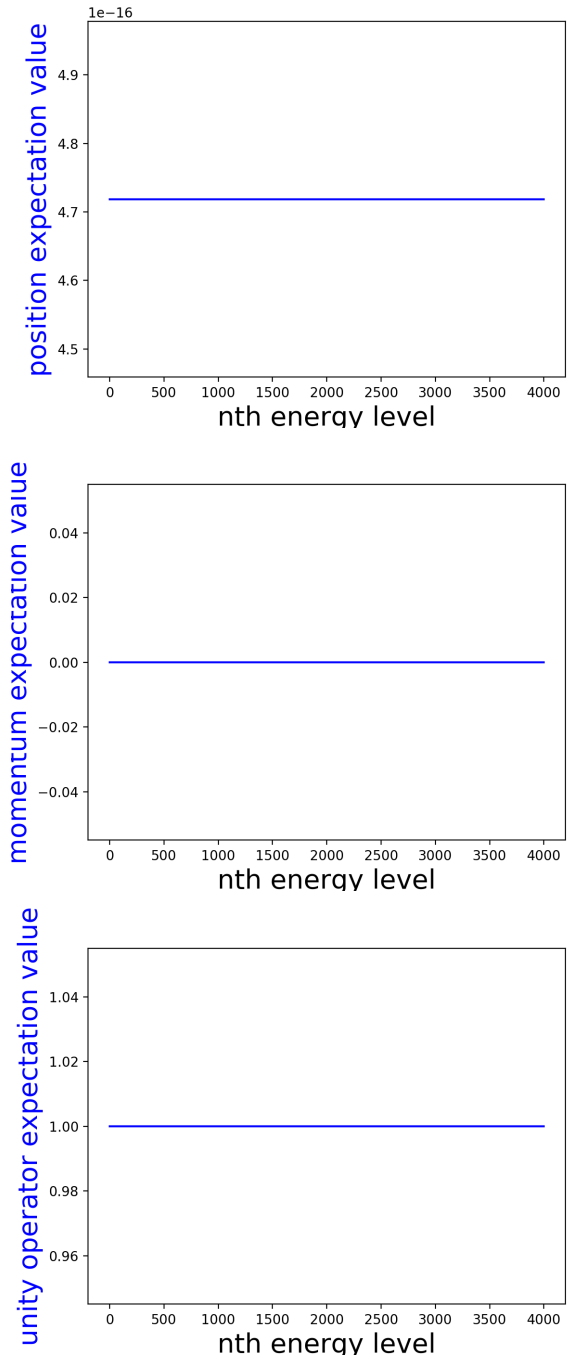

FIG. 2: Theses figures show the numerically calculated expectation values for the eigenfunctions of the square well. The momentum and position expectation values for all eigenfunctions where numerically determined to be zero within numerical accuracy agreeing with the analytical expectation values. The expectation value for the unity operator evaluated to unity as it should, serving as a code validation.

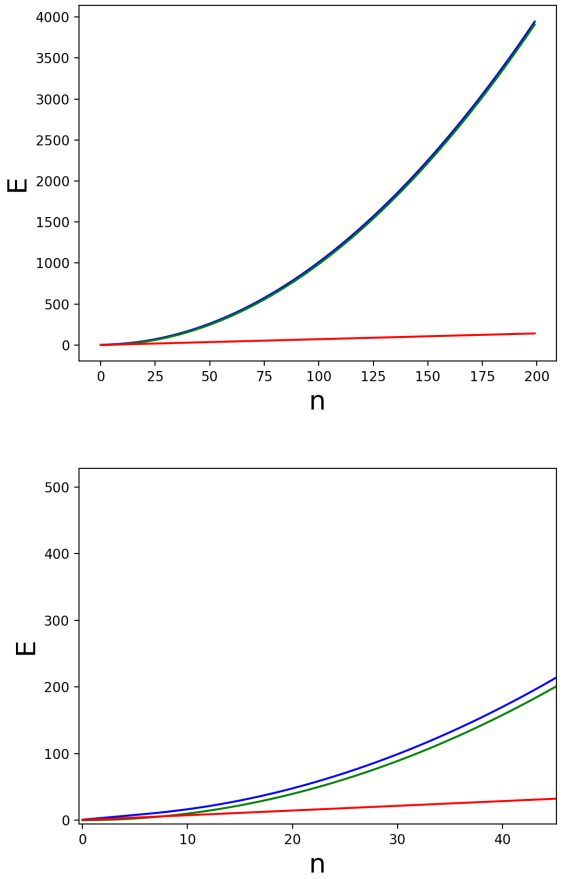

FIG. 3: This plot shows the numerically calculated energies and the analytical energies for the harmonic oscillator. The harmonic oscillator energies are in red. The square well energies are in green. The blue curve represent the numerically determined energies. The Bottom graph show a zoom in of the top graph for low energy eigenvalues. It can be seen that the numerical results agree linearly with the analytical harmonic oscillator energies in the low energy eigenvalue, but than diverge away from the harmonic oscillators to converge with the square well energies. This is because at a certain energy level the harmonic oscillator wave functions start touching the zero boundary conditions imposed in the code. Thus the potential effectively just becomes a square well at higher energy eigenvalues.

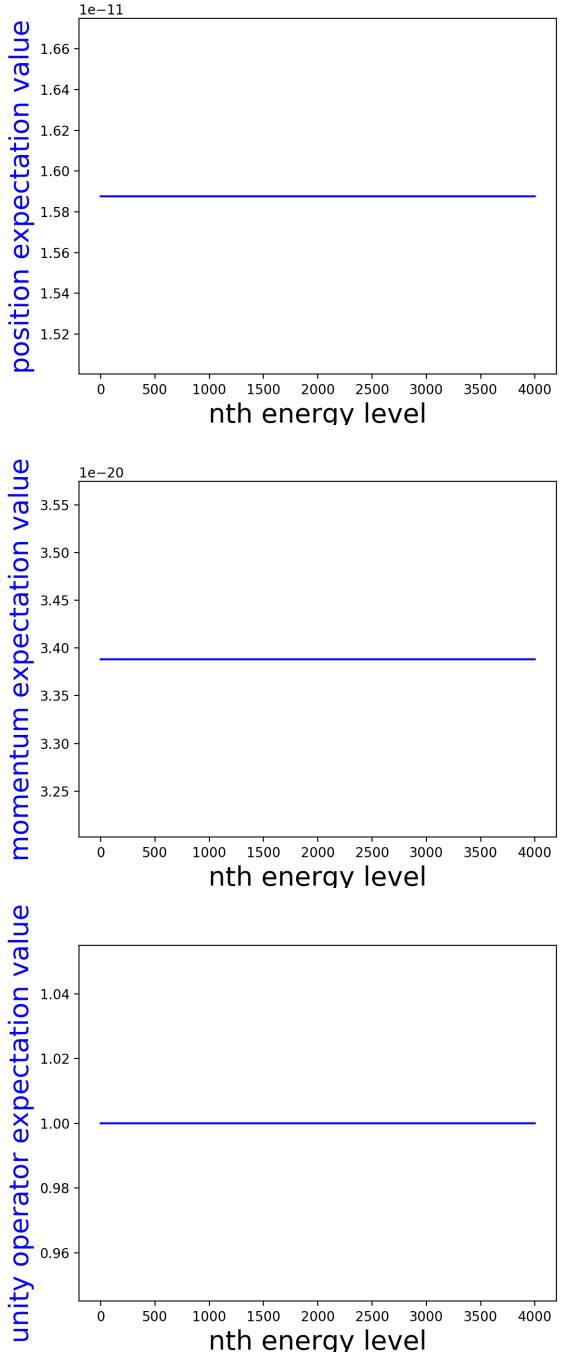

FIG. 4: Theses figures show the numerically calculated expectation values for the eigenfunctions of the harmonic oscillator. The momentum and position expectation values for all eigenfunctions where numerically determined to be zero within numerical accuracy agreeing with the analytical expectation values. The expectation value for the unity operator evaluated to unity as it should, serving as a code validation.

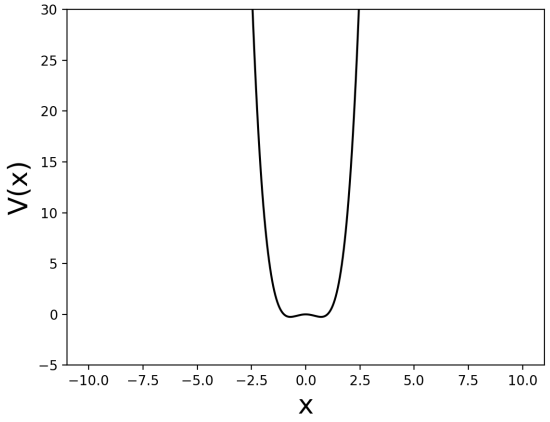

FIG. 5: This is a plot of a shallow quartic well potential. It has a small potential barrier uprising in the middle

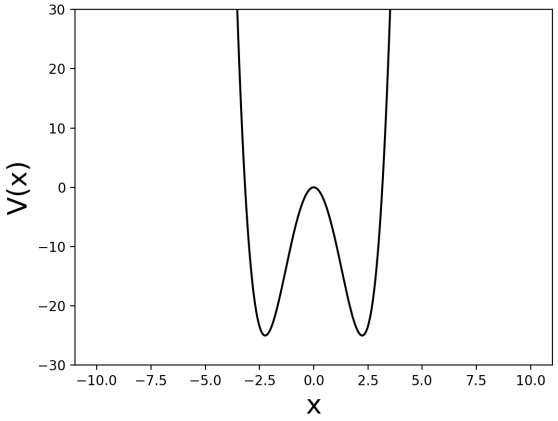

FIG. 6: This is a plot of a deep quartic well potential. It has a large potential barrier uprising in the middle

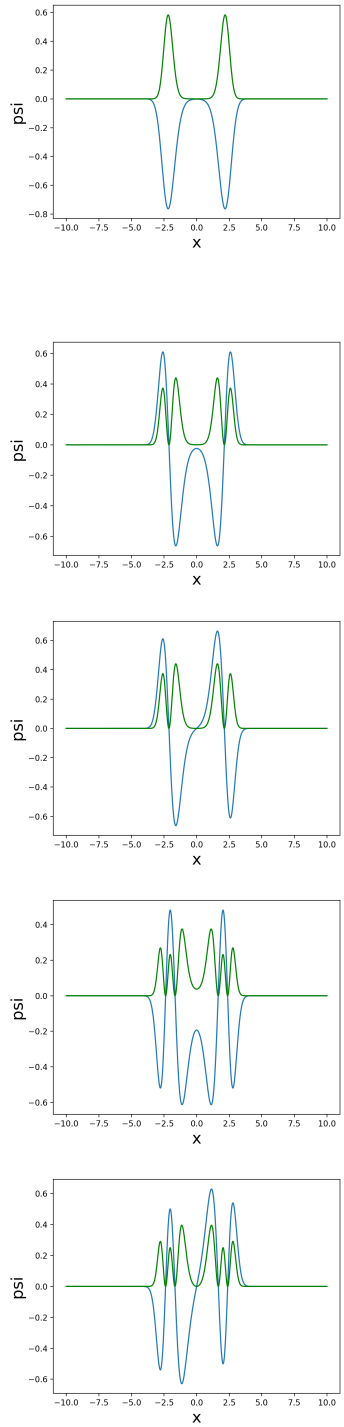

FIG. 7: These are the plots of the first six wave function solutions to the deep well quartic potential. The wave functions are in blue and the probability density functions are in green. It can be seen how the wave function penetrates the middle potential barrier by observing the probability density function in the vicinity of the middle of the potential. It can be seen that the tunneling probability increases for the higher energy wave functions.

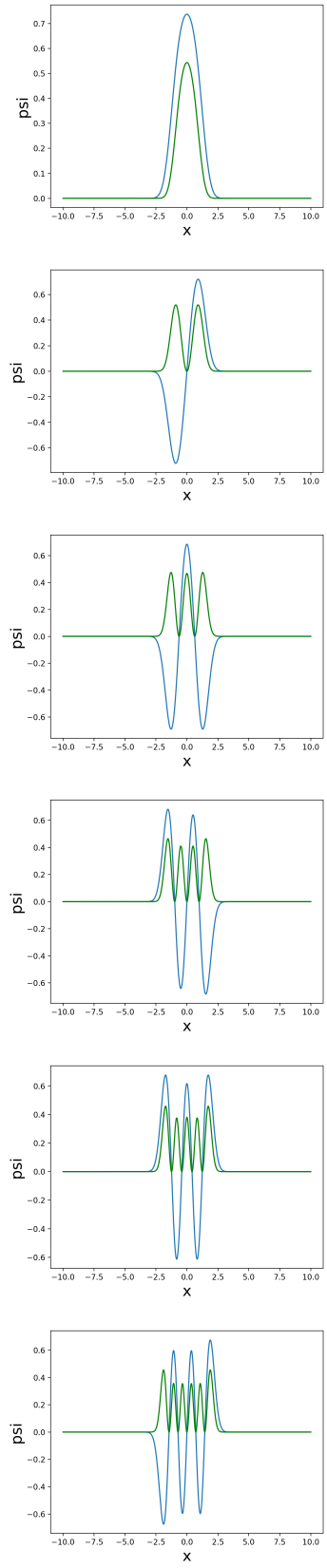

FIG. 8: These are the plots of the first six wave function solutions to the shallow well quartic potential. The wave functions are in blue and the probability density functions are in green. It can be seen how the wave function easily floods over the middle potential barrier by observing the probability density function in the vicinity of the middle of the potential. Thus in this case the quartic well is more like a harmonic oscillator with a small perturbation at the bottom of the well.

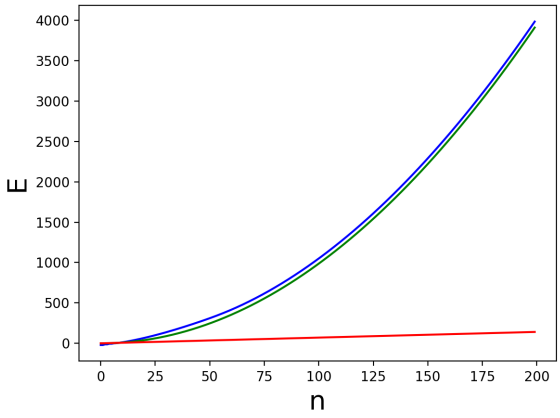

FIG. 9: This plot shows the numerically calculated energies for the deep quartic well potential. The analytical energies for the harmonic oscillator and square well are shown for comparison. The harmonic oscillator energies are in red. The square well energies are in green. The blue curve represent the numerically determined energies.

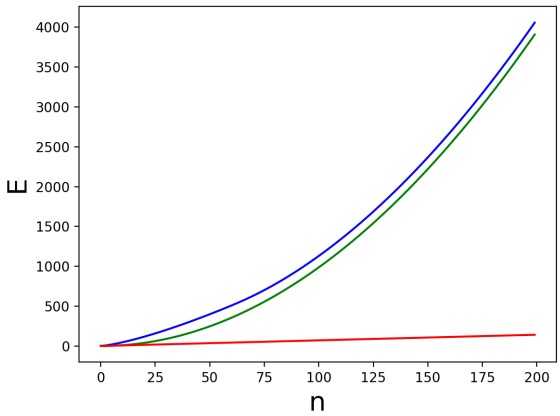

FIG. 10: This plot shows the numerically calculated energies for the shallow quartic well potential. The analytical energies for the harmonic oscillator and square well are shown for comparison. The harmonic oscillator energies are in red. The square well energies are in green. The blue curve represent the numerically determined energies.

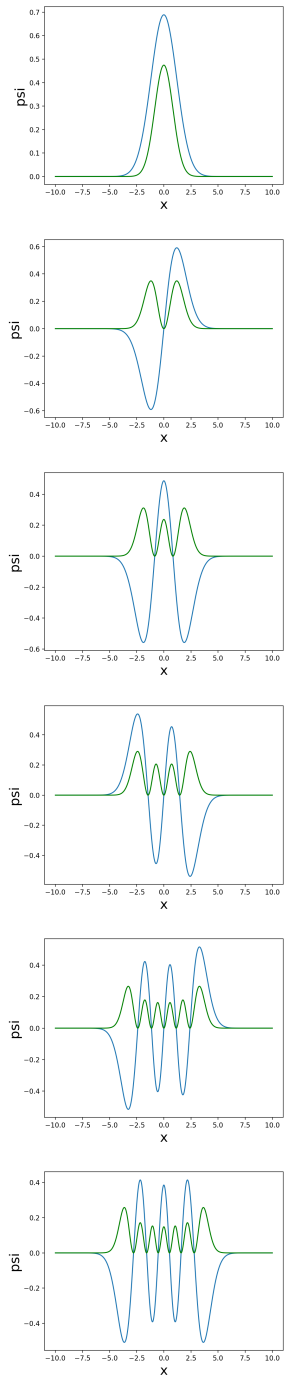

FIG. 11: First six wave function solutions to the Harmonic Oscillator potential. The wave functions are in blue and the probability density functions are in green.

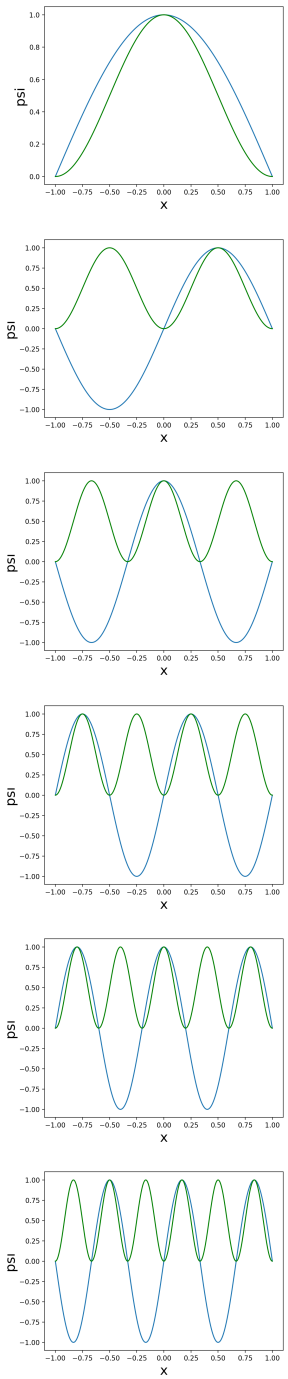

FIG. 12: First six wave function solutions to the Infinite Square Well potential.The wave functions are in blue and the probability density functions are in green.