The Stationary Schrödinger Equation

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1 Abstract

In this experiment the *One-Dimensional Stationary Solution* to the *Schrödinger Equation* was investigated using numerical methods by creating a C++ program. Using the *3-Point Numerov* algorithm the Schrödinger Equation was solved for a symmetric potential energy function to find the Eigenvalues and Eigenfunctions of an *Infinite Square Well* potential energy function. These solutions were compared with the analytically calculated solutions and were found to agree. The ground state energy was found to be $\varepsilon_1 = -0.90130956$, which was in perfect agreement with the analytical solution. The solutions were normalised and graphs for the wavefunctions were plotted using *Gnuplot*.

A *Step Potential* energy function was also investigated, and its energy eigenvalues were found using numerical methods. The orthogonality of these solutions was checked, and all eigenstates were found to be orthogonal. Finally a *Linear Potential* energy function was used and the experiment was repeated.

2 Introduction & Theory

2.1 The Schrödinger Equation

The *Time-Independent Schrödinger Equation* is given by

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) \tag{1}$$

where

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) \tag{2}$$

is the wavefunction, $V(x)$ is the potential energy function and m is the mass of the particle.

This equation can be normalised to give

$$\frac{d^2\hbar\psi(x)}{d\tilde{x}^2} + \gamma^2[\varepsilon - \nu(\tilde{x})]\psi(\tilde{x}) = 0 \tag{3}$$

where $\tilde{x} = x/L$ is the dimensionless spatial variable, $\nu(\tilde{x}) = V(\tilde{x})/V_0$ for $-1 \le \tilde{x} \le +1$ is the dimensionless potential energy function, $\varepsilon = E/V_0$ is the dimensionless energy and

$$\gamma^2 = \frac{2mL^2V_0}{\hbar^2} \tag{4}$$

is a dimensionless constant where we set $\gamma^2 = 100$

Differentiating, and then substituting equation (2) into equation (1) gives the equation for the *Energy Eigenvalues*

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} + V_0 \tag{5}$$

2.2 The 3-Point Numerov Algorithm

The equation above can be numerically integrated using the 3-Point Numerov formula

$$\psi_{n+1} = \frac{2(1 - \frac{5}{12} l^2 k_n^2)\psi_n - (1 + \frac{1}{12} l^2 k_{n-1}^2)\psi_{n-1}}{1 + \frac{1}{12} l^2 k_{n+1}^2} \tag{6}$$

where $l = 1/(N-1)$ is the step size for the discretise spatial variable and N is the number of points, and $k_n = \gamma^2[\varepsilon - \nu(x_n)]$ for our equation above.

The Numerov algorthim will give us a third point if we define two neighbouring points. Thus our algorithm can "shoot" from both sides of our potential well to calculate the wavefunction $\psi(\tilde{x})$.

2.3 The Euler Difference

We may numerically compute the approximate slope of a function $f(x)$ using *The Euler Difference* where

$$\psi'(x) \simeq \frac{\psi(x+l) - \psi(x)}{l} \tag{7}$$

2.4 Simpson's Rule

Furthermore, we may numerically compute the approximate integral of a function $\int_a^b f(x)dx$ using *Simpson's Rule* where

$$\begin{aligned} \int_{x_0}^{x^N} f(x)dx &\simeq \frac{l}{3}\left(f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \cdots + 2f_{N-2} + 4f_{N-1} + f_N\right) \\ &= \frac{l}{3}\left(f_0 + 2\sum_{j=1}^{N/2-1} f_{2j} + 4\sum_{j=1}^{n/2} f_{2j-1} + f_N\right) \end{aligned} \tag{8}$$

3 Experimental Method

3.1 Symmetric Potential

Using equations (4) and (5) above, an analytical solution for ε_n was found in terms of γ where $V(x) = -V_0$. The *Ground State Energy Eigenvalue* was then calculated.

The program was then compiled and run without any editing for a number of trial energies. The wavefunctions $\psi(x)$ were plotted for these trial energies using Gnuplot.

The program was then edited using *gedit*. Code was written to print the difference in the slopes ψ_{left} and ψ_{right} at the *Matching Point* using the Euler Difference. By using trail energies it was investigated weather the difference in the slopes was minimised for the ground state energy.

The code was then further edited by adding a *for loop* with an *if* statement inside to minimise the difference in ψ_{left} and ψ_{right} at the matching point for any trial energy E below the eigenvalue up to a predefined accuracy.

The accuracy of this method was compared to the analytical solutions.

The code was further edited to minimise the difference in the slopes for the E_2 eigenvalue.

Again, the code was edited by changing the matching point and adding a *for loop* to rescale ψ_{right} so that $\psi_{right}(x_{matching\ point}) = \psi_{left}(x_{matching\ point})$.

The first six energy eigenvalues were then found and compared with the analytical solutions.

3.2 Normalisation

The code was edited to allow it to use *Simpson's Rule for Numerical Integration* to normalise the wavefunctions. The graphs of these six normalised wavefunctions were then plotted.

3.3 Step Potential

The potential energy function in the program was edited to give a *Step Potential* such that $\nu(x) = -1$ for $0 < \tilde{x} < 0.5$ and $\nu(x) = 0$ for $0.5 < \tilde{x} < 1$. The ground state energy for this potential was then found by changing the matching point.

Next the first six energy eigenvalues were found for the step potential. A graph of each wavefunction was then plotted.

The data for each energy eigenstate was saved and was then imported into *Open Office Calc*, and using Simpson's Rule the probabilities were numerically integrated for the six energy eigenstates to check the orthogonality of some of them.

3.4 Linear Potential

Finally, the potential energy function was again edited, this time to provide a *Linear Potential*. Once again, the first six energy eigenstates were found and graphs of each were plotted.

4 Results & Analysis

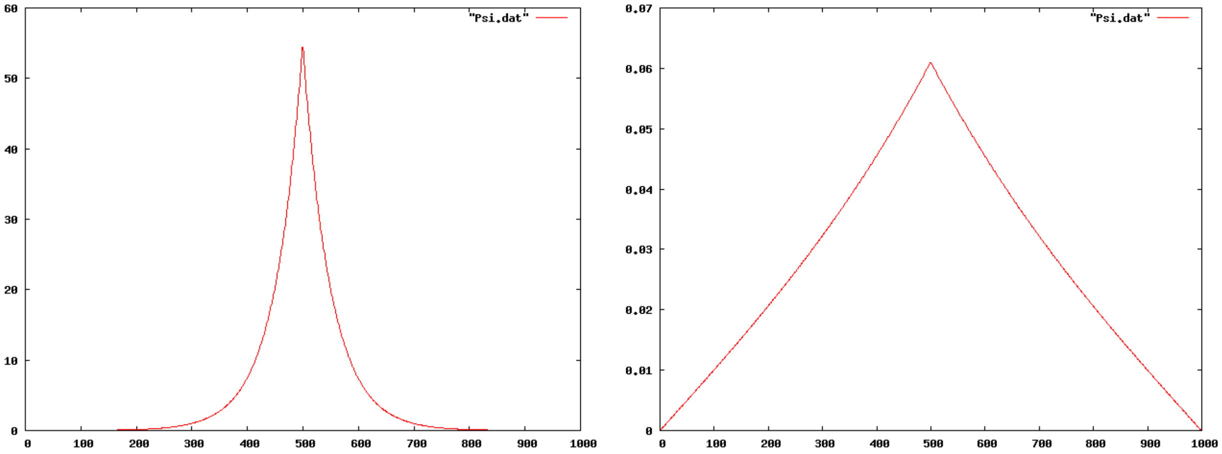
4.1 Symmetric Potential

The following expression was found for the energy eigenvalues

$$\varepsilon_n = \frac{\pi^2 n^2}{\gamma^2} - 1 \tag{9}$$

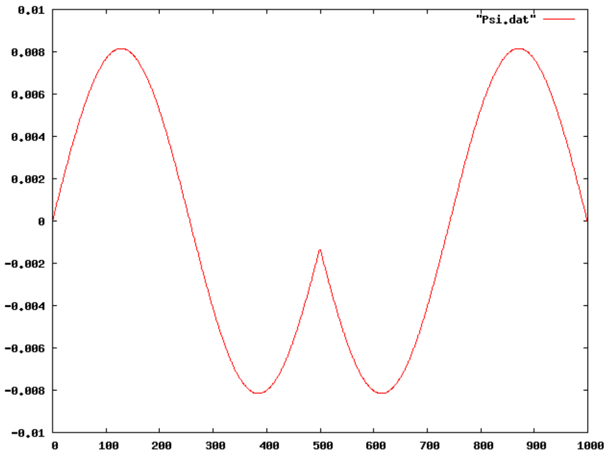
This gave a value of $\varepsilon_1 = -0.90130956$ units for the ground state energy.

The following graphs were plotted for trial energies both above and below the ground state energy

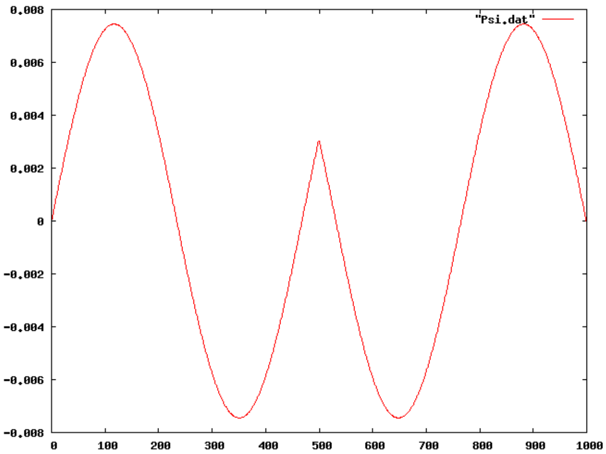


(a) E=-5

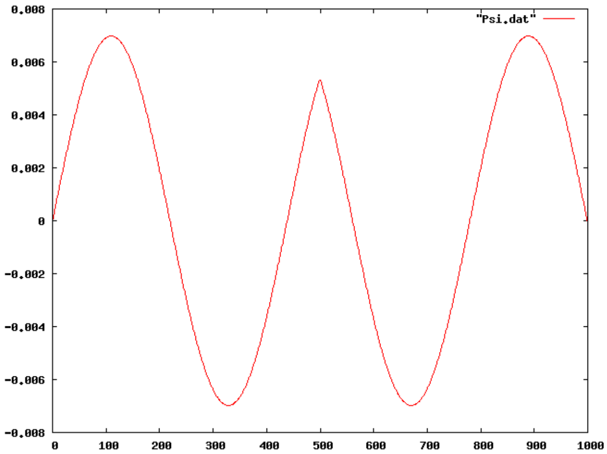
(b) E=-1.05



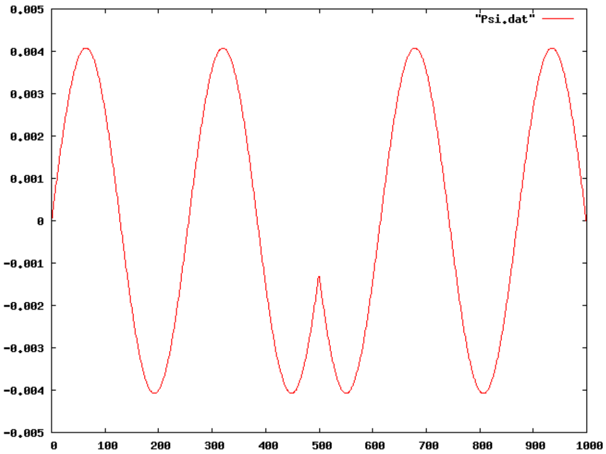
(c) E=0.5



(d) E=0.8



(e) E=1.05



(f) E=5

The following data was obtained for the difference in the slopes of ψ_{left} and ψ_{right} for varying trial energies

Trial Energy	Slope Difference
-5	2200
-1.05	0.338
-0.9013	0.000
0.8	0.82
5	0.190

We were able to get a value of $\varepsilon_1 = -0.90130956$ accurate to nine decimal places to the analytically calculated value. It would be possible to get a value accurate to $\varepsilon_{machine}$, the machine error constant, $\simeq 10^{-23}$, however our calculator only reads to nine decimal places.

The matching point was changed to $5N/12 + 1$, and this worked for all energy eigenstates.

The first six energy eigenvalues found analytically and using the C++ program were as follows

Energy Eigenstate	Analytic Solution	C++ solution
ε_1	-0.901303956	-0.901303956
ε_2	-0.605215824	-0.605215824
ε_3	-0.111735603	-0.111735604
ε_4	0.579136704	0.579136703
ε_5	1.467401100	1.467401099
ε_6	2.553057584	2.553057582

4.2 Normalisation

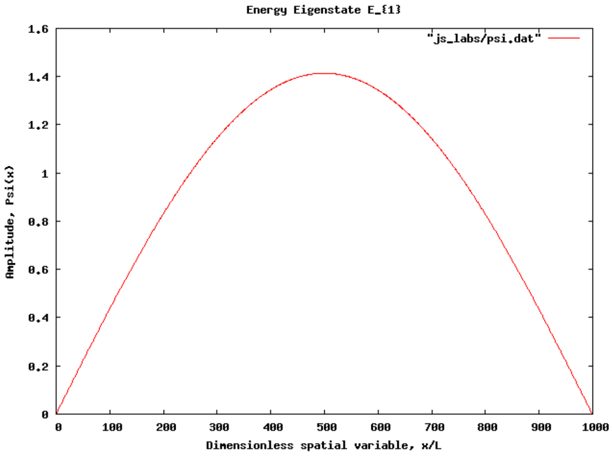
Using the relation

$$\psi(x)' = \frac{\psi(x)}{\sqrt{A}}$$

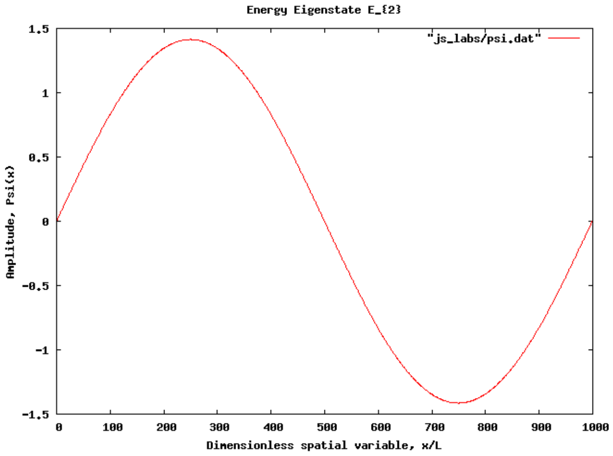
where $|\psi(x)'|^2 = 1$ the following normalisation constants A were found numerically

Energy Eigenstate	Normalisation Constant, A
ε_1	50.5595×10^{-5}
ε_2	12.6400×10^{-5}
ε_3	5.6179×10^{-5}
ε_4	3.1601×10^{-5}
ε_5	2.0225×10^{-5}
ε_6	1.4046×10^{-5}

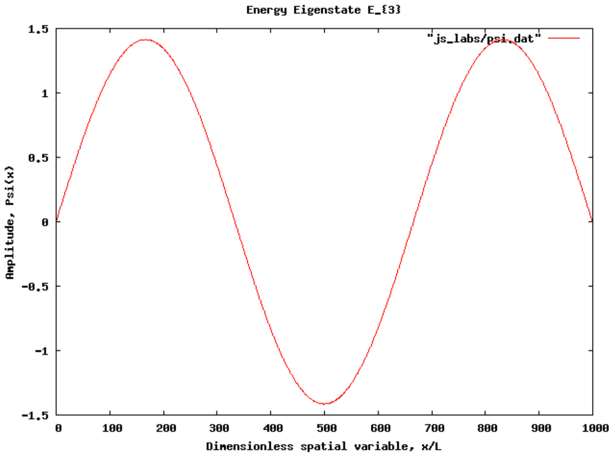
The following normalised graphs were then plotted using Gnuplot



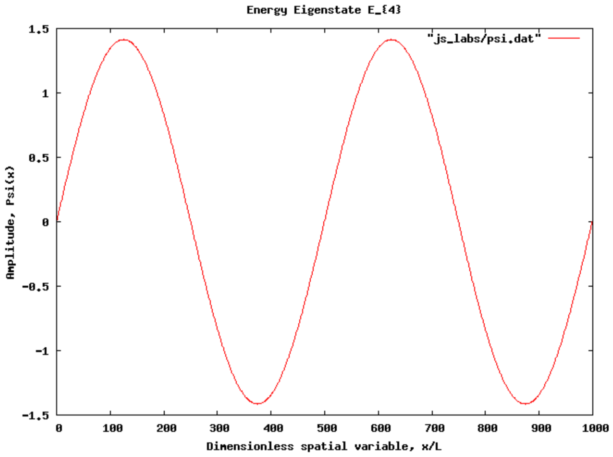
Energy Eigenstate E_{1}



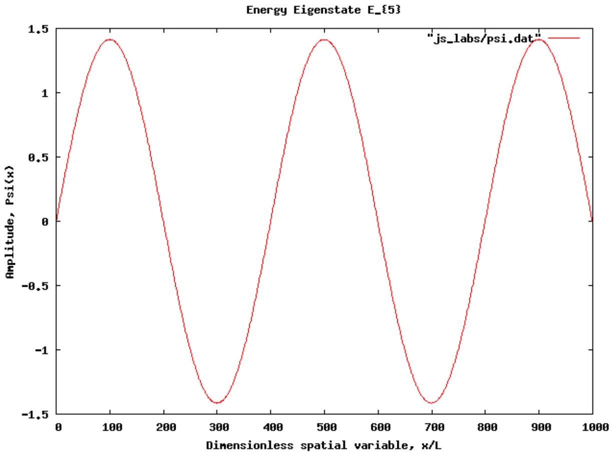
Energy Eigenstate E_{2}



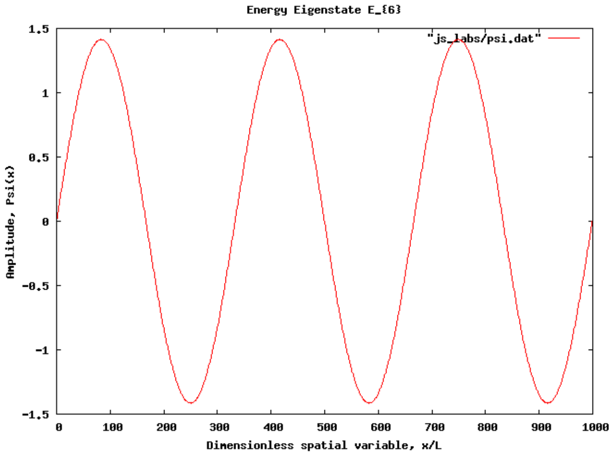
Energy Eigenstate E_{3}



Energy Eigenstate E_{4}



Energy Eigenstate E_{5}



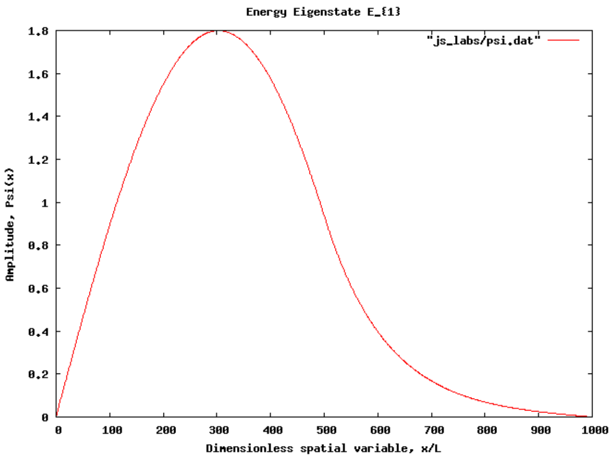
Energy Eigenstate E_{6}

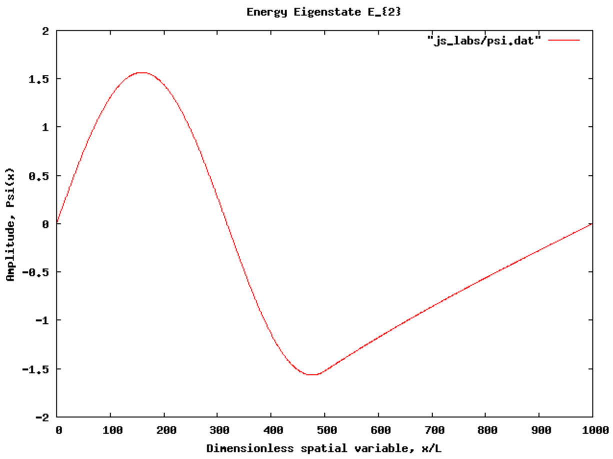
4.3 Step Potential

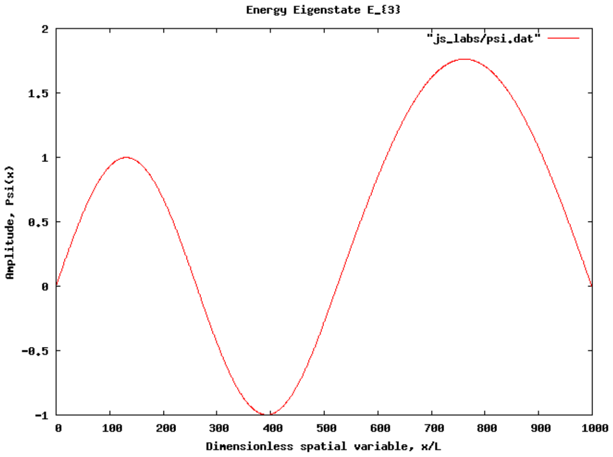
For the Step Potential the following values for the first six energy eigenvalues were numerically computed

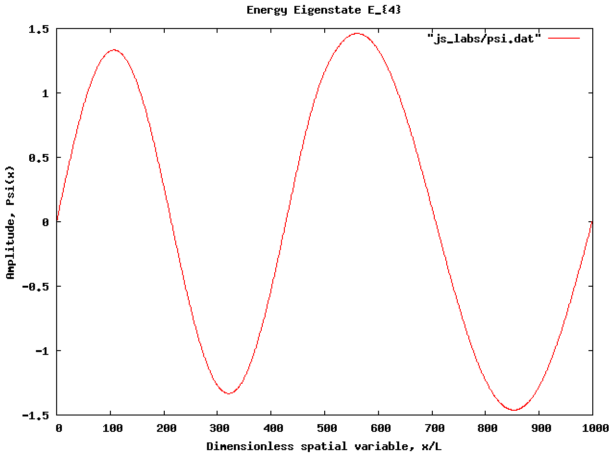
Energy Eigenstate	Energy
ε_1	-0.731329365
ε_2	-0.023988678
ε_3	0.436729626
ε_4	1.152688182
ε_5	1.959921830
ε_6	3.095349541

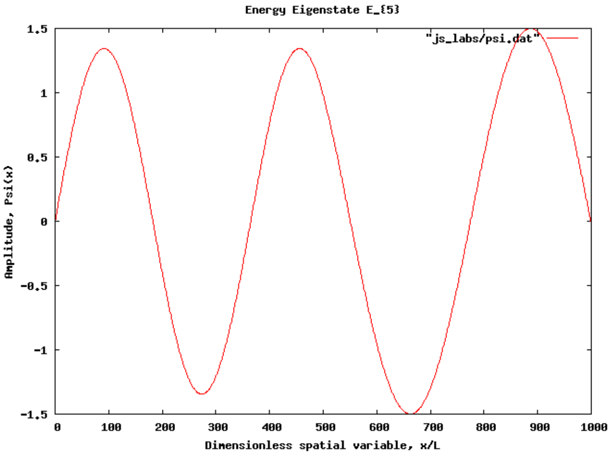
And their normalised graphs were plotted

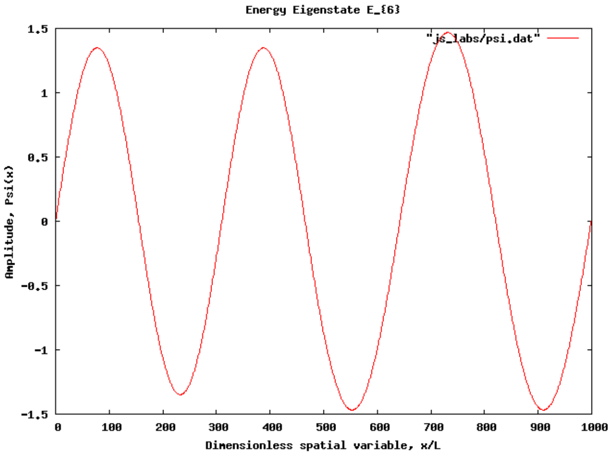












The orthogonality of the energy eigenstates was investigated by numerically computing

$$\int_{x_0}^{x^N} \psi_i(x)\psi_j(x)dx$$

for $i \neq j$. The following results were found, to three significant figures

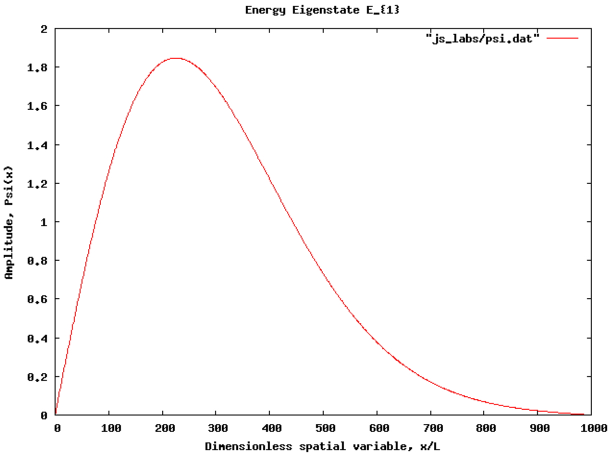
Energy Eigenstates	Probability
$\int_{x_0}^{x^N} \psi_1(x)\psi_2(x)dx$	-0.000142
$\int_{x_0}^{x^N} \psi_1(x)\psi_3(x)dx$	0.000195
$\int_{x_0}^{x^N} \psi_1(x)\psi_4(x)dx$	0.000341
$\int_{x_0}^{x^N} \psi_1(x)\psi_5(x)dx$	0.000146
$\int_{x_0}^{x^N} \psi_2(x)\psi_3(x)dx$	-0.000099
$\int_{x_0}^{x^N} \psi_2(x)\psi_4(x)dx$	-0.000092
$\int_{x_0}^{x^N} \psi_3(x)\psi_4(x)dx$	-0.000191
$\int_{x_0}^{x^N} \psi_5(x)\psi_6(x)dx$	0.000088

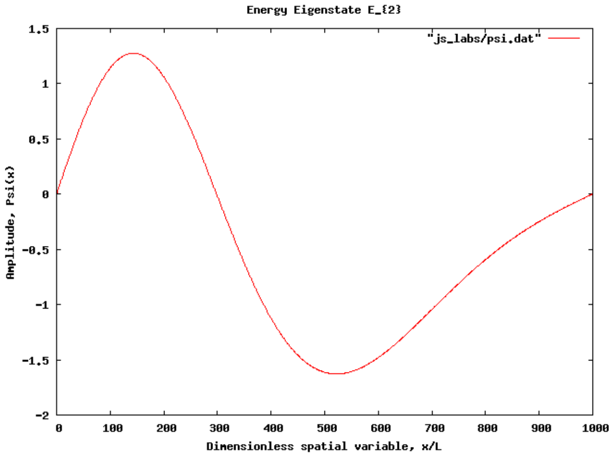
4.4 Linear Potential

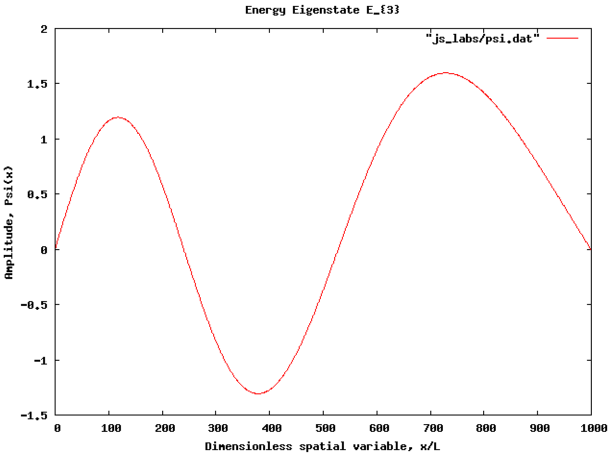
And finally for the Linear Potential the following energy eigenvalues were numerically computed

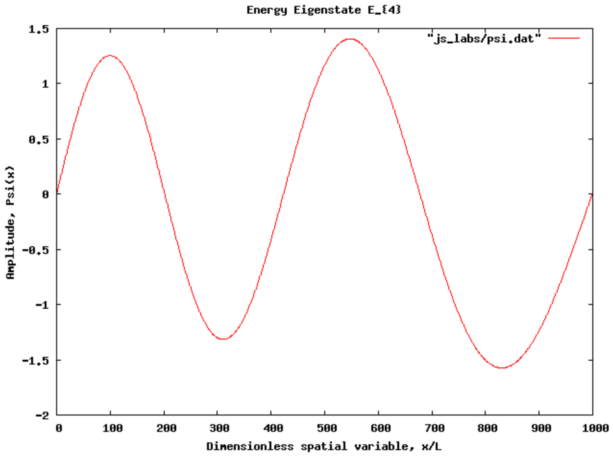
Energy Eigenstate	Energy
ε_1	-0.200361835
ε_2	0.401537681
ε_3	0.951206587
ε_4	1.626016836
ε_5	2.499172565
ε_6	3.575583994

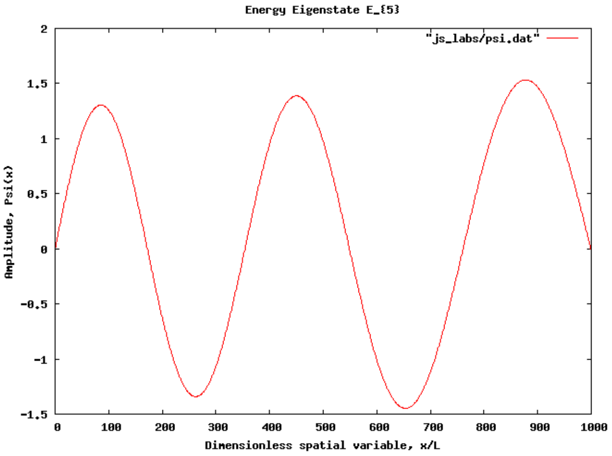
And their normalised graphs were plotted

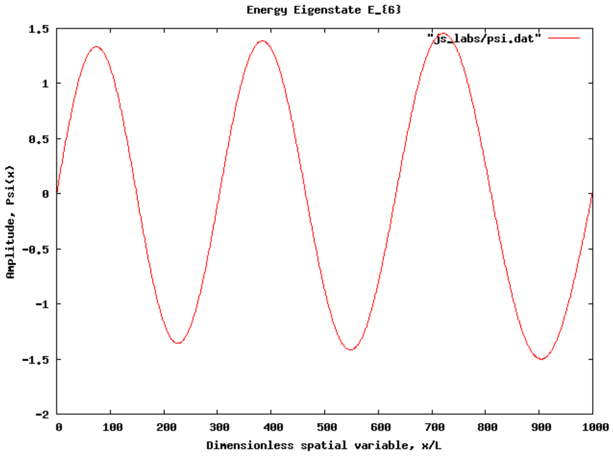












5 Error Analysis

As our experiment was preformed on a computer, the fundamental error is $\varepsilon_{machine}$, the machine error constant, $\simeq 10^{-23}$.

Furthermore, there is errors in our calculations due to the nature of numerical methods. The Numerov Algorithm has an error of order $\simeq l^6$ however due to the accumulation over many steps the total error is of order $\simeq l^4$.

In our program our predefined accepted error was $m = 1 \times 10^{-9}$, and after the absolute value of the energy increment was below this value the program stopped computing. It is possible to decrease this number as far as $\varepsilon_{machine}$, given enough computing power.

6 Conclusions

For the symmetric potential energy function, the value found for the ground state energy by numerical methods was $\varepsilon_1 = -0.90130956$. This was in perfect agreement to nine places of decimal with the analytical value of $\varepsilon_1 = -0.90130956$.

This was verified to be the ground state energy as the difference in the slopes of ψ_{left} and ψ_{right} was minimum for a trial energy of $E = -0.9013$.

The original minimisation procedure would not work for the E_2 energy eigenstate because the matching point of $N/2$ is a point of inflection for this $\psi(x)$. Thus the slopes of ψ_{left} and ψ_{right} do not have opposite sign, and so our algorithm will not work. The algorithm will work for the E_3 energy eigenstate because here the matching point of $N/2$ is again an extremum, and thus the slopes have opposite sign here. An easy way to search for the

E_2 energy eigenstate is to change the matching point to $N/4$, as here $\psi(x)$ is an extremum.

Even after rescaling, this minimisation algorithm will fail for the E_2 energy eigenstate for a matching point of $N/2$ because it is a point of inflection.

We found that the values for the first six energy eigenvalues agree in most cases, with an error of only $\simeq 10^{-9}$ in those cases which did not completely agree.

For the step potential it was found that two energy eigenvalues are negative. We needed to choose a matching point outside of the 'bump' due to the fact that the probability of finding a particle there is very low, as the wavefunction drops off exponentially. This solution to $\psi(x)$ corresponds to *Quantum Tunnelling*. It was found that for energies below +1, the particle was unlikely to be found on the right. However, as the energy was increased and became greater than +1 the wavefunctions approached those of the symmetric potential, and the particle was now likely to be found anywhere, as it had enough energy to overcome the potential step.

It was found that the probability of any two different eigenstates was of order $\simeq 10^{-4}$. This verifies that the eigenstates are orthogonal.

Finally, the energy eigenvalues for a linear potential were able to be computed numerically. The wavefunctions for this potential were found to be similar to those of the step potential. This is because the potential increased to the right, and so for low energies, the particle was not likely to be found there. Once again, as the particle energy became greater than +1 the wavefunction approached that of the symmetric potential as the particle had enough energy to be climb the potential slope.