Computer vs. Pencil: Applications of Numerical Methods in Quantum mechanics

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I. INTRODUCTION

This report uses a combination of numerical and analytical methods to solve a problem in [1] using the variational principle and the WKB/semi-classical approximation. We find the energy of ground and excited states using the two different methods along with the corresponding wavefunction and discuss how we were able to use numerical methods to reduce the human labor required to solve this problem.

II. NUMERICAL METHODS

Numerical methods have long served as a way to approximate challenging mathematical problems to high levels of precision. Numerical algorithms were used as early as 1650 BC to find roots for simple equations which were not easily solved analytically [2]. Numerical and analytic methods each offer distinct advantages and disadvantages when applied to physics problems. Analytical methods are formulated rigorously, and provide exact solutions to problems. These solutions provide deep insights and serve as benchmarks for verifying numerical methods. Analytic methods often require simplifications like linearity or symmetry to make a problem solvable. Many problems in physics are formulated as differential equations, for which a small selection are analytically solvable. These analytical solutions must be found by a human doing the math, whereas the ability to program in languages such as Python could lead to quick implementation of numerical methods which must be diligently checked for errors.

Numerical methods are broadly applicable, making them useful for solving problems that are very challenging or impossible to solve analytically. They are particularly effective in modeling problems with irregular boundary conditions where analytic solutions may not exist. They are also useful when computing a large number of somewhat-trivial integrals, as we see when using the variational principle. Numerical methods come with limitations. They are approximate and introduce errors into your solutions. They can also require significant computational resources, particularly for high-precision or large-scale problems, and may suffer from stability issues if improperly designed or assumptions being made are not true, as we see when using the WKB approximation. Numerical solutions often lack the general insights provided by closed-form analytic expressions and present as a "black-box" answer to the problem which you are solving.

Testing numerical methods is crucial to ensure their accuracy, stability, and reliability. This involves validating numerical results against analytic solutions when available. An example in the context of quantum mechanics is checking that the normalization integral for a wavefunction which you believe is normalized is in fact equal to one. It is also of use to display numerical solutions graphically when possible, to verify if there is any strange behaviour which you do not expect. I used the trapezoidal rule, implemented in libraries like NumPy (‘numpy.trapz‘) to numerically solve integrals. This method approximates integrals by summing the areas of trapezoids under a curve. Packages like NumPy make implementing these methods very simple, adding to the value they have to physicists. The accuracy of the trapezoidal rule depends heavily on the density of sampling points, with coarse discretization leading to significant errors [3]. To ensure its reliability, testing involves comparing results with known analytic integrals and evaluating performance on edge cases like discontinuities or irregular data spacing if you identify that this may be a concern.

I also used Scientific Python (SciPy) optimization tools to find the roots of equations to determine the energy of states. It uses advanced numerical methods to find the roots of a specified function. In this case, I found the input function by analytically solving an integral, and then found the roots numerically. This is a good demonstration of how numerical and analytic methods are used in unison. Numerical methods expand the scope of solvable problems, but must be carefully implemented and tested in conjunction with analytical solutions to find well informed solutions to problems.

III. VARIATIONAL METHOD

In this report I will solve Problem 8.30, from the 3^{rd} edition of Griffith's and Schroeter's Introduction to Quantum Mechanics textbook [1]. I will first give a summary description of the information provided and what is asked in this problem.

When applying the variational method the biggest decision to make is determining the trial wavefunction you will use to calculate the expectation value of the Hamiltonian, $\langle\psi_{trial}|\, H\, |\psi_{trial}\rangle$. The problem suggests that we

take our trial wavefunction to be of the form

$$\psi(x) = \sum_{n=1}^{N} c_n \phi_n(x), \tag{1}$$

where the c_n are the variational parameters, and the ϕ_n form an orthonormal set $\langle \phi_m | \phi_n \rangle = \delta_{mn}$. The text states that if $\psi(x)$ is not necessarily normalized we find that the variationally calculated energy correction is:

$$\epsilon = \frac{\sum_{mn} c_m^* H_{mn} c_n}{\sum_n |c_n|^2}, \tag{2}$$

where $\mathrm{H}_{mn} = \langle \phi_m | \, H \, | \phi_n \rangle$. Further, we find that

$$\sum_n H_{jn} c_n = \epsilon c_j. \tag{3}$$

Verifying this fact is the nature of part a of problem 8.30.

A. P-8.30 a

To derive equation 3, we take the derivative of ϵ with respect to c_j^*. We can treat c_j^* and c_j as independent variables when taking the derivative . The next thing we must consider is that for any complex number z, the modulus squared is:

$$|z|^2 = zz^*. \tag{4}$$

Using this fact, we can rewrite ϵ as

$$\epsilon = \frac{\sum_{mn} c_m^* H_{mn} c_n}{\sum_n c_n c_n^*}. \tag{5}$$

Now, we must simply apply the quotient rule treating c_j^* as the independent variable. Note that this will cause all $m \neq j$ terms to vanish from each sum, leaving us with a fixed value of j for the given index. We find that

$$\frac{\partial \epsilon}{\partial c_j^*} = \frac{\sum_n H_{jn} c_n}{\sum_n |c_n|^2} - \frac{\sum_{mn} c_m^* H_{mn} c_n}{(\sum_n |c_n|^2)^2} c_j. \tag{6}$$

Now we if we set this equation to zero and multiply by $\sum_n |c_n|^2$ we get

$$\sum_n H_{jn} c_n = \frac{\sum_{mn} c_m^* H_{mn} c_n}{\sum_n |c_n|^2} c_j \tag{7}$$

which we can recognize to be

$$\sum_n H_{jn} c_n = \epsilon c_j \tag{8}$$

as we expected.

B. P-8.30 c. Linear Potential

We want to consider a particle in an infinite square well with a sloping floor such that

$$\begin{cases} \infty & x < 0 \\ \frac{V_o x}{a} & 0 \leq x \leq a \\ \infty & x > a \end{cases} \tag{9}$$

is the potential of the system, where $V_o = 100 \frac{\hbar^2}{ma^2}$. We will use a linear combination of the first ten stationary states of the infinite square well as our orthogonal basis states. That is

$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \tag{10}$$

which form an orthonormal set as previously discussed. We want to use this information to calculate the upper bound on the ground state energy. To do this, we must compute the matrix elements H_{mn}. We must take some care in calculating this expectation value using our 10 basis vectors. We can write our Hamiltonian as

$$H = \frac{p^2}{2m} + V(x), \tag{11}$$

where p^2 = -$\hbar^2 \frac{\partial^2}{\partial^2 x}$ is the momentum operator squared in one dimension. We can treat the two terms in 11 seperately, and add them together to fully describe the H matrix. This is of interest, since the $p^2/2m$ term only has non-zero elements along the diagonal. This is seen in the following calculation:

$$\langle \phi_m | \, \frac{p^2}{2m} \, | \phi_n \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi x}{a}\right) \frac{p^2}{2m} \sin\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{n^2 \hbar^2 \pi^2}{ma^3} \int_0^a \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx$$

and using the orthogonality of the sinusoids, we find that

$$\langle \phi_m | \, \frac{p^2}{2m} \, | \phi_n \rangle = \frac{n^2 \hbar^2 \pi^2}{2ma^2} \delta_{mn},$$

noting that when $m = n$, we do an integral of a sine-squared function, and get a factor of $a/2$. This shows that the contribution from the kinetic energy term of the Hamiltonian is $\frac{n^2 \hbar^2 \pi^2}{2ma^2}$ along the diagonal. Next we must consider the contribution from the potential, which has non-zero diagonal and off-diagonal parts. These are found by the integral

$$\langle \phi_m | \, V(x) \, | \phi_n \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi x}{a}\right) \frac{V_o x}{a} \sin\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{2V_o}{a^2} \int_0^a \sin\left(\frac{m\pi x}{a}\right) x \sin\left(\frac{n\pi x}{a}\right) dx.$$

We can compute this integral numerically for each pair of m and n, noting that m, n= 1,2,...,10. Combining the terms of the Hamiltonian's expectation value we find that

$$H_{mn} = \langle \phi_m | \frac{p^2}{2m} | \phi_n \rangle + \langle \phi_m | V(x) | \phi_n \rangle . \quad (12)$$

This is a 10 x 10 matrix, which we can use to find the energy shift ϵ and then the optimized variational wavefunction. It is possible to express equation 8 as an eigenvalue problem:

$$\begin{pmatrix} H_{11} & H_{12} & \dots & H_{110} \\ H_{21} & H_{22} & \dots & H_{210} \\ \vdots & \vdots & \ddots & \vdots \\ H_{101} & H_{102} & \dots & H_{1010} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_{10} \end{pmatrix} = \epsilon \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_{10} \end{pmatrix}$$

where the smallest eigenvalue of this matrix is our best bound on the ground state energy. We can then use the corresponding eigenvector to that eigenvalue to tell us the best wavefunction of the form of equation 1.

I found that the upper bound on the energy of the linear-potential ground state was $E_{g.s.} \leq 39.98195449883025 \frac{\hbar^2}{ma^2}$ (keeping all digits representing the maximum floating point precision that my computer could compute). This is 0.00014 % different from the exact solution of the problem as stated in [1], which is a very good sign that the variational method worked well.
I chose to complete these integrals using the numerical python (NumPy) package's trapezoidal integrator. I also used the linear algebra capabilities built into python to find the eigenvalues and eigenvectors of H.

C. P-8.30 c. Quadratic Potential

We now want to solve the same problem using the potential

$$\begin{cases} \infty & x < 0 \\ \frac{V_o x^2}{a^2} & 0 \leq x \leq a \\ \infty & x > a \end{cases} \quad (13)$$

where $V_o = 100 \frac{\hbar^2}{ma^2}$ still. We find that the kinetic term of the Hamiltonian is unchanged, and that the potential term becomes

$$\langle \phi_m | V(x) | \phi_n \rangle = \frac{2}{a} \int_0^a \sin(\frac{m\pi x}{a}) \frac{V_o x^2}{a^2} \sin(\frac{n\pi x}{a}) \, dx$$

$$= \frac{2V_o}{a^3} \int_0^a \sin(\frac{m\pi x}{a}) x^2 \sin(\frac{n\pi x}{a}) \, dx.$$

As opposed to writing out all of these integrals, I will strictly compute each result numerically to build up the Hamiltonian matrix. When doing this I find that the lower bound on the ground state energy for the quadratic potential is 21.214285147758144 $\frac{\hbar^2}{ma^2}$. Figure 1 shows both the linear and quadratic potential wave-functions plotted from $x = 0$ to $x = a$ (here $a = 1$ to keep our units of energy generalized). Since the formulation of the question is identical for both questions, we can assume that we have a similar level of error in the quadratic potential as well compared to the exact solution, which we did not find for this potential.

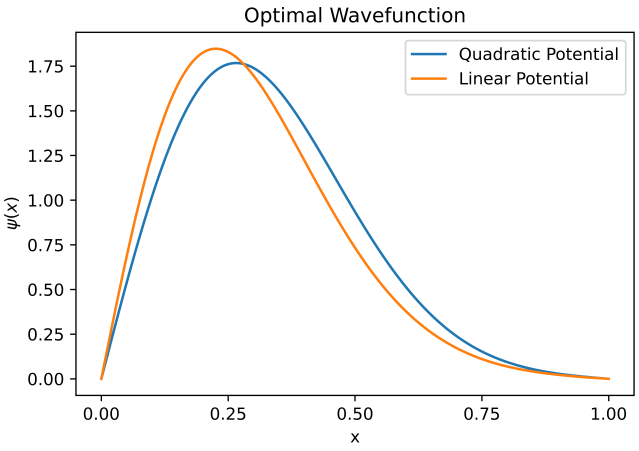

FIG. 1. Variational wavefunction plotted against position showing the result for the linear potential and the quadratic potential, recalling the rest of the potential is a infinite square well with Dirichlet boundary conditions. We see that they both resemble a similar shape, with the quadratic wavefunction peaking closer to the center of our well.

IV. WKB APPROXIMATION

We now want to solve this problem using the WKB approximation. The Dirichlet boundary conditions state that the wavefunction must vanish at the walls of the infinite potential well. Assuming that $E > V(x)$ inside of the well, our quantization condition becomes

$$\int_0^a p(x)dx = n\pi\hbar, \quad (14)$$

where n = 1,2,3 ... and $p(x) = \sqrt{2m(E - V(x))}$. We will use this for both example potentials to find the approximate allowed energies which then tell us our wavefunction.

A. Linear Potential

First using the linear potential in equation 14 we have

$$\sqrt{2m} \int_0^a \sqrt{(E - V_o x/a)} = n\pi\hbar.$$

This integral can be solved using the substitution u = $(E - V_o x/a)$ to get

$$\sqrt{2m}(-\frac{2a}{3V_o})(E - V_o x/a)^{3/2}\Big|_0^a$$

and we find that

$$\sqrt{2m}\frac{2a}{3V_o}(E^{3/2} - (E - V_o)^{3/2}) = n\pi\hbar$$

which can now be solved for E. We do this using the SciPy root_scalar function when n = 4. This solution does not work for n < 4 because the energy is not strictly greater than the potential throughout the entire well for these states, which we have assumed to be the case. We could treat this case using the connection formulas with a turning point at $x = E_{n<4} * a/V_o$. This treatment would be quite complicated, so we will therefore analyze an excited state which satisfies $E > V(x)$ throughout the well. Using the same units as before, we find that the first excited state to satisfy this assumption has energy

$$E_4 = 131.69\frac{\hbar^2}{ma^2}.$$

From the Dirichlet boundary conditions, the WKB wavefunction has the form

$$\psi(x) \approx \frac{1}{\sqrt{p(x)}}[C_1 \sin(\phi(x)] \tag{15}$$

where $\phi(x)$

$$\phi(x) = \int_0^x p(x)dx/\hbar \tag{16}$$

$$\phi(x) = \frac{2\sqrt{2ma}}{3V_o\hbar}[E^{3/2} - (E - V_o x/a)^{3/2}].$$

Our last step to getting the wavefunction is to normalize $\psi(x)$. Doing this numerically, we find that the wavefunction is

$$\psi(x) \approx \frac{1}{\sqrt{p(x)}}[4.955 * \sin(\phi(x)] \tag{17}$$

which we have numerically checked to be properly normalized. The wavefunction is show in figure 2.

B. Quadratic Potential

We can now apply the exact same treatment for the potential described in 13. Our quantization condition remains the same and we can use equation 14 to find the energies that will again satisfy $E > V(x)$:

$$\sqrt{2m}\int_0^a \sqrt{(E - V_o x^2/a^2)} = n\pi\hbar.$$

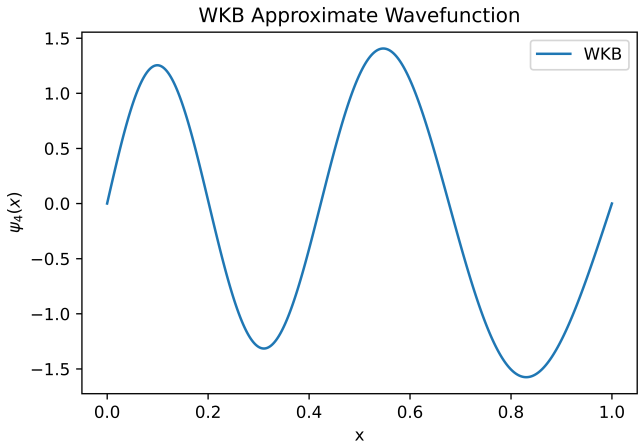

FIG. 2. WKB wavefunction of the third excited state plotted against position showing the result for the linear potential infinite square well. We see that the wavefunction is a sinusoidal as expected, and satisfies the Dirichlet boundary conditions.

We can solve this integral using a trig substitution and we find that as before we must use an excited state to satisfy out assumptions. Here we find that the $n = 5$ state has energy

$$E_{n,quad} = 158.69\frac{\hbar^2}{ma^2}.$$

We then find the argument of the sinusoid to be

$$\phi(x)_{quad} = \frac{aE\sqrt{m}\Big[\arcsin\frac{x\sqrt{V_o}}{a\sqrt{E}} + \frac{1}{2}\sin(2\arcsin\frac{x\sqrt{V_o}}{a\sqrt{E}})\Big]}{\sqrt{2V_o}\hbar}.$$

Lastly, when normalizing numerically we find that the wavefunction for the quadratic potential is

$$\psi(x) \approx \frac{1}{\sqrt{p(x)}}[5.219 * \sin(\phi(x)_{quad})]. \tag{18}$$

The normalized wavefunction is shown in figure 3.

V. CONCLUSION

We were able to bound the ground state energy of the system with the linear and quadratic potential using the variational principle. We found that the linear potential ground state energy was within 0.00014% of the exact solution stated in [1]. This result indicates how powerful the variational method can be. We then used the WKB approximation to solve the same problem. We were not able to easily employ the WKB approximation for states with energies less than that of our potential well, so we used the WKB approximation to solve for excited states. This shows us that for this problem either the variational method or possibly a perturbative approach would be of interest to solve for states where $E < V(x)$ at some point,

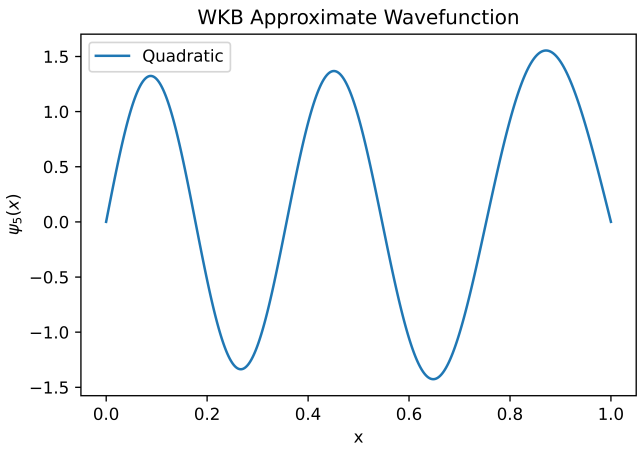

FIG. 3. WKB wavefunction of the fourth excited state plotted against position showing the result for the quadratic potential infinite square well. Wavefunction satifies the Dirichlet boundary conditions as expected.

but for excited states we can easily apply the WKB approximation to find the approximate energies and wavefunctions. We were able to leverage numerical methods in both of these approaches, to solve integrals, compute eigenvalues and eigenvectors, and to find roots of equations to arrive at solutions with very little error, much quicker than we could have using analytic methods to arrive at the same solution. Importantly, we were able to quickly plot graphs to help us verify our results and check that solutions obey boundary conditions. This is an important way for us to check our numerical methods, which act as a black box solution when you are using already written packages such as those available in Python.

[1] Darrell Schroeter David Griffiths. *Introduction to Quantum Mechanics, third edition.*
[2] Kendall Atkinson. Britannica. 2024.
[3] William H. Press, Saul A. Teukolsky, William T. Vetterling, and Brian P. Flannery. *Numerical Recipes: The Art of Scientific Computing.* Cambridge University Press, 3rd edition, 2007.