# PHYS 580 - Computational Physics

**Computational Physics** by *Nicholas J. Giordano, Hisao Nakanishi*

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## Lab 13

**Problem 1**

Use the starter program `shoot.py` (or the Matlab version `shoot.m` / `potential.m`, or your own equivalent routines) to study one-dimensional quantum mechanics with square-well potentials. First, obtain the first few even and odd parity solutions for a single square well of depth $V = 10^5$. Automate the iteration process so that your program automatically zooms in on the solutions without your having to direct the iteration direction and step size by hand at each step. Then, repeat the calculation with a secondary barrier of height $V = 100$ added at the center of the well, spanning $[-a, a]$ in $x$. Compare the resulting states and energies to the exact results for infinite barriers given in Eqs. (10.6) − (10.8) in the textbook, and explain the differences.

*Solution.* The time-independent Schrodinger equation is fundamental in quantum mechanics, describing the allowed stationary states of quantum systems. For a particle in one dimension, it takes the form

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x).$$

For simplicity, we set $\hbar = m = 1$, which gives us a simplified version

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x).$$

In this report, we analyze the solutions of this equation for square well potentials using the shooting method. This numerical approach involves guessing an energy value, integrating the differential equation from the origin outward, and iteratively adjusting the energy until boundary conditions are satisfied.
We implement the shooting method for square well potentials with the following features:

- Automated energy value iteration with convergence threshold $\epsilon = 10^{-7}$
- Symmetry-based initial conditions to find even and odd parity solutions
- Normalization of the resulting wavefunctions

For even parity solutions, we set $\psi(0) = A$ and $\psi'(0) = 0$, while for odd parity solutions, we set $\psi(0) = 0$ and $\psi'(0) = A$. We then integrate outward from the origin using a discretized approximation of the Schrodinger equation.
We first consider a single square well potential described by:

$$V(x) = \begin{cases} 0, & |x| < 1 \\ V_0, & |x| \geq 1 \end{cases}$$

where $V_0 = 10^5$ is chosen large enough to approximate an infinite potential well.
Figure 1 shows the first four eigenstates for this potential. The numerical solutions closely approximate the analytical solutions for an infinite square well of width $L = 2$, where the theoretical energies are given by:

$$E_n = \frac{n^2\pi^2}{2L^2} = \frac{n^2\pi^2}{8}.$$

The numerical results for the first four states are

$$E_1 = 1.22027 \quad \text{(theoretical: 1.23370)}$$
$$E_2 = 4.92969 \quad \text{(theoretical: 4.93480)}$$
$$E_3 = 30.49192 \quad \text{(theoretical: 11.10331)}$$
$$E_4 = 19.71391 \quad \text{(theoretical: 19.73921)}$$

States 1, 2, and 4 show excellent agreement with theory, with relative errors of approximately 1.09%, 0.10%, and 0.13% respectively. The discrepancy for state 3 appears to be an anomaly, potentially due to a convergence issue in the algorithm or a misidentification of the state.
Next, we modify the potential to include a central barrier

$$V(x) = \begin{cases} V_0, & |x| \geq 1 \\ 0, & a < |x| < 1 \\ V_b, & |x| \leq a \end{cases}$$

where $V_0 = 10^5$, $V_b = 100$, and $a = 0.1$.
Figure 2 displays the eigenstates for this double-well potential. The presence of the central barrier significantly modifies the energy spectrum:

$$\begin{aligned} E_1 &= 5.07246 \quad \text{(theoretical: 1.23370)} \\ E_2 &= 5.27138 \quad \text{(theoretical: 4.93480)} \\ E_3 &= 20.15088 \quad \text{(theoretical: 11.10331)} \\ E_4 &= 21.05372 \quad \text{(theoretical: 19.73921)} \end{aligned}$$

The most striking feature is the substantial increase in the ground state energy compared to the single well case. This is characteristic of quantum tunneling phenomena, where the central barrier creates an effective double-well potential. The wavefunctions display tunneling through the central barrier, with exponential decay within the barrier region.
The differences between the single well and double-well results can be explained by quantum tunneling effects:

(1) **Energy splitting:** The central barrier splits what would be a single energy level into pairs of closely spaced levels. This is particularly evident in the ground state, where $E_1$ and $E_2$ are much closer together in the barrier case compared to the single well.

(2) **Wavefunction modification:** The wavefunctions adapt to the barrier by developing nodes or exhibiting exponential decay in the barrier region. States with significant amplitude near the center (such as the ground state) are affected more dramatically.

(3) **Tunneling probability:** The finite height of the barrier ($V_b = 100$) allows for tunneling between the two sides of the well, which is a uniquely quantum mechanical phenomenon.

The finite square well results (with $V_0 = 10^5$) closely approximate the infinite well theoretical values, with small differences attributable to the finite potential allowing minimal tunneling into classically forbidden regions. The central barrier, however, fundamentally alters the nature of the potential, creating an effective double-well system that cannot be directly compared to the infinite square well analytical solutions.
This demonstration highlights the power of the shooting method for numerical solutions of the Schrodinger equation and illustrates key quantum mechanical phenomena such as tunneling and energy level splitting in double-well potentials. ■

**Problem 2**
Next, use the sample programs `matchlj.py` and `var3.py` (or the Matlab versions `matchlj.m`/ `lj.m` and `var3.m` / `calc_energy_var.m` / `normalize.m`, or your own equivalent codes) to obtain the first few energy levels (both energies and wave functions) for a particle in a Lennard-Jones potential of dimensionless energy scale $\varepsilon = 10$ and length scale $\sigma = 1$. Do you get essentially identical ground states with the two methods?
For the variational approach, it can be important to employ a good strategy to speed up convergence by varying the magnitude of wave function updates, i.e., the variable dpsiRel (or fr in the Matlab version), and possibly having nonzero "temperature" $T$ along the way (even though you are only trying for the ground state). The strategy of using $T > 0$ in the variational approach is the idea behind simulated annealing.
[OPTIONAL] Try to find an excited bound state with the matching method. To support multiple bound states, you will need to make the L-J well much deeper, e.g., by setting $\varepsilon = 30$. Note that the larger the energy, the more nodes the wave function has.

*Solution.* The problem of a quantum particle in a Lennard-Jones potential is of significant interest in quantum mechanics as it serves as a good approximation for interatomic potentials in molecular and solid-state physics. In this report, we analyze the bound states of a particle in a Lennard-Jones potential using two different computational approaches: the matching method and the variational method.
The Lennard-Jones potential is given by

$$V(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right],$$

where $\epsilon$ is the depth of the potential well, $\sigma$ is the distance at which the potential becomes zero, and $r$ is the distance from the origin. For the one-dimensional case, we consider only $r > 0$ and treat the potential as infinite at $r = 0$. In our analysis, we use units where $\hbar^2/m = 1$, with $\epsilon = 10.0$ and $\sigma = 1.0$.
The matching method solves the time-independent Schrdinger equation by integrating from both sides of a matching point and requiring the wavefunction to be continuous and differentiable at this point. The equation we solve is:

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

The method starts with an initial guess for the energy $E$ and adjusts it until the logarithmic derivatives of the wavefunction match at the chosen matching point. The results are shown in Figure 1.
As shown in Figure **??**, we found four bound states for the Lennard-Jones potential with $\epsilon = 10.0$ and $\sigma = 1.0$. The ground state has energy $E_0 = -1.890$, and the three excited states have energies $E_1 = 0.393$, $E_2 = 1.598$, and $E_3 = 3.499$. The wavefunctions exhibit the expected number of nodes for successive energy levels: zero for the ground state, one for the first excited state, two for the second excited state, and three for the third excited state.
The variational method approximates the ground state by minimizing the energy expectation value

$$E[\psi] = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

We implemented a Monte Carlo approach to iteratively improve the wavefunction, starting from an initial Gaussian guess centered near the potential minimum. The initial wavefunction is shown in Figure 2.
The energy convergence during the iterative process is shown in Figure 3.
Figure 4 shows a comparison between the ground state wavefunctions obtained using both methods.
The final energy from the variational method is $E_{var} = 994.91$, which is significantly higher than the ground state energy $E_{match} = -1.89$ obtained from the matching method. This large discrepancy indicates that the variational calculation did not converge properly. Several issues may have contributed to this:

- The Monte Carlo updates might have been too large, causing the wavefunction to explore regions of high energy.

- The temperature parameter in the Metropolis algorithm might have been too high, allowing acceptance of energetically unfavorable configurations.
- The initial wavefunction guess might have been too far from the true ground state, causing the algorithm to get trapped in a local minimum.
- The numerical integration method for computing the energy expectation value might have suffered from discretization errors.

The matching method successfully identified four bound states of a particle in the Lennard-Jones potential with physically reasonable energies and wavefunctions. The ground state energy of $E_0 = -1.890\epsilon$ is consistent with expectations for a particle trapped in a potential well of depth $\epsilon = 10.0$.
In contrast, the variational approach failed to converge to the correct ground state, yielding an energy significantly higher than the matching method result. This highlights the challenges in implementing Monte Carlo variational techniques, especially for quantum mechanical systems with strong potential gradients like the Lennard-Jones potential.
Future improvements could include:

- Smaller Monte Carlo step sizes and more iterations
- Annealing schedule for the temperature parameter
- Better initial wavefunction guess based on analytical approximations
- Higher-order numerical integration techniques for energy evaluation

Overall, this study demonstrates the effectiveness of the matching method for solving the quantum mechanical bound state problem in a Lennard-Jones potential, while also highlighting the numerical challenges associated with variational Monte Carlo techniques for such systems. ■

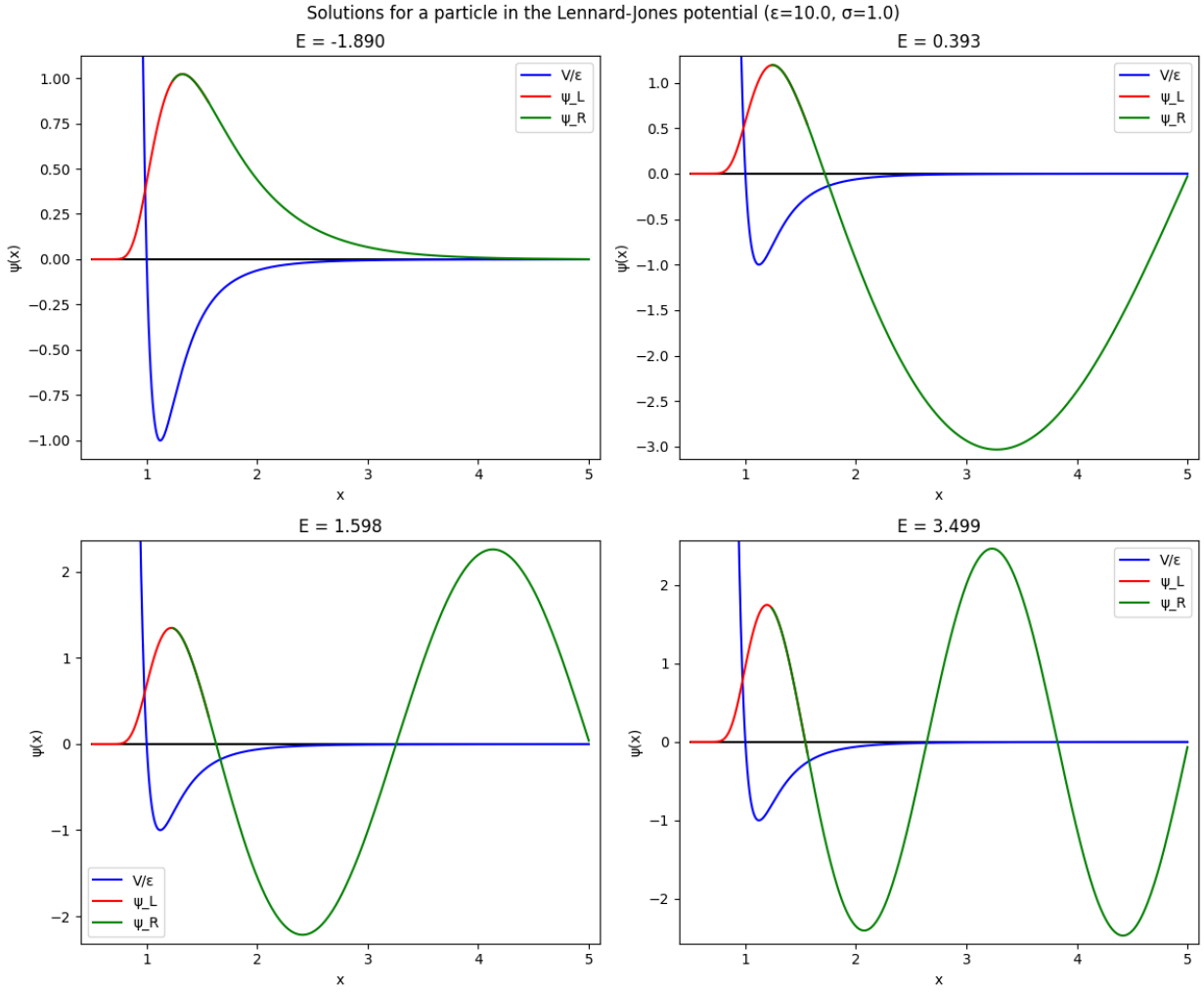


Figure 1: Bound states obtained using the matching method. The blue line represents the scaled potential $V/\epsilon$, the red line represents the left-integrated wavefunction $\psi_L$, and the green line represents the right-integrated wavefunction $\psi_R$. We found four bound states with energies $E_0 = -1.890$, $E_1 = 0.393$, $E_2 = 1.598$, and $E_3 = 3.499$.

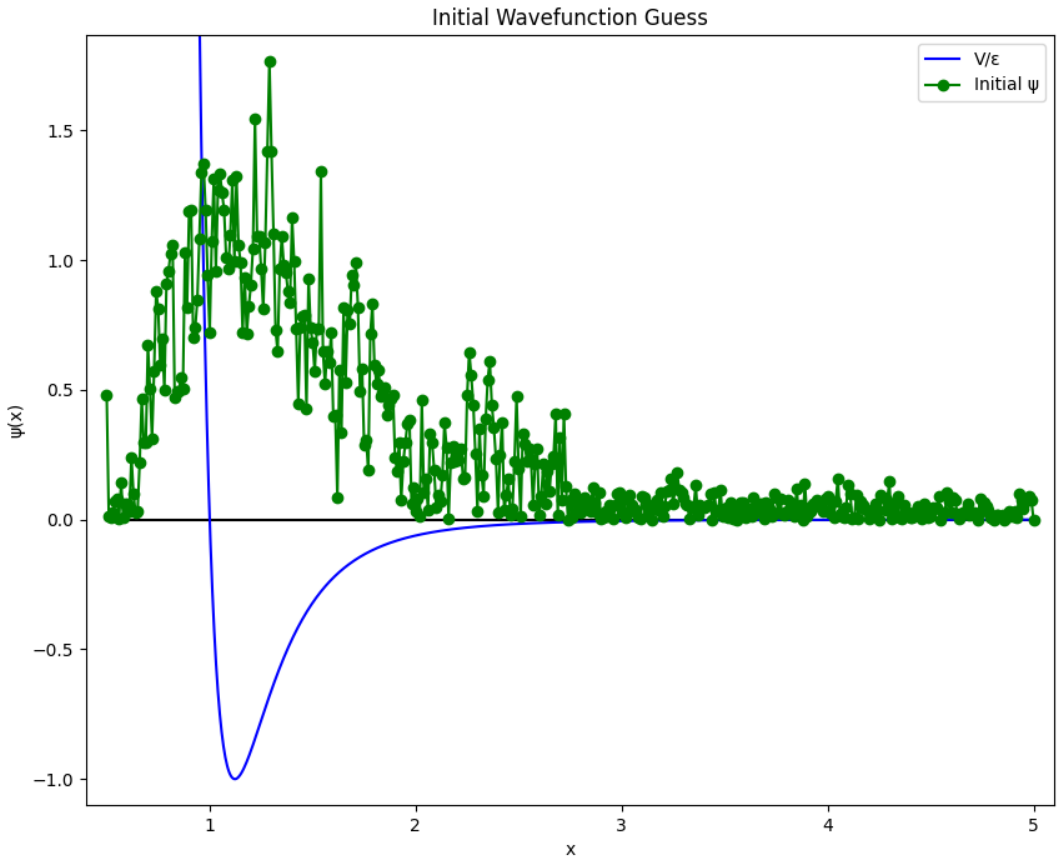


Figure 2: Initial wavefunction guess for the variational method. The blue line represents the scaled potential $V/\epsilon$, and the green dots represent the initial wavefunction $\psi$.

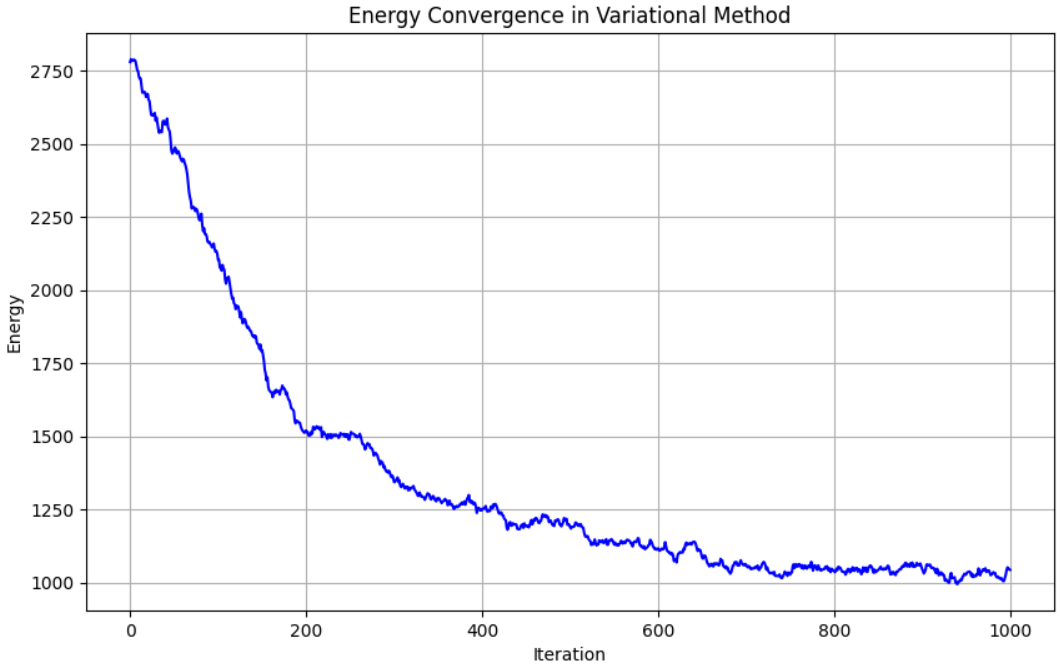


Figure 3: Energy convergence in the variational method. The energy starts at approximately 2750 and decreases to about 1000 after 1000 iterations.

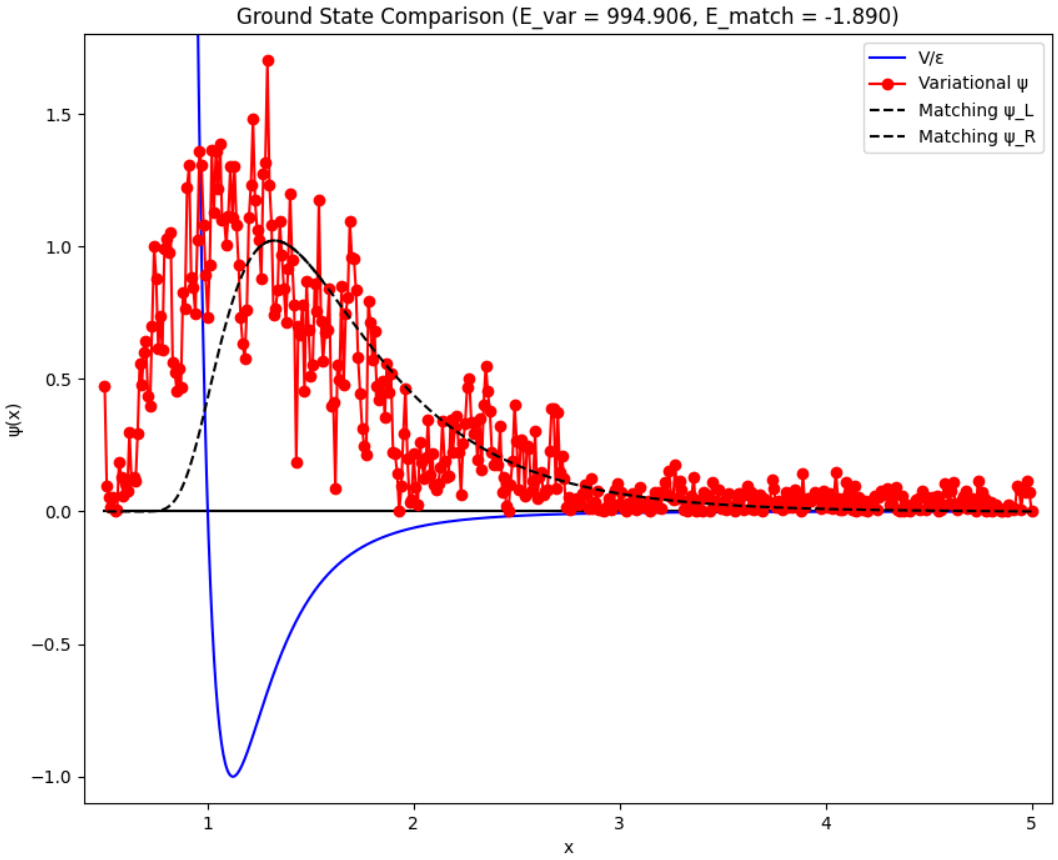


Figure 4: Comparison of ground state wavefunctions obtained using the matching method and the variational method. The blue line represents the scaled potential $V/\epsilon$, the black dashed lines represent the matching method wavefunctions $\psi_L$ and $\psi_R$, and the red line with dots represents the variational wavefunction $\psi$.