Variational Methods

Conor Sheehan

May 2024

1 Introduction

The Schrödinger equation is a fundamental equation in quantum mechanics that describes how the quantum state of a physical system changes over time. For many systems, especially those involving multiple particles, solving the Schrödinger equation analytically is infeasible due to its complexity. This is where numerical methods, such as the variational method, come into play.

1.1 What is the Variational Method?

The variational method is a powerful technique used to approximate the ground state energy of a quantum system. The core idea behind the variational method is the variational principle, which states that for any trial wavefunction Ψ_{Trial}, the expected value of the Hamiltonian (the energy operator) is always greater than or equal to the true ground state energy E_0. This functional (Function which takes a function as an argument) can be written as follows:

$$E_0 \leq \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \tag{1}$$

1.2 Variational Method Proof

The Variational method always produces a value greater than, or equal to the Exact ground state energy. It is only equal when the trial wavefunction matches the analytically correct wavefunction perfectly. Mathematically, we can prove that the energy of a trial wavefunction will always be greater than E_0:

We're going to start from the ground up, with our trial wavefunction ψ_T. Just to state some facts, we're assuming ψ_T is normalised, also also can be written as a sum of it's eigenvectors and their corresponding expansion coefficients:

$$\langle\psi_T|\psi_T\rangle = 1 \tag{2}$$

$$|\psi_T\rangle = \sum_{i=0}^{n} c_n|\phi_n\rangle \tag{3}$$

We can write the expectation value of the Hamiltonian, with respect to our trial wavefunction as:

$$E_T = \frac{\langle \psi_T | \hat{H} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} \tag{4}$$

We're not going to write the denominator from now on, as our trial wavefunction has been normalised to 1, as we stated in (2). I just put it in there so we could see that we're actually writing (1). Anyway, if we expand the trial wavefunctions in the numerator as a summation of their eigenstates as stated in (3) above:

$$E_T = \left\langle \sum_n c_n^* \phi_n^* | \hat{H} | \sum_m c_m | \phi_m \right\rangle \tag{5}$$

Rewriting (5) and also using orthogonality:

$$= \sum_n \sum_m c_n^* c_m \langle \phi_n^* | \hat{H} | \phi_m \rangle = \sum_n \sum_m c_n^* c_m \delta_{n,m} E_m \tag{6}$$

Where $\delta_{n,m}$ is the Kronecker delta, and is 0 except for $n = m$ i.e. orthogonality. So this summation is only non-zero for $n = m$. We can write (6) as:

$$= \sum_n |c_n|^2 E_n \tag{7}$$

which for all $n > 0$:

$$E_T = \sum_n |c_n|^2 E_n \geq \sum_n |c_n|^2 E_0 = E_0 \tag{8}$$

2 Trial Wavefuncion Parameter Optimization

So, our first problem to solve here. For a given potential, we want to use a trial wavefunction, and implement the Variational Method to optimise a parameter within that equation. This essentially requires the implementation of the FDM method we've used previously, to calculate the energy expectation value for a trial wavefunction. This must be done iteratively over a parameter range, with the minimum energy being the optimal value, as this is closest to the exact ground state energy. Algorithmically (making that word up by the way):

- Ensure that the Trial wavefunction is normalised.
- Discretize the x-axis. We're only going to use the 1 dimension, any more is a bit dramatic.
- Calculate the Energy expectation value:

$$\langle \psi_T | \hat{H} | \psi_T \rangle = \langle \psi_T | \hat{T} + \hat{V} | \psi_T \rangle \tag{9}$$

$$= \sum_{i=0}^{N} \left(-\frac{\hbar^2}{2m} \frac{2\psi_i - \psi_{i-1} - \psi_{i+1}}{\Delta x^2} + V(x_i) \right) \Delta x \tag{10}$$

- Alter the parameter within ψ you're investigating. Calculate E again, and so on, and so forth. The minimal value of E obtained gives the optimal value of the parameter is question.

2.1 Our Specific Scenario

We're going to use the following normalised wavefunction and the QHO potential $V(x) = \frac{1}{2}x^2\omega^2 m$:

$$\psi(x) = \left(\frac{2}{\pi x_0}\right)^{\frac{1}{4}} e^{-\left(\frac{x}{x_0}\right)^2} \tag{11}$$

We're going to be lazy, and set $\hbar$ & ω & m to 1. The variable we are to investigate is x_0. We're going to look at it in the interval $\in$ [0.5,2]. As we can

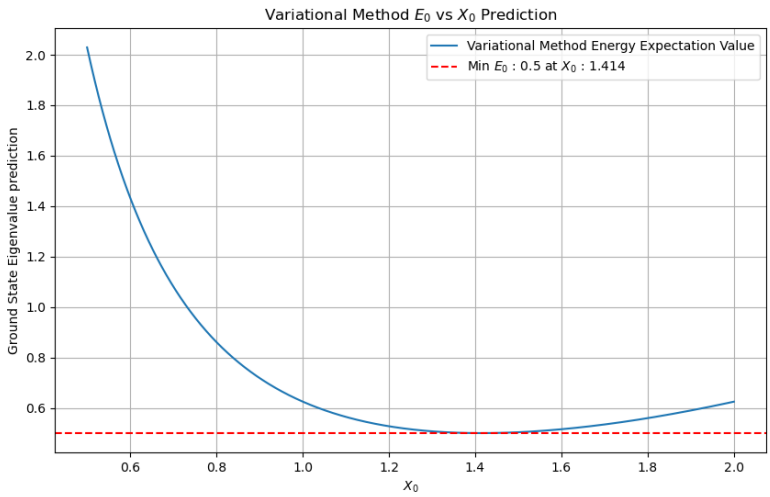


Figure 1: Variational Method Energy Expectation Value Result

see in the above figure, we find the optimal X_0 at 1.414, or $\sqrt{2}$. We know that our Variational method ha calculated the right Energies anyway, as we know from previous studies, that the Eigenvalues of the QHO are given by $\left(\frac{n+1}{2}\right)\hbar\omega$. We have set both those constants to 1, and as we're at $n = 0$, a value of 0.5 is exactly what we we're looking for.

This is a cool way to optimise parameters, but what if we could numerically calculate the value some other way? Not just picking the minimum of a graph? There is another way I am happy to announce to the world. You can breathe a sigh of relief. We are going to use a method called Gradient Descent, to be a bit more clever about picking our x_0 values.

2.2 Gradient Descent Approach

OK, so see how we simply iterated $x_0$in the Python Matplotlib graph in figure 1? Nothing wrong with this approach at all. But I just wanted to try this method as I think it's cool.

So the clue is in the name. Gradient Descent. We have some parameter we want to analyse in order to minimise some function value (in this case energy) and we want to slide down this graph until we get to that point. How do we do that? As follows:

- Evaluate $E(x)$ for some initial guess x_0
- Evaluate the Gradient at this point by the following formula: (which is just a dressed of version of the Cartesian slope formula)

$$gradient = \frac{f(x_0 + \epsilon) - f(x_0)}{\epsilon} \tag{12}$$

  Where ϵ is a very small value, of about 1E-5 for us.

- We then calculate the next point we want to check using this gradient, and a 'Learning Rate'

$$X_{i+1} = X_i - (LearningRate) * Gradient \tag{13}$$

  The negative sign above ensures that the new x value will 'swing' back around in case we overshoot the minimum. Learning Rate is a user input parameter, where I used 0.1. This parameter can be anything, but using a value too small, will take forever (slow learning), and using a value too large, you could end up 'yo-yoing' about either side of the minimum indefinitely if the tolerance isn't wide enough. Therefore, by reading around I found 0.1 to be a good compromise.

- We repeat the above steps, until $|x_i - x_{i-1}|$ is less than some tolerance.

See the Gradient Descent method in action there in figure 2. We can see our first guess at 0.5, and all subsequent iterations near the bottom of the graph, right where we want them. We we're also only about 0.009 off the 'true' value, and we only needed 49 iterations as opposed to the 1500 iterations I used firstly.

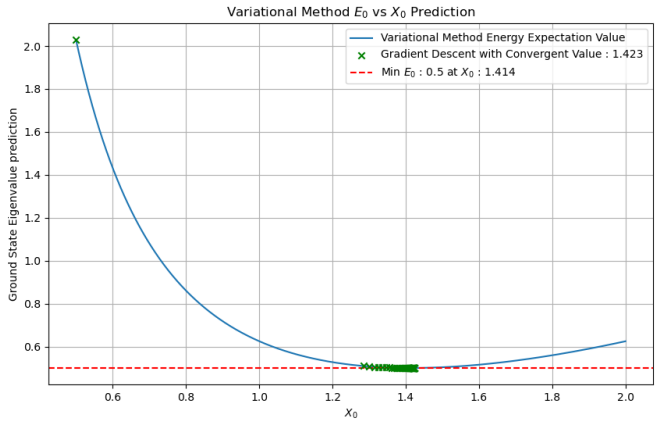


Figure 2: Variational Method Energy Expectation Value Result with Gradient Descent

To really drive home how this works (for me more than anything), in the above figure I've plotted the first 2 points in the Gradient Descent approach, with their gradients to give an idea visually of the method.

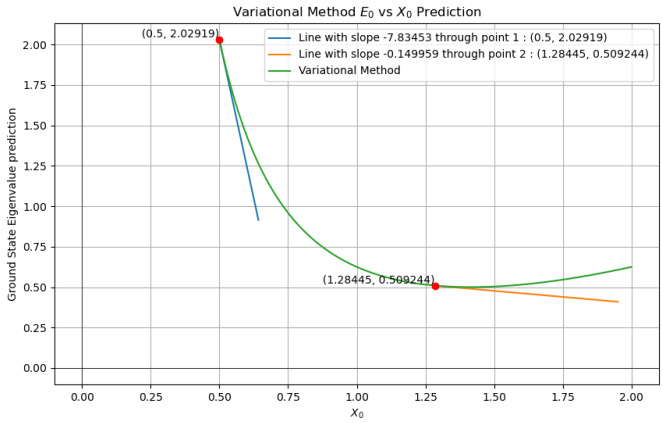


Figure 3: Gradient Descent Action shot

3 Wave Function Perturbation

In this section, we're going to go a bit wacky. What we want to do, is to try to get an exact wavefunction solution from an analytical one. What we are going

to do is as follows:

- Firstly, same as before, discretize the x axis.
- For our trial ψ calculate E using the FDM approach.
- For some random point on our trial ψ, perturb it by some small amount δ. Calculate the energy of this new wavefunction.
- If it is less than the previous energy, keep this updated ψ, as by the Variational Principle it is closer to the exact solution.
- If it isn't less, change the updated value back. Repeat this process until a final E_0 is found.

3.1 Our Specific Scenario

So for us now, we're going to move away from the QHO. We're going to look at the Leonnard Jones potential, which is as follows:

$$V(x) = 4\epsilon \left(\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6} \right) \tag{14}$$

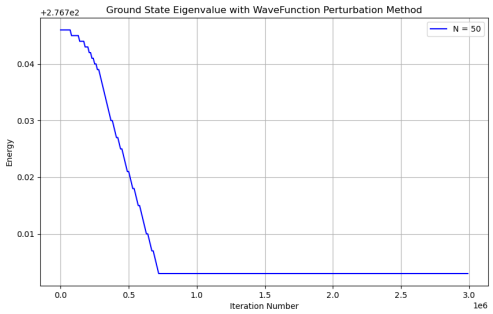
This equation models the Potential interaction between two non-bonding atoms, seperated by a distance x, ϵ is the well depth and a measure of how strongly the two particles attract each other, and σ is the distance at which the intermolecular potential between the two particles is zero.
Our trial wavefunction is going to be as follows:

$$\psi(x) = \left(\frac{32}{\pi x_0^6}\right)^{\frac{1}{4}} e^{-\frac{x}{x_0}^2} \tag{15}$$

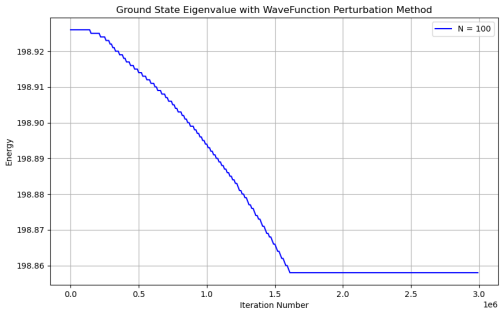
See below 3 consecutive graphs. One for a discretized x-axis with 50, 100 and 200 intervals respectively. The Energy seems to be inversely related, with less intervals converging to a higher energy, while also converging quicker. The higher energy, to me makes sense.

Mathematically, as you can see in (10) above, the calculation of the energy involves a summation of all elements in the calculated Hamiltonian vector, each of which is multiplied by Δx. Therefore, with smaller N, grid sizes get bigger, increasing the overall summation.

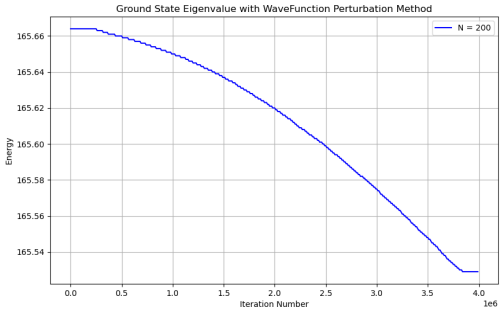
Also, intuitively, the Variational method produces a graph larger than the true analytical value. If there are less grid points, this approximation will be less accurate. Therefore increasing N and subsequently the accuracy makes sense to me.



(a) N = 50 called in Variational Method Constructor



(b) N = 100 called in Variational Method Constructor



(c) N = 200 called in Variational Method Constructor

Figure 4: Effect of discretization of x-axis on Wavefunction Perturbation & Variational Method approach

Overall however, the same affect can be seen in each graph. The Wavefunction is continuously modified and adapted, until a final baseline value is hit. This is the Variational method in full flow, being used to alter the Trial Wavefunction to a more accurate one.