1-Dimensional Particle in a Box

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1 Introduction

In the realm of quantum mechanics, the one-dimensional particle in a box serves as a fundamental and insightful model. Imagine confining a particle, such as an electron, within a one-dimensional region, often represented as a box. Within this boundary, the particle experiences no potential energy, akin to being free, while outside the box, the potential energy is infinite, effectively preventing the particle from escaping.

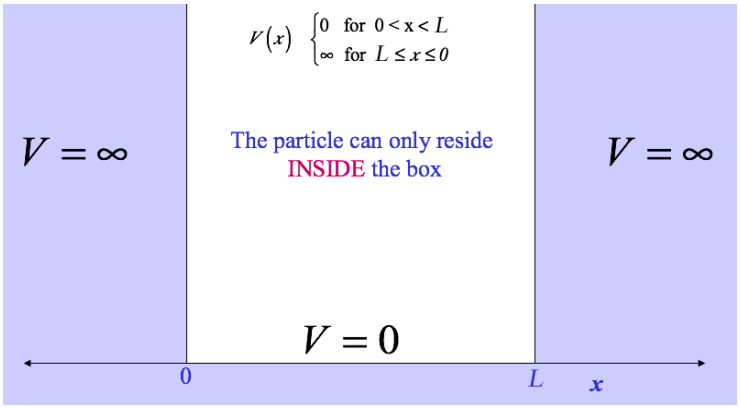

Figure 1: Our Particle in a box visualisation

2 Relevance

This simple yet profound model finds applications across various domains of physics and chemistry. Understanding the behavior of particles in constrained environments like this provides crucial insights into the principles governing quantum systems. Moreover, the particle in a box concept serves as a cornerstone in understanding more complex quantum phenomena, including molecular bonding, semiconductor physics, and the behavior of electrons in solid-state devices.

3 Solution

In order to obtain a solution for this conundrum, we first begin with the Schrodinger equation in (1) below. More specifically the time-independant version shown in (2) below.

$$\hat{H}\Psi = \hat{E}\Psi \tag{1}$$

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

We want to find a solution to the wavefunction Ψ here. Based on figure 1 and our own intuition, we know that Ψ must equal zero at $x = 0$ and L. We also know that V is 0 within these boundaries, as this is a free particle within the box.

This leaves us with the following second order differential equation seen below in (3).

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi = E\Psi \tag{3}$$

This ODE has been studied extensively, and has a general solution seen below in (4).

$$\Psi(x) = A.sin(kx) + B.cos(kx) \tag{4}$$

Using our boundary conditions, we figure out that B is 0 here. Therefore we're left with only the first term. We now need to determine both k, and the normalisation factor A. We'll go for k first. We know that at x = L Ψ must equal 0. See below:

$$0 = A.sin(kL) \tag{5}$$

Knowing that this only occurs when the argument of sin is $n\pi$ where $n \in N$ we know that k must be:

$$k = \frac{n\pi}{L} \tag{6}$$

Therefore we currently have:

$$\Psi(x) = A.sin(\frac{n\pi x}{L}) \tag{7}$$

Now for A. We know that Ψ must be square integrable over the interval, i.e. the particle must exist within our confines, therefore the following relationship is true:

$$\int_L^0 |\Psi(x)|^2 \, dx = 1 \tag{8}$$

Leaving us with:

$$A^2 \int_0^L sin^2(\frac{n\pi x}{L})dx = 1 \tag{9}$$

Using the double angle identity: $sin^2(x) = 1 - 2cos(2x)$ in (9), integrating, and applying limits leaves us with:

$$A = \sqrt{\frac{2}{L}} \tag{10}$$

Leaving us with our final wavefunction:

$$\Psi(x) = \sqrt{\frac{2}{L}} sin(\frac{n\pi x}{L}) \tag{11}$$

By subbing (11) into (3), we can calculate our Energy Eigenvalues to be given by:

$$E_n = \frac{h^2 n^2}{8mL^2} \tag{12}$$

4 Solution Graphs and Discussion

This project obtained graphs for the first 10 Eigenstates of a U-235 particle in a 1-D box. Below, the graphs for n *in* [1,5,10] can be seen. To be explicit, this is function (11). L of 200 Angstroms was used, and the mass of U-235 of 235AMU was used. I only used this as this is the fissile material used in Nuclear Reactors which I find really interesting.

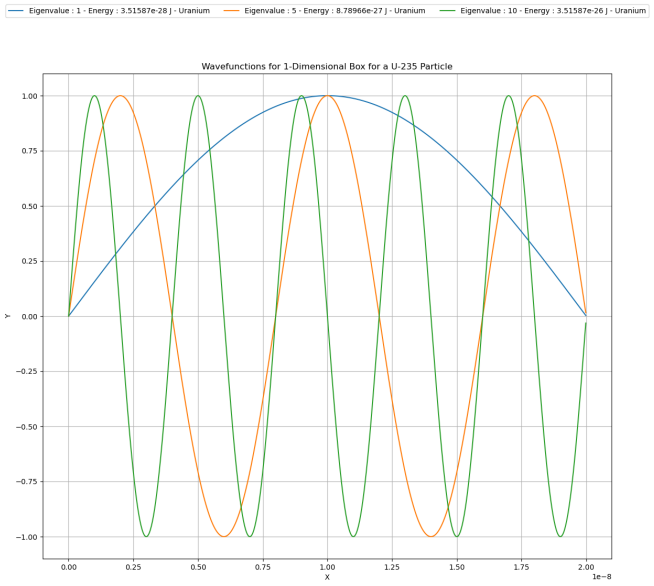

Figure 2: Eigenfunctions for U-235 n *in* [1,5,10]

Visually one can see the cycles of the Sine function, with π, 5π and 10π radians of the sine wave present within the box in each solution respectively. We can also see that the solution obeys the boundary conditions at the box walls also, with $\Psi = 0$ at both x=0 and x=L.

We also obtained plots for the Energy Eigenvalues for an Electron, Neutron, U-235, and Pu-239 (which is a beta decay daughter nucleus of U-235). The values from 1 to 30 inclusive can be seen below: I had initially plotted all 4 graphs

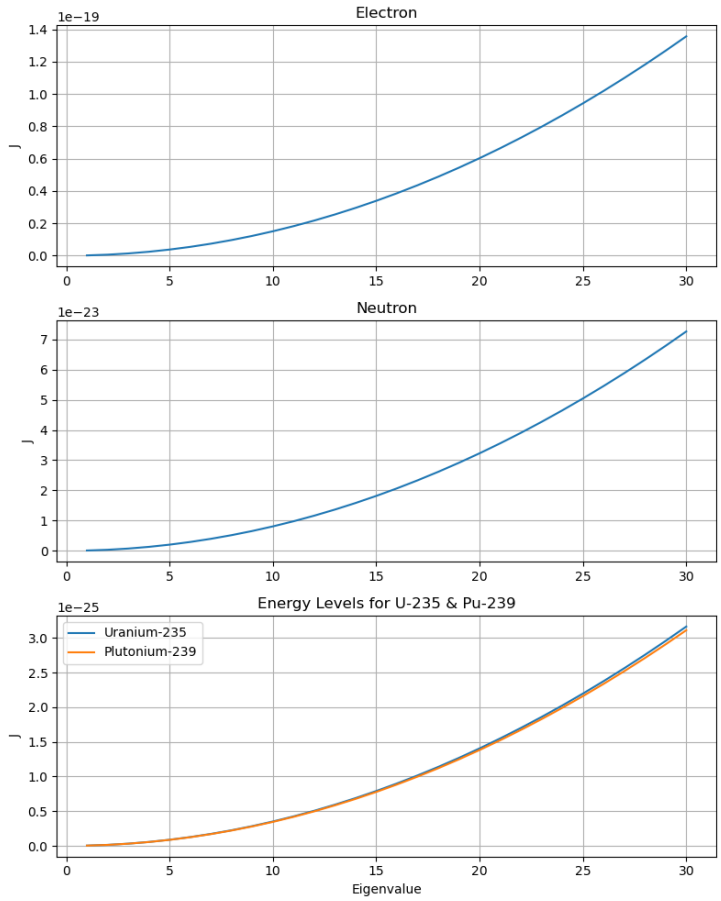

Figure 3: Energies for each particle for $\in$ [1,30]

on the same axes, but note the y axes for each. The energy of an electron far exceeds that of a neutron, and subsequently both Uranium and Plutonium in this example.
All 4 particles can be seen to follow the quadratic relationship between E and n. Remember the energies were given by:

$$E_n = \frac{h^2 n^2}{8mL^2} \tag{13}$$

The inverse relationship between mass and Energy can also be seen here. Given that Plutonium-239 has a larger Atomic Number than Uranium, it makes sense

that Pu has a slightly tapered graph at higher energy levels as can be seen below.

5 Monte Carlo Methods

For the final segment of this project, we will use Monte Carlo methods to estimate the ground state energy E_1 for Plutonium-239, as well as the expectation value for the position operator $\hat{x}$.

We will first look at the Energy calculation using Monte Carlo methods.

5.1 Ground State Energy calculation using Monte Carlo methods

Monte Carlo methods offer a computational approach for estimating energy levels of a particle in a one-dimensional box. By randomly sampling positions within the box according to the system's wavefunction, these methods enable the computation of average energy values. This approach provides an efficient alternative for estimating energy levels, particularly in cases where analytical solutions are challenging to obtain or computationally intensive to compute.

So lets get this show on the road and map out our method. We know that we have our wavefunction below:

$$\Psi(x) = \sqrt{\frac{2}{L}} sin(\frac{n\pi x}{L}) \tag{14}$$

We are going to calculate the Ground State energy E_1 for Pu-239. Therefore n = 1, m = m_{Pu239}, and we're going to set L = 200 Angstroms.

The Monte Carlo segment of this step, will involve sampling random points x_i for 0 <= x <= L, where the probability of a point being sampled is uniform for all points. At each point, we will calculate the Energy E_i. The energy at a given point is given below:

$$E_i = \hat{T}_i + \hat{V}_i \tag{15}$$

But, as we know V = 0 in this box. Therefore:

$$E_i = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x_i) = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \Psi(x_i) \tag{16}$$

So, we can calculate the energy per point. How does this let us calculate the entire energy I hear you think? We compute the average energy ⟨E⟩ of the system by averaging the total energies E_i over all sampled positions:

$$\langle E \rangle = \frac{1}{N}\sum_{i=1}^{N} E_i \tag{17}$$

So, we have a Pseudo Algorithm outlined.

- Randomly select N points x_i from $\in$ [0,L]
- Calculate the total Energy per point E_i using equation (16)
- Sum, and then average each energy, according to (17).
- Compare to the analytical value E_1, already calculated for the initial segment of this project.

5.1.1 Solution and Discussion

This section graphs both the Monte Carlo Estimation of the Eigen-Energies from 1 to 10, as well as the known Analytical Energies. Here we see that the

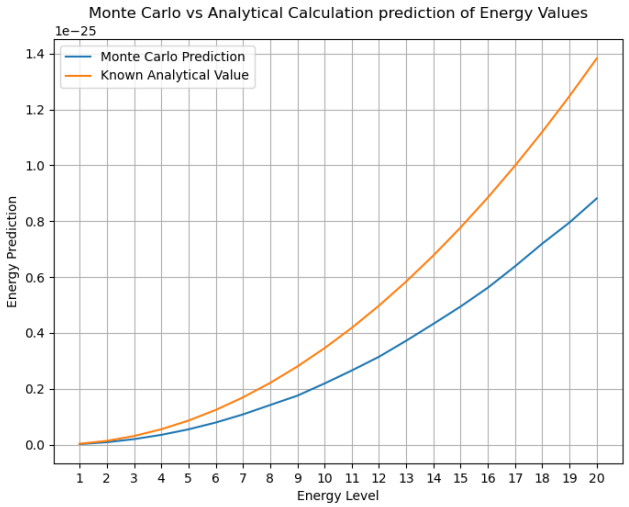

Figure 4: Comparison of Monte Carlo Energy Value per Energy Level against known analytical solution value

Monte Carlo estimation is quite accurate, of the correct order of magnitude at least! However, we can see that as we extend into higher energy levels this approximation method becomes more inaccurate. Not massively, but when we're dealing with energies as small as we have here, these errors matter.

The main reason for this I feel, stems from the wavefunction. In this case, it is a Sine wave. As we increase the n above, we add 1 π radian to the sine argument, meaning an extra half cycle in the region 0 to L. As we proceed, $\Psi(x)$ begins to rapidly oscillate. This will affect the sampling of the wavefunction that is critical to the Monte Carlo method.

As the graph changes rapidly, the finite number of samples we have, we'll get a less accurate representation of Ψ with our samples. This therefore affects the final averaged energy per eigenvalue.

5.2 Position Operator Expectation Value Calculations using Monte Carlo methods

So, we want to calculate the expectation value of the position operator $\hat{x}$. We'll first analytically calculate this, and then compare our Monte Carlo approximation. We're going to work with n=1 the ground state.

For n = 1, we have the wavefunction:

$$\Psi(x) = \sqrt{\frac{2}{L}} sin\left(\frac{\pi x}{L}\right) \tag{18}$$

The expectation value for an operator in QM is given by:

$$\langle \hat{x} \rangle = \frac{\langle \Psi | \hat{x} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{19}$$

For us, we know Ψ is square integrable, therefore the denominator is 1. The top can also be rewritten as an integral.

$$\langle \hat{x} \rangle = \int_0^L \hat{x} |\Psi(x)|^2 \tag{20}$$

Using (18), and that $\hat{x} = x$:

$$\langle \hat{x} \rangle = \frac{2}{L} \int_0^L sin^2\left(\frac{n\pi}{L}\right) \tag{21}$$

Using the double angle formula: $2sin^2(x) = 1 - 2cos(2x)$ and subsequently integrating by parts, and applying limits we are left with:

$$\langle \hat{x} \rangle = \frac{L}{2} \tag{22}$$

Which surprise, in our case will be 100 Angstroms. Even looking at figure 2 we should have predicted this visually anyway. So, using Monte Carlo how will we do this? Were going to start with equation (21) above. To rewrite this for Monte Carlo Integration, we'll first take a quick look at the logic behind Monte Carlo integration.

Say we have a function $f(x) = -x^3 + 6x^2 - x + 17$. Say we want to approximate this integral between 2, and 5. Analytically we could integrate this area, see below: However, we wish to take a different approach. The idea behind

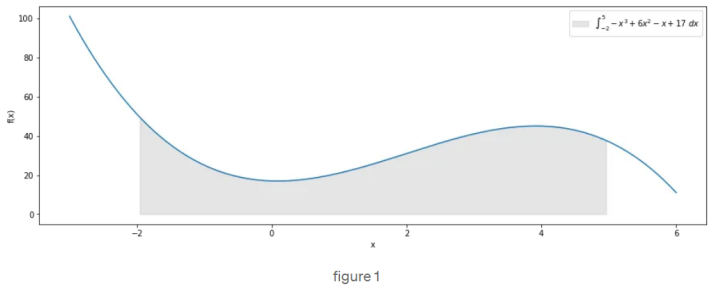

Figure 5: Analytical Integral of example function

Monte Carlo integration is to take N random x_i, within the integral limits, and calculate the rectangle area $f(x_i) * (b - a)$.

$$\langle f \rangle = (b-a)\frac{1}{N-1}\sum_{i=0}^{N} f(x_i) \tag{23}$$

Then, the average rectangle area will approximate to the definite integral, for sufficiently large N. See below: Now, finally applying equation (23) to equation

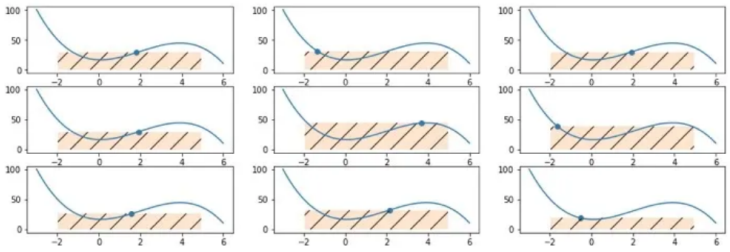

Figure 6: Monte Carlo Integral of example function

(21), we must calculate the value for n = 1:

$$\langle \hat{x} \rangle = \frac{2}{L}\frac{L}{N-1}\sum_{i=1}^{N} x_i \left| sin\left(\frac{n\pi}{L}\right)\right|^2 = \frac{2}{N-1}\sum_{i=1}^{N} x_i \left| sin\left(\frac{n\pi}{L}\right)\right|^2 \tag{24}$$

Therefore, we have a pseudo-algorithm:

- Firstly, calculate a uniform distribution of N points x_i within $0 < x < L$, similarly to before.
- At each random point, the RHS of (23) can be evaluated. These can be totalled into a sum.
- This sum can then be divided by N-1, the number of points to give us hopefully, L/2

Enough babbling, lets get to it.

5.3 Result and Discussion

Rejoice, I finally fixed the program. I had been out by a factor of a half for ages, until I rechecked the maths of Eq. (23) and realised I had ignored the 2 from Ψ's normalization factor. For N = 10,000, and an L of 200 Angstrom's, we have an expected position of 100.06 Angstroms, approximately 0.500See below for proof in case you don't believe me...

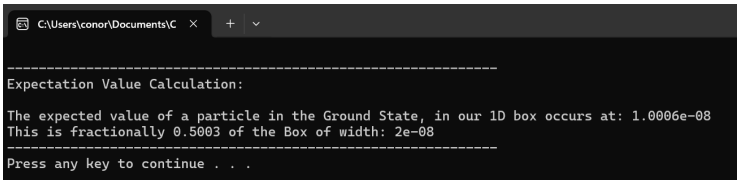

Figure 7: Monte Carlo prediction for expectation value of position operator $\langle \hat{x} \rangle$