

Identical Particle Interaction using Perturbation Theory

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Abstract

We present numerically exact solutions for the time-independent Schrödinger equation of a system of two identical fermions confined in an infinite potential well that have the same charge and repel each other. First, a method of finite differences is employed to solve the system of 2 identical fermions that don't interact with each other to plot the wavefunction and probability density curves. Next, perturbation theory is applied to find the correction to the energies and wavefunctions in order to account for potential due to the repulsion between the two electrons in addition to the infinite potential well. We find that the wavefunction for the 2 electrons after applying the perturbation is distinctively different from that of the unperturbed system and hence conclude that the repulsion between 2 electrons in any system is not negligible and should be accounted for.

Keywords: Perturbation theory, Fermions, coulombic repulsion, Schrödinger Equation, Python, Computation, Identical particles, finite difference

Introduction

In quantum mechanics, perturbation theory is a set of approximation schemes directly related to mathematical perturbation for describing a complicated quantum system in terms of a simpler one. The idea is to start with a simple system for which a mathematical solution is known, and add an additional perturbing Hamiltonian representing a weak disturbance to the system. If the disturbance is not too large, the various physical quantities associated with the perturbed system (e.g. its energy levels and eigenstates) can be expressed as "corrections" to those of the simple system. These corrections, being small compared to the size of the quantities themselves, can be calculated using approximate methods. In this project, we solve the time independent Schrodinger's equation for a system of two identical fermions inside an infinite potential well for two cases: 1) non interacting fermions (no perturbation) and 2) interacting fermions (perturbed). For both these cases, the wavefunction and probability density curves are computationally obtained using Python and the energy correction terms are calculated for the different energy levels of the two particles.

Theory

Method of Finite Differences

A three-point finite difference method for solving second order differential equations is used in our project. The finite difference method is a way of approximating the derivatives with finite differences to solve differential equations.

For the method of finite differences, the range of integration $[a,b]$ is divided into m sub-intervals of length h each. The values of the numerical solution at these mesh points are denoted by y_i , $i = 0, 1, 2, \dots, m$.

Two approximations are made:

$$i) \quad y_i' = \frac{y_{i+1} - y_{i-1}}{2h} \text{ and } y_i'' = \frac{y_{i-1} - 2y_i + y_{i+1}}{h^2}$$

ii) The differential equations are only enforced at the mesh points.

Consider the second order differential equation:

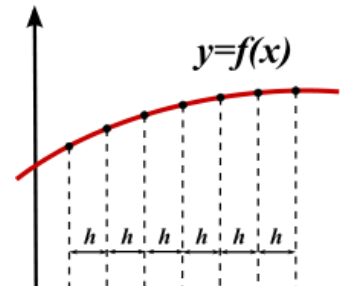


Figure 1. Discretization of space

$x_0 \ x_1 \ x_2 \ x_3 \ x_4 \ x_5 \ x_6$

$$y'' = f(x, y, y')$$

with boundary conditions $y(a) = \alpha$ and $y(b) = \beta$

Approximating the derivatives at the mesh points, the problem becomes,

$$\frac{y_{i-1} - 2y_i + y_{i+1}}{h^2} = f(x_i, y_i, \frac{y_{i+1} - y_{i-1}}{2h})$$

$$y_0 = \alpha$$

$$y_m = \alpha$$

Now, the Schrödinger's equation in 1-dimension is given by,

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

By using the finite difference approximation for this second order differential equation, we get

$$\frac{-\hbar^2}{2m} \psi_i'' + V_j \psi_i = E \psi_i$$

For $i = 0, 1, 2, \dots, m$.

$$\frac{-\hbar^2}{2m} \left[\frac{\psi_{i-1} - 2\psi_i + \psi_{i+1}}{h^2} \right] + V_j \psi_i = E \psi_i$$

Now, the particle is confined in the region $[a, b]$, therefore,

$$y_0 = 0$$

$$y_m = 0$$

The discretized Schrödinger's equation can now be written in a matrix form to obtain a system of linear equations given by,

$$\frac{-\hbar^2}{2m} \begin{bmatrix} -2 & 1 & 0 & 0 & 0 & 0 & \dots & m \\ 1 & -2 & 1 & 0 & 0 & 0 & \dots & m \\ 0 & 1 & -2 & 1 & 0 & 0 & \dots & m \\ 0 & 0 & 1 & -2 & 1 & 0 & \dots & m \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_{m-1} \end{bmatrix} + \begin{bmatrix} V_1 & 0 & 0 & 0 & 0 & 0 & \dots & 0 \\ 0 & V_2 & 0 & 0 & 0 & 0 & \dots & 0 \\ 0 & 0 & V_3 & 0 & 0 & 0 & \dots & 0 \\ 0 & 0 & 0 & V_4 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{m-1} \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_{m-1} \end{bmatrix} = E \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_{m-1} \end{bmatrix}$$

$$\frac{-\hbar^2}{2m} \begin{bmatrix} -2 + V_1 & 1 & 0 & 0 & 0 & 0 & \dots & m \\ 1 & -2 + V_2 & 0 & 0 & 0 & 0 & \dots & m \\ 0 & 1 & -2 + V_3 & 1 & 0 & 0 & \dots & m \\ 0 & 0 & 1 & -2 + V_4 & 1 & 0 & \dots & m \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 + V_{m-1} \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_{m-1} \end{bmatrix} = E \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_{m-1} \end{bmatrix}$$

$$H\psi = E\psi$$

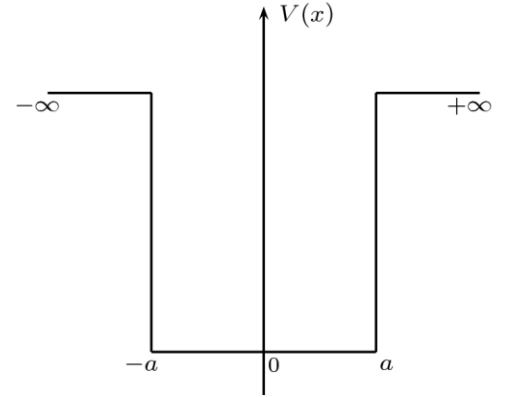


Figure 2. Infinite Potential Well

This is now an Eigenvalue problem that can be solved easily to find the eigenfunctions and their corresponding eigenvalues. This method proves to be extremely useful for finding the eigenfunctions and eigenvalues numerically.

Infinite Potential Well

The potential is given by:

$$\begin{aligned} V(x) &= 0 & \text{if } -W < x < W \\ V(x) &= \infty & \text{if } x > W \text{ and } x < -W \end{aligned}$$

The particle is bounded in a well and cannot escape it as it would need an energy of more than $V(x)$ which at the boundaries is $\pm \infty$, therefore,

$$\psi(-W) = 0 \quad \text{and} \quad \psi(W) = 0$$

The general solution of this Schrodinger's Equation for a particle confined in an infinite potential well is given by,

$$\psi_n = \sqrt{\frac{2}{A}} \cos \frac{n\pi x}{A} \quad n = 1, 3, 5, \dots$$

----- (1)

Figure 3. Infinite Well

$$\psi_n = \sqrt{\frac{2}{A}} \sin \frac{n\pi x}{A} \quad n = 2, 4, 6, \dots$$

----- (2)

The energy of the particle is given by:

$$E = \frac{n^2 h^2}{8mA^2} \quad n = 1, 2, 3, \dots$$

----- (3)

2-Particle System (Identical Particles)

For a single particle system, we take $\Psi(r, t)$, where r represents the spatial coordinate of the particle and t is the time. But when we have a system of 2-particles, we need to take the coordinates of both the particles into consideration, and hence, the function becomes:

$$\Psi(r_1, r_2, t)$$

Where r_1 is the spatial coordinate of particle-1, and r_2 is the spatial coordinate of particle-2.

As we take the case of free-particles, $V = 0$, hence, the Schrodinger equation becomes:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

----- (4)

where H is the Hamiltonian of the whole thing and can be represented as:

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r_1, r_2, t)$$

Where ∇ is the Laplacian operator, and,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \text{----- (5)}$$

As we know that the equation should be normalized, hence,

$$\int |\Psi(r_1, r_2, t)|^2 d^3r_1 d^3r_2 = 1 \quad \text{----- (6)}$$

We can represent the relation between time-dependent spatial wave function with time-independent spatial wave function as:

$$\Psi(r_1, r_2, t) = \psi(r_1, r_2) e^{-\frac{iEt}{\hbar}} \quad \text{----- (7)}$$

And this spatial wave function satisfies the TISE:

$$\frac{-\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi \quad \text{----- (8)}$$

And E is the total energy.

Solving this TISE (eqⁿ 8) is difficult and can be further divided into two cases:

Case 1: Non-Interacting Particles

In this case, the two particles are not interacting with each other but are subjected to some external form. In this case, the potential energy is the sum of the individual potential energies of the two particles.

$$V(r_1, r_2) = V(r_1) + V(r_2) \quad \text{----- (9)}$$

And equation 8, can be solved using the separation of variables:

$$\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) \quad \text{----- (10)}$$

(ψ_a and ψ_b are basically states of particle 1 and 2 respectively)

Plugging equation 10 in equation 8, and solving the equation in such a way that we get r_1 and r_2 separately, and then finding $\psi_a(r_1)$ and $\psi_b(r_2)$, which basically satisfies the one-particle Schrodinger equation:

$$\frac{-\hbar^2}{2m_1} \nabla_1^2 \psi_a(r_1) + V_1(r_1)\psi_a(r_1) = E_a(r_1)\psi_a(r_1) \quad \text{----- (11)}$$

$$\frac{-\hbar^2}{2m_2} \nabla_2^2 \psi_b(r_2) + V_2(r_2)\psi_b(r_2) = E_b(r_2)\psi_b(r_2) \quad \text{----- (12)}$$

And, total energy, $E = E_a + E_b$, hence, we can move ahead and write that,

$$\Psi(r_1, r_2, t) = \psi_a(r_1)\psi_b(r_2)e^{-\frac{i(E_a+E_b)t}{\hbar}} \text{----- (13)}$$

$$\Psi(r_1, r_2, t) = (\psi_a(r_1)e^{-\frac{iE_a t}{\hbar}})(\psi_b(r_2)e^{-\frac{iE_b t}{\hbar}}) = \psi_a(r_1, t)\psi_b(r_2, t) \text{----- (14)}$$

Any linear combination of these solutions would satisfy the time-dependent Schrodinger's Equation.

Case 2: Interacting Particles with a Central Potential

In this case, the two particles are interacting with a potential that depends on their distance of separation, i.e.,

$$V(r_1, r_2) \rightarrow V(|r_1 - r_2|) \text{----- (15)}$$

This potential can be anything, in our project we take the Coulomb's Potential here, i.e.,

$$V = \frac{-e^2}{4\pi\epsilon_0 r}$$

Now analysis of such an interaction is not as easy as what we had done before, because not only an external force is present, there is a mutual interaction. For example, in an helium atom, there are two electrons and they feel the Coulomb's force of attraction towards the nucleus (with a charge of $2e$) while repelling each other. Here,

$$V(r_1, r_2) = \frac{1}{4\pi\epsilon_0} \left(-\frac{2e^2}{|r_1|} - \frac{2e^2}{|r_1|} + \frac{e^2}{|r_1 - r_2|} \right) \text{----- (16)}$$

To solve such a complicated equation, we need to know some more things, whether the particles are distinguishable or identical. Hence, we'll first look at that case and leave this equation here as it is.

Fermions

In quantum mechanics, it is very difficult to distinguish between two particles, for example,

$$\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2)$$

We can say that one particle is in the state $\psi_a(r_1)$ and the other is in the state $\psi_b(r_2)$ but we cannot say explicitly that out of the two, which exact particle is in this exact state. So, to be able to successfully do so, we construct a wave function, and this helps in distinguishing between two almost identical particles: bosons (eg: photons and mesons) and fermions (eg: protons and electrons) by just looking at the signs of the wave function.

$$\psi_{\pm}(r_1, r_2) = A[\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)] \text{----- (17)}$$

Here, bosons, particles with *integer* spins, are represented using a *plus* sign. Whereas, fermions, particles with *half-integer* spins, are represented using a *minus* sign.

There is a very special principle called, ***Pauli's exclusion principle***, which states that no two identical fermions can occupy the same state.

This principle can be verified by taking an example, let's have two identical fermions, and let them occupy the same state, i.e., $\psi_a = \psi_b$.

Plugging these values in equation 17,

$$\psi_-(r_1, r_2) = A[\psi_a(r_1)\psi_a(r_2) - \psi_a(r_1)\psi_a(r_2)] = 0$$

This says that no wave function exists for such a case, hence, verifying Pauli's exclusion principle.

Now, let's define a new term, ***exchange operator***, P , which interchanges two particles (one in state ψ_a and the other in state ψ_b). $Pf(r_1, r_2) = f(r_2, r_1)$.

We do know that, $P^2 = 1$ and the eigenvalues of P are ± 1 . Now, if the two particles are identical, $m_1 = m_2$ and $V(r_1, r_2) = V(r_2, r_1)$, this shows that P and H (which is the Hamiltonian) are compatible observables, i.e.,

$$[P, H] = 0$$

Hence, we can find solutions to the Schrodinger's Equation that are either *symmetric* (eigenvalue = + 1) or *antisymmetric* (eigenvalue = -1) under exchange:

$$\psi(r_1, r_2) = \pm \psi(r_2, r_1) \quad \text{----- (18)}$$

A new law is stated, ***symmetrization requirement***, it states that for identical particles, the wave function is not merely allowed, but is required to satisfy equation 18, with a *plus* sign for *bosons*, and a *minus* sign for *fermions*. Equation 17 is a special case for this general statement.

Exchange Forces

Now, we come back to our original problem. Let's state the basic things we discussed before: there are two particles, one in state ψ_a and the other in state ψ_b . Let us say that these are orthogonal and normalized. If these two particles are distinguishable, then we can combine the wave functions as so:

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) \quad \text{----- (19)}$$

If they are identical bosons, we get the normalized wavefunction as:

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)] \quad \text{----- (20)}$$

(we get $A = \frac{1}{\sqrt{2}}$ as the normalization constant when we normalize the equation)

Similarly, for two identical fermions, we get:

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)] \quad \text{----- (21)}$$

The expectation value of the distance of separation between the two particles is $\langle x_1 - x_2 \rangle$.

We calculate the expectation value of the square of the distance of separation:

$$\langle (x_1 - x_2)^2 \rangle = \langle (x_1)^2 \rangle + \langle (x_2)^2 \rangle - 2\langle x_1 x_2 \rangle \quad \text{----- (22)}$$

Case 1: Distinguishable Particles: With respect to the wavefunction in equation 19,

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a$$

And,

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b$$

As a result,

$$\langle x_1 x_2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b$$

Finally, we get,

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \quad \text{----- (23)}$$

Case 2: Identical Particles: With respect to the wavefunction in equation 20 and 21,

$$\begin{aligned} \langle x_1^2 \rangle &= \frac{1}{2} \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \\ &\quad \pm \int x_1^2 \psi_a(x_1) * \psi_b(x_1) dx_1 \int \psi_b(x_2) * \psi_a(x_2) dx_2 \\ &\quad \pm \int x_1^2 \psi_b(x_1) * \psi_a(x_1) dx_1 \int \psi_a(x_2) * \psi_b(x_2) dx_2 \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b] \end{aligned}$$

Similarly,

$$\langle x_2^2 \rangle = \frac{1}{2} [\langle x^2 \rangle_b + \langle x^2 \rangle_a]$$

As we can see, $\langle x_1^2 \rangle = \langle x_2^2 \rangle$, *surprising?* Well, **NO**, because the two particles are identical.

$$\begin{aligned}
\langle x_1 x_2 \rangle &= \frac{1}{2} \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \\
&\quad \pm \int x_1 \psi_a(x_1) * \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2) * \psi_a(x_2) dx_2 \\
&\quad \pm \int x_1 \psi_b(x_1) * \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2) * \psi_b(x_2) dx_2 \\
&= \frac{1}{2} [\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}] = \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2
\end{aligned}$$

$$\text{Where, } \langle x \rangle_{ab} = \int x \psi_a(x) * \psi_b(x) dx \quad \text{----- (24)}$$

Finally,

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2 \quad \text{----- (25)}$$

If we see the difference between equation 23 and equation 25, we get,

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 |\langle x \rangle_{ab}|^2 \quad \text{----- (26)}$$

Perturbation Theory (Non-Degenerate)

Perturbation theory is a set of approximation schemes comprising of mathematical methods to find an approximate solution to a problem for describing a system. The basic idea is that we first consider a system which is simple enough for which we already know the mathematical solution. Then we add a perturbing representing a weak disturbance to the system. Depending on the disturbance and the different physical quantities that are associated to the perturbed system it can be expressed as corrections to those systems.

So, generally we can formulate this as follows:

Suppose we solve the TISE for some potential and obtain a set of orthonormal eigenfunctions ψ_n^0 and corresponding eigenvalues E_n^0 .

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \quad \text{----- (27)}$$

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad \text{----- (28)}$$

This is the problem that we are well familiar with, and this case is called **unperturbed** (take Figure 1 for example, infinite potential well).

Now, what happens we slightly disturb the system, i.e., perturb the potential. The Hamiltonian changes

$$H = H^0 + \lambda H' \quad \text{----- (29)}$$

Where, H is the total Hamiltonian, H^0 is the Hamiltonian for unperturbed case, and H' is the extra change that we get when perturbation is done. λ is a small parameter.

So, now we have a new equation:

$$H\psi_n = E\psi_n \quad \text{----- (30)}$$

We solve this equation using equation 27, the solution of which we already know.

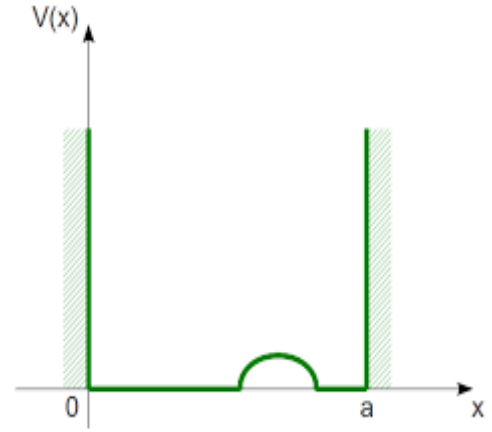


Figure 3. Infinite potential well with perturbation

Here, this point is to be stressed that H' is small compared to H . The eigenstates and eigenvalues of H do not differ much from H^0 .

Taking Taylor Series as a reference, we can expand the solution of perturbation H' ,

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \dots$$

And,

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

The first-order correction to the energy is given by:

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle \quad \text{----- (31)}$$

First-order correction to the wave function is given by:

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0 \quad \text{----- (32)}$$

If we think about it, two non-interacting particles in an infinite potential well is basically an example of an *unperturbed* system, whereas when these two particles interact, there is a shift in the potential, in a way, their mutual interaction cause *perturbation*.

We have covered the background of all, but now let's focus on the main problem, *how to analytically solve a Schrodinger's equation for 2 particles in an infinite potential well, for both cases, interacting and non-interacting?*

The entire next section is going to cover that.

Analytical solution for 2 Particles in an Infinite Potential Well

Now, we have two particles in an infinite potential well. We again have two possible conditions, interacting and non-interacting.

Case 1: Non-Interacting

We know that for one particle in an infinite potential well, the wavefunction is represented as:

$$\psi_n(a) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad \text{----- (33)}$$

$$\text{And, } E_n = n^2 \left[\frac{\pi^2 \hbar^2}{2ma^2} \right] = n^2 K \quad \text{where } K = \left[\frac{\pi^2 \hbar^2}{2ma^2} \right]$$

Now, we derived this before, when we have 2 particles,

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$$

$$\text{And,} \quad E = E_a + E_b$$

For *distinguishable* particles,

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2) = \frac{2}{a} \sin\left(\frac{n_1 \pi x_1}{a}\right) \sin\left(\frac{n_2 \pi x_2}{a}\right)$$

$$\text{And,} \quad E_{n_1 n_2} = (n_1^2 + n_2^2)K$$

For *identical bosons*,

$$\psi_{n_1 n_2}(x_1, x_2) = A \left(\frac{2}{a} \sin\left(\frac{n_1 \pi x_1}{a}\right) \sin\left(\frac{n_2 \pi x_2}{a}\right) + \frac{2}{a} \sin\left(\frac{n_1 \pi x_2}{a}\right) \sin\left(\frac{n_2 \pi x_1}{a}\right) \right)$$

For *identical fermions*,

$$\psi_{n_1 n_2}(x_1, x_2) = A \left(\frac{2}{a} \sin\left(\frac{n_1 \pi x_1}{a}\right) \sin\left(\frac{n_2 \pi x_2}{a}\right) - \frac{2}{a} \sin\left(\frac{n_1 \pi x_2}{a}\right) \sin\left(\frac{n_2 \pi x_1}{a}\right) \right)$$

Case 2: Interacting

Now, when the two particles interact with each other, the potential is slightly moved up or down. For example, in a Helium atom, the two electrons are attracted towards the nucleus, but there is also another form of interaction present, the electron repel each other. This mutual interaction

causes a disturbance in the potential; hence, perturbation occurs. Here, potential disturbance is equal to the Coulombic potential between two electrons, i.e,

$$H' = V = \frac{-e^2}{4\pi\epsilon_0 r}$$

So, our Hamiltonian changes as such, $H = H^0 + H'$

We use the unperturbed case (when there was so such interaction) to help find the change in the value of H and ψ , as it was discussed before.

The first-order correction to the energy is given by:

$$E_n^1 = \langle \psi_m^0 | H' | \psi_n^0 \rangle \quad \text{----- (31)}$$

First-order correction to the wave function is given by:

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0 \quad \text{----- (32)}$$

$$E = E^0 + E'$$

$$\psi = \psi^0 + \psi'$$

This corrected value of ψ is then put in the equation, as we did to solve the non-interacting case just before this.

Results and Discussion

Non-interacting fermions

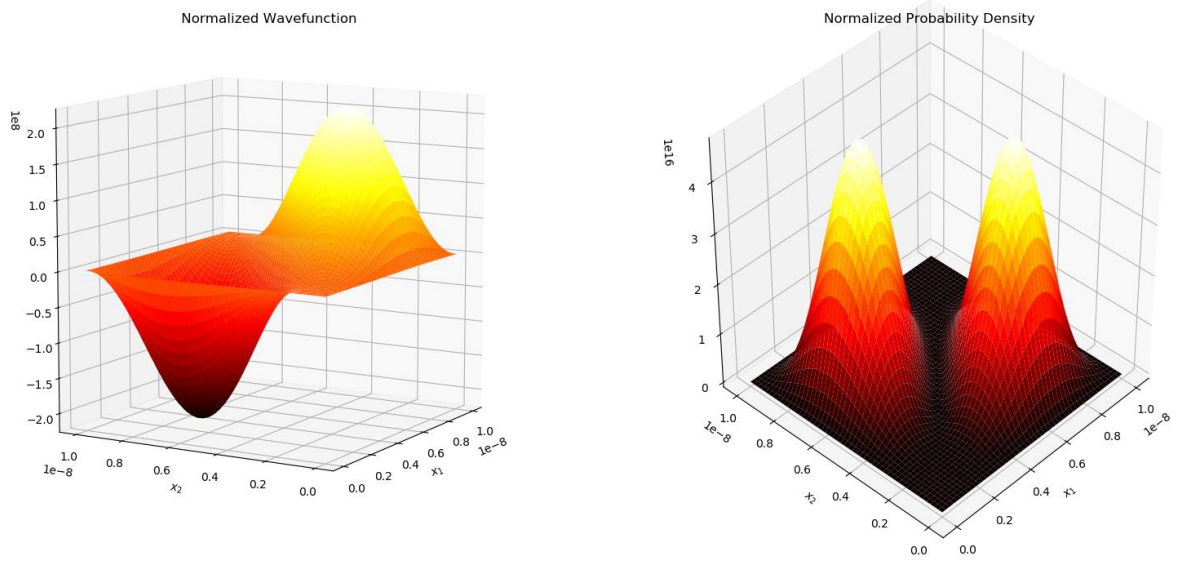


Figure 5. Identical fermions (parallel spins) in ground state in an infinite potential well.

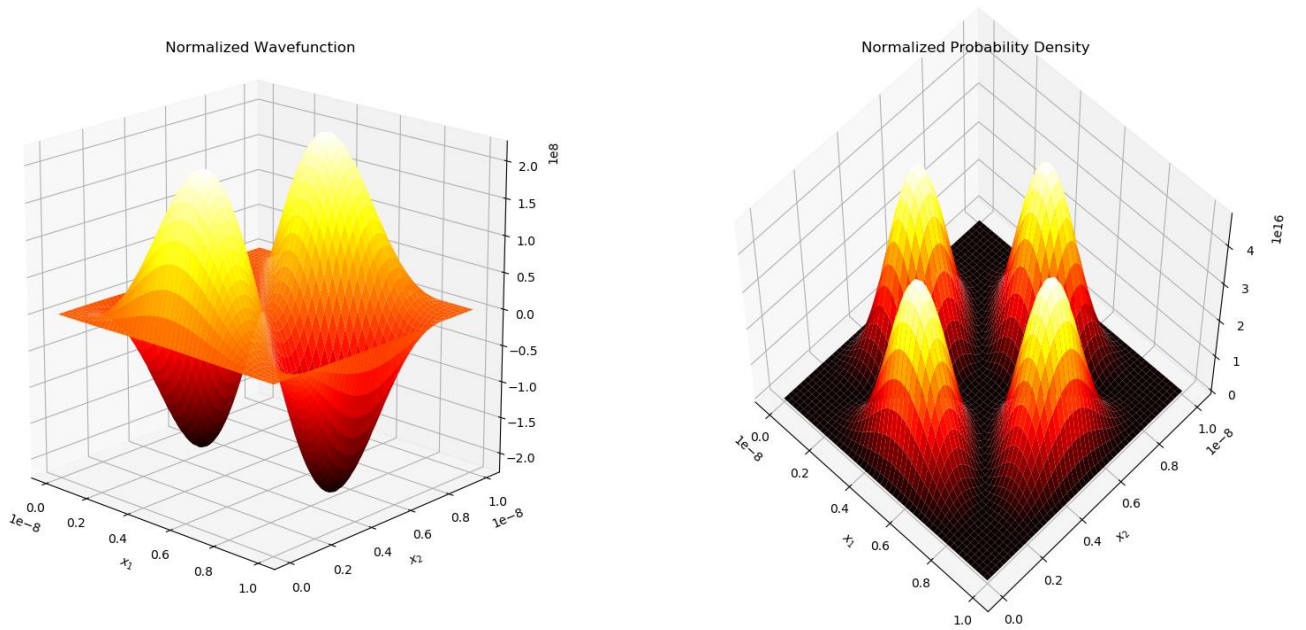


Figure 4. Identical fermions (parallel spins) in first excited state in infinite potential well

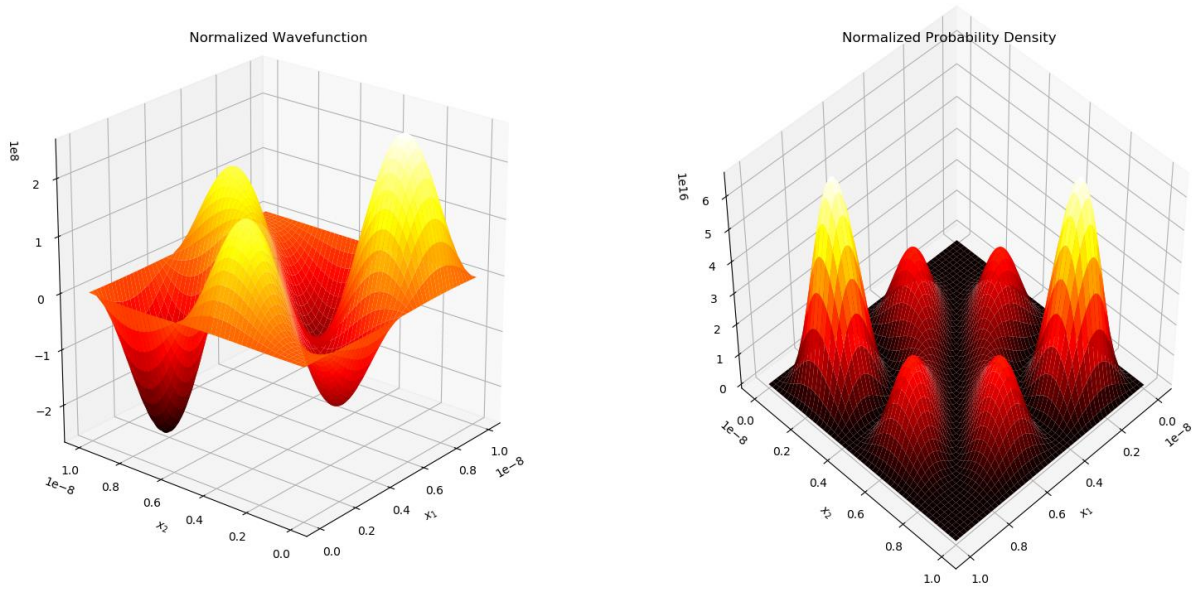


Figure 6. Identical fermions (parallel spin) in second excited state in infinite potential well.

In the ground state of the 2-particle system of identical fermions, we see that there is a line of 0 probability $x_1 = x_2$, i.e., the probability of finding both particles in the same position is 0 owing to the fact that the particles have parallel spins. In the first excited state, there is a nodal line (line of 0 probability) $x_2 = W - x_1$ (where W is the well width) in addition to the nodal line $x_1 = x_2$. Thus, the probability of finding both the particles simultaneously in the coordinates along these lines will be 0. In the second excited state, there are two nodal *curves* in addition to the nodal line $x_1 = x_2$.

$$\psi_{n_1 n_2}(x_1, x_2) = [\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_2}(x_1)\psi_{n_1}(x_2)]$$

This is the equation for the combined wavefunction of 2 indistinguishable fermions. It is then obvious that the 2 electrons cannot have the same value of n_1 and n_2 . Thus, the ground state of such a system is actually $(n_1, n_2) = (1, 2)$ followed by $(1, 3)$ and $(2, 3)$ in that order.

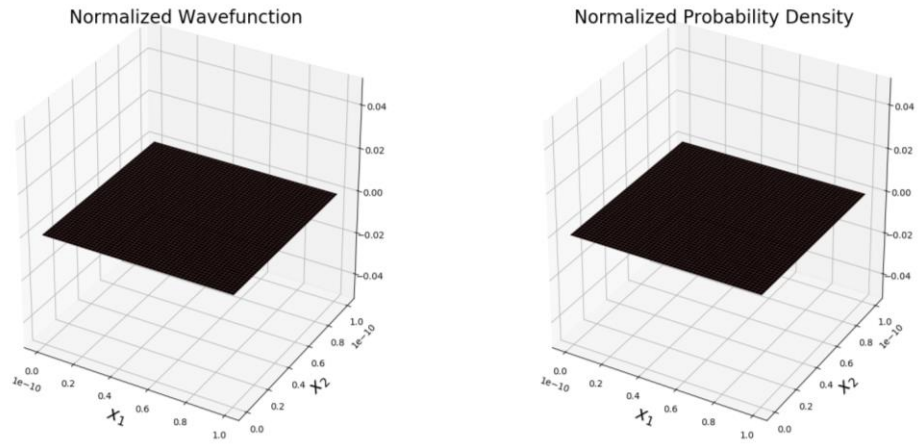


Figure 7. $\psi_{n_1 n_2}(x_1, x_2)$ when $n_1 = n_2$. The wavefunction and probability density curve is 0.

Interacting Fermions

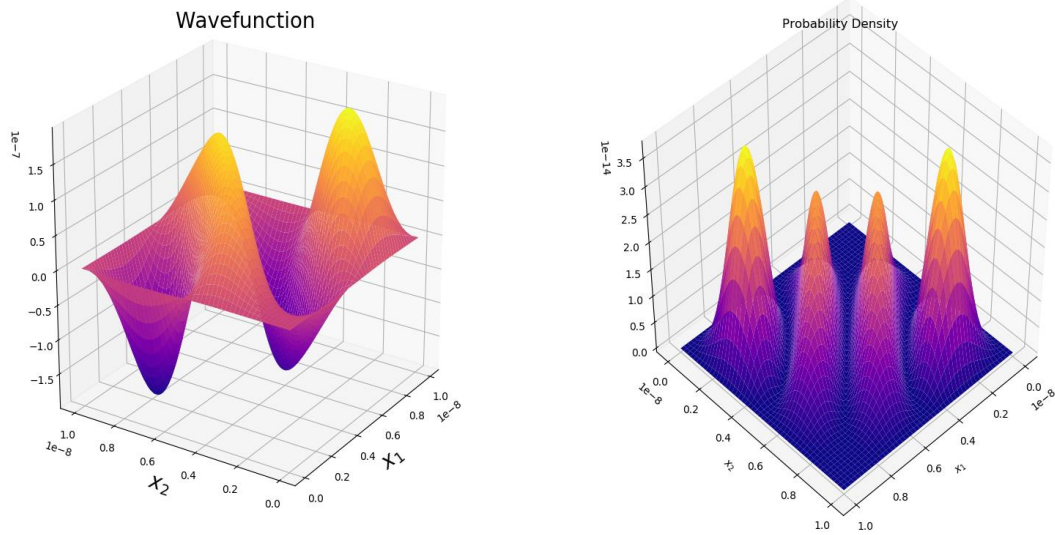


Figure 8. Interacting identical fermions (parallel spin) in ground state in an infinite well.

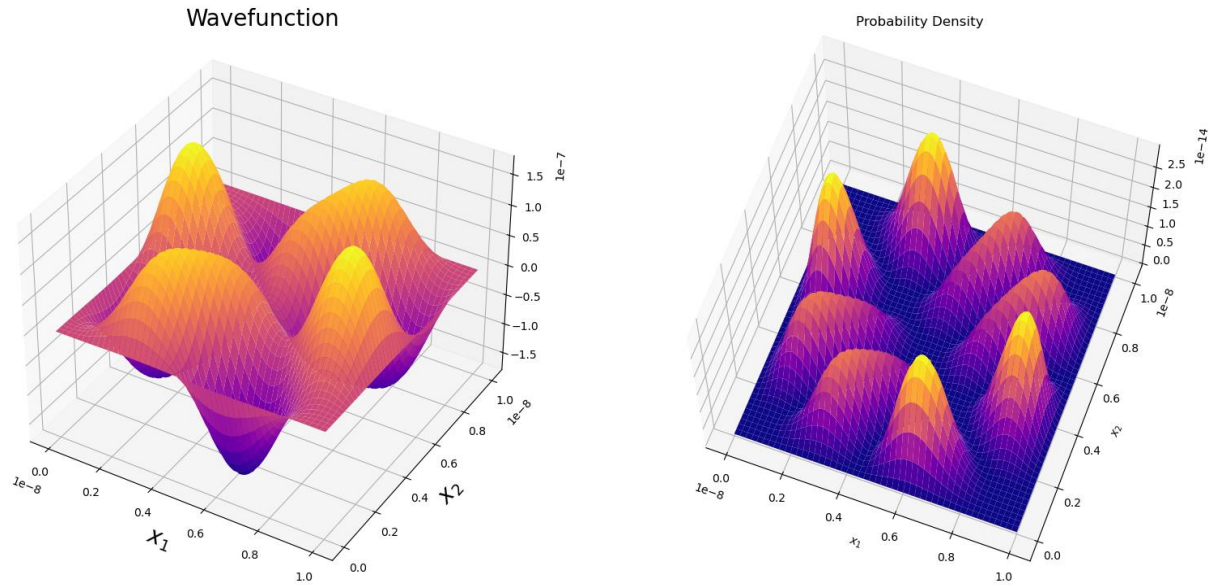


Figure 9. . Interacting identical fermions (parallel spin) in first excited state in an infinite well.

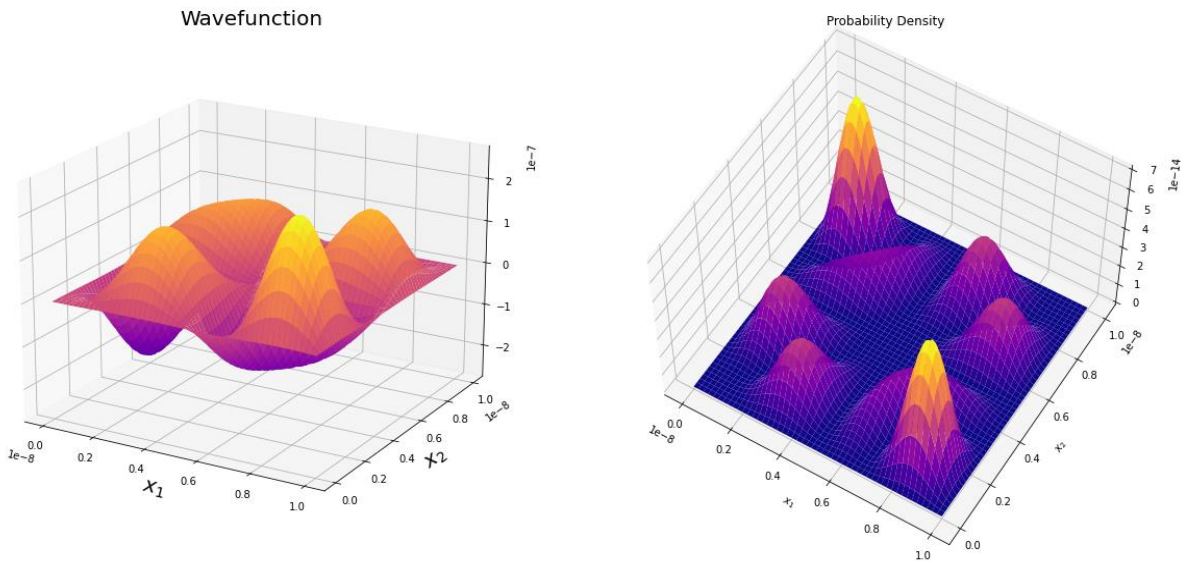


Figure 10. Interacting identical fermions (parallel spin) in second excited state in an infinite well

Table 1: Energy terms for different energy levels of the 2 electrons

Energy level of 1 st electron	Energy level of 2 nd electron	Total Energy (eV)	Corrected Energy (eV)	Change in Energy (eV) $\times 10^{-12}$
1	2	0.018622178543690665	0.018622178548350684	4.660018181190934
1	3	0.03724421005233811	0.037244210058159935	5.821821776761213
2	3	0.048417502474588876	0.04841750247980843	5.219554968381771

It is observed that after considering the interaction of the fermions, the nodal curves in each of the three energy levels increased by a value of two. For example, in the ground state of the 2-particle system, the number of nodal curves is one when we ignore their interaction, however, on considering an interaction between them, the number of nodal planes increases to 3. Similarly, the number of nodal curves in the second excited state for non-interacting fermions is 3 but the number of nodal planes in the probability density curve of interacting fermions is 5. Thus, considering the coulombic repulsion between two identical fermions (or electrons) gives rise to two extra regions or curves where the probability of finding the electrons is zero.

Applications

1. Calculating the probability of transition between states of a continuous spectrum under the action of a constant (time-independent) perturbation. This may include various interactions like collision.
2. Corrections in dipole moment as a function of uniform electric field can be calculated using perturbation theory and applying Hellmann-Feynman theorem.
3. When a molecule is rotating freely in the gas phase or in solution, it has some polarizability. The formula of this polarizability can be found out from the expression for the second order correction to the energy.
4. Dispersion forces are caused by the interaction between electric dipoles on different species. These dipoles are not permanent but are brought about by instantaneous fluctuations in the charge distribution of the species. These are way too weak to be considered a chemical bond, but it has a great significance. Perturbation theory can be used to calculate the interaction energy due to dispersion between two species.

Further Work

We have applied perturbation theory to a system of 2 identical fermions confined in an infinite potential well to find the corrected energies and wave functions of the various energy levels. In the future, we would like to apply this framework to the Helium atom that consists of 2 electrons that are attracted to the nucleus while at the same time repel each other via coulombic forces.

Conclusion

In this project, we have plotted the wavefunction and probability density curves of 2 indistinguishable fermions trapped in an infinite potential well. To simplify the problem, we have considered that the fermions have parallel spin values. Identical fermions – like electrons repel each other by coulombic forces. This additional potential term which is a function of the distance between the two electrons complicates the solution of the TISE. Hence, we have used perturbation theory to computationally produce the wavefunction and probability density curves of 2 electrons in an infinite potential well that interact with each other (Coulombic repulsion).

References

1. Griffiths, D. J. (1960). *Introduction to quantum mechanics*. Pearson International Edition (Pearson Prentice Hall, Upper Saddle River, 2005).
2. Iyengar, S. D. (2019). *Numerical Treatment of Schrödinger's Equation for One-Particle and Two-Particle Systems Using Matrix Method*. Embry-Riddle Aeronautical University.
3. Salter, E. A., Trucks, G. W., & Cyphert, D. S. (2001). Two charged particles in a one-dimensional well. *American Journal of Physics*, 69(2), 120-124.
4. Diestler, D. J., & McKoy, V. (1967). Quantum Mechanics of One-Dimensional Two-Particle Models. Electrons Interacting in an Infinite Square Well. *The Journal of Chemical Physics*, 47(2), 454-467.
5. Peter Atkins, Ronald Friedman (2005). *Molecular quantum mechanics*.

Acknowledgement

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Appendix: Program

```
import numpy as np
import matplotlib.pyplot as plt
from numpy.linalg import eig
from mpl_toolkits.mplot3d import Axes3D

# 2 identical non-interacting fermions (spin-
# 1/2 fermions) in an infinite potential well
#modelling the eigenfunctions and energy levels

#note that identical means - they cannot be distinguished, i.e. their spin
#s are parallel

#Solving the TISE for 1 particle in an infinite potential well using finite
#difference method

#initial constants
hbar = 1.05*(10**-34)
m = 9.1*(10**-31)          #electron mass in atomic units
#well width
W = 10*(10**-9)
#step size
n = 1000

#x-axis points and y-axis points
x = np.linspace(0,W,n)
y = np.linspace(0,W,n)

#print(x)
#number of grid points
h = x[1] - x[0]

#Kinetic energy matrix

K = np.zeros((n,n))

s,t = np.shape(K)
for i in range(s):
    for j in range(t):
        if i==j:
            K[i,j] = -2
for i in range(s):
    for j in range(t-1):
        if j==(i+1):
            K[i,j] = 1
for i in range (1,s):
```

```

        for j in range(t):
            if j==(i-1):
                K[i,j] = 1

Potential Energy function
def P(x):
    return 0

#Potential Energy Matrix
V = np.zeros((n,n))
for i in range(s):
    for j in range(t):
        if i==j:
            V[i,j] = P(x)
        else: continue
#Hamiltonian

H = (-hbar**2/(2*m*(h**2)))*K + V

#Solving eigenvalue problem
eigval, eigvec = eig(H)

#sorting eigenvalues in asceding order and arranging eigenvectors too
idx = np.argsort(eigval)
eigval = eigval[idx]
eigvec = eigvec[:,idx]

#Plotting
level1 = int(input('Enter energy level of electron 1:'))
level2 = int(input('Enter energy level of electron 2:'))
#mesh points for plotting in 3-D
xx, yy = np.meshgrid(x,y)

if level1 != level2:

    #Wavefunction matrix
    Z = np.zeros((n,n))
    for i in range(n):
        for j in range(n):
            Z[i,j] = (eigvec[i:i+1,level1-1]*eigvec[j:j+1,level2-1]
1] - eigvec[j:j+1,level1-1]*eigvec[i:i+1,level2-1])

    #Probability Density matrix
    Z2 = np.zeros((n,n))

```

```

for i in range(n):
    for j in range(n):
        Z2[i,j] = np.abs(Z[i,j])**2

#Normalization constant
A = np.trapz(np.trapz(Z2,x),y)

Z = (1/np.sqrt(A))*Z
Z2 = (1/A)*Z2

fig= plt.figure()
ax = fig.add_subplot(1, 2, 1, projection='3d')
p = ax.plot_surface(xx,yy,Z, cmap='hot')
ax.set_xlabel("$x_1$")
ax.set_ylabel("$x_2$")
ax.set_title(' Normalized Wavefunction')

ax = fig.add_subplot(1, 2, 2, projection='3d')
p = ax.plot_surface(xx,yy,Z2, cmap='hot')
ax.set_xlabel("$x_1$")
ax.set_ylabel("$x_2$")
ax.set_title('Normalized Probability Density')

E_total = (eigval[level1-1] + eigval[level2-1])*(6.242*(10**18))
print('Total Energy (in eV):',E_total)

else:
    print("No state possible. Identical fermions cannot occupy the same energy level!")
    Z = np.zeros((n,n))
    for i in range(n):
        for j in range(n):
            Z[i,j] = 0
    fig= plt.figure()
    ax = fig.add_subplot(1, 2, 1, projection='3d')
    p = ax.plot_surface(xx,yy,Z, cmap='hot')
    ax.set_xlabel("$x_1$",fontsize = '20')
    ax.set_ylabel("$x_2$",fontsize = '20')
    ax.set_title('Normalized Wavefunction', fontsize = '20')

#ANALYTICAL
def psix(x,l,a):
    return np.sin((l*np.pi*x)/a)
def psiy(y,l,a):
    return np.sin((l*np.pi*y)/a)

```



```
def PSI(x,y,a,l1,l2):
    return (np.sqrt(2)/a)*(psix(x, l1, a)*psiy(y, l2, a) - psix(x, l2, a)*
psiy(y, l1, a))
```

```
#fig = plt.figure()
#ax = fig.add_subplot(1, 2, 1, projection='3d')
#p = ax.plot_surface(xx,yy,PSI(xx,yy,W,level1,level2), cmap='cool')
```

```
    #***
```

```
#Perturbation: considering the potential due to the interaction between 2
electrons
```

```
e = 1.6*(10**-19)
eo = 8.85*(10**-12)
```

```
    #FIRST ORDER CORRECTION TO ENERGY
```

```
P = np.zeros((n,n))
for i in range(n):
    for j in range(n):
        if i != j:
            P[i,j] = Z2[i,j]*((e**2)/(4*np.pi*eo*np.abs(i-
j)))*(6.242*(10**18))
        else:
            P[i,j] = Z2[i,j]*0
```

```
#print(P)
```

```
E_correction = (np.trapz(np.trapz(P,x),y))
```

```
E_corrected = (E_correction + E_total)
print('Corrected Energy (in eV):', E_corrected)
print("Correction in energy (in eV):",E_correction)
```

```
    #                FIRST ORDER CORRECTION TO WAVE FUNCTION
#function that gives the wavefunction and probability density of any energy
level
```

```
def Psi(l1,l2):

    #Wavefunction matrix
    Z = np.zeros((n,n))
    for i in range(n):
        for j in range(n):
            Z[i,j] = (eigvec[i:i+1,l1-1]*eigvec[j:j+1,l2-
1] - eigvec[j:j+1,l1-1]*eigvec[i:i+1,l2-1])
```

```

#Probability Density matrix
Z2 = np.zeros((n,n))
for i in range(n):
    for j in range(n):
        Z2[i,j] = np.abs(Z[i,j])**2

E_total = (eigval[l1-1] + eigval[l2-1])

return{'psi':Z,'psi2':Z2, 'energy':E_total}

# function that returns the scalar term in the formula for perturbed
wavefunctions

def K(l1,l2):

    #well width
    W = 10*(10**9)

    #step size
    n = 1000

    #x-axis points and y-axis points
    x = np.linspace(0,W,n)
    y = np.linspace(0,W,n)

    #print(x)

    psi1 = Psi(1,2)['psi']          #enter l1 and l2 depending on the
energy level at which you want the perturbed wavefunction
    psim = Psi(l1,l2)['psi']

    K = np.zeros((n,n))
    for i in range(n):
        for j in range(n):
            if i != j:
                K[i,j] = psi1[i,j]*psim[i,j]*(1/(np.abs(i-j)))
            else:
                K[i,j] = 0

    knum = np.trapz(np.trapz(K,x),y)

```

```

kdenom = Psi(1,2) ['energy'] - Psi(11,12) ['energy']

k = knum/kdenom

return k

#calculating perturbed wavefunction

Psi_perturbed = K(1,3)*Psi(1,3) ['psi'] + K(2,3)*Psi(2,3) ['psi'] + K(1,4)*Psi(1,4) ['psi'] + K(2,4)*Psi(2,4) ['psi'] + K(3,4)*Psi(3,4) ['psi'] + K(1,5)*Psi(1,5) ['psi'] + K(2,5)*Psi(2,5) ['psi'] + K(4,4)*Psi(4,4) ['psi']

#calculating perturbed prob density
prob_density = np.zeros((n,n))
for i in range(n):
    for j in range(n):
        prob_density[i,j] = np.abs(Psi_perturbed[i,j])**2

#well width
W = 10*(10**9)

#step size
n = 1000
#x-axis points and y-axis points
x = np.linspace(0,W,n)
y = np.linspace(0,W,n)

#mesh points for plotting in 3-D
xx, yy = np.meshgrid(x,y)
fig= plt.figure()
ax = fig.add_subplot(1, 2, 1, projection='3d')
p = ax.plot_surface(xx,yy,Psi_perturbed, cmap='plasma')
ax.set_xlabel("$x_1$", fontsize = '20')
ax.set_ylabel("$x_2$", fontsize = '20')
ax.set_title('Wavefunction', fontsize = '20')

ax = fig.add_subplot(1, 2, 2, projection='3d')
p = ax.plot_surface(xx,yy,prob_density, cmap='plasma')
ax.set_xlabel("$x_1$")
ax.set_ylabel("$x_2$")
ax.set_title('Probability Density')

```