1. Schrodinger's Equation

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

Where,

$$\hbar = \frac{h}{2\pi}$$

$$h = Planck's\ constant = 6.626 \times 10^{-34}\ J\ s$$

$$m = mass\ of\ the\ particle$$

$$\psi = wave\ equation$$

$$V(z) = Potential\ function$$

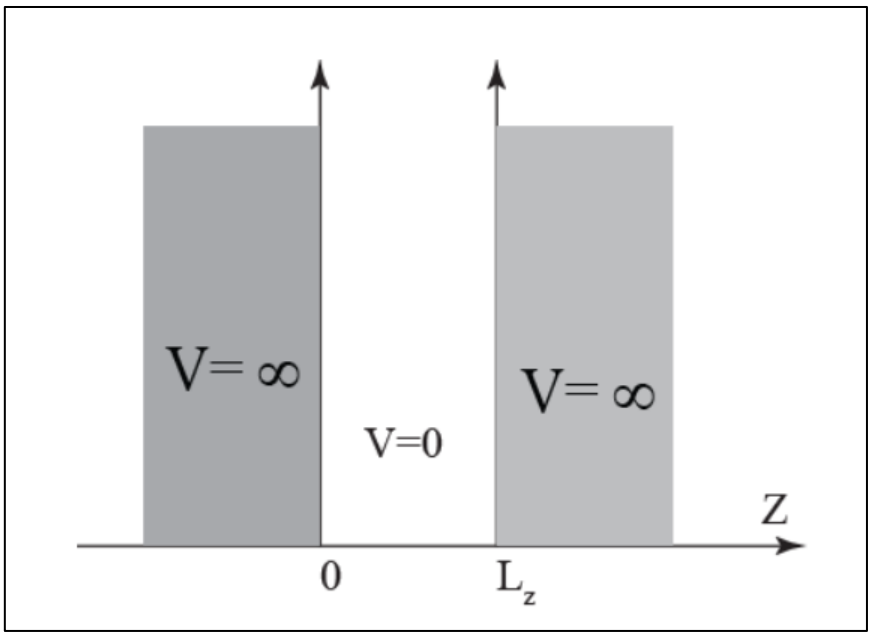
$$E = Energy$$

2. MATLAB Simulations

MathWorks MATLAB R2018b was used to do the simulations. Simply run them and input the required parameters (e.g.: *L*, *n*, v_0). They have the usual meaning, unless mentioned otherwise. Codes are divided into several sections, so that it is easier to comprehend.

2.1 Particle in a Box

Here, the inside potential is assumed to be zero and the outside potential is assumed to be infinite.



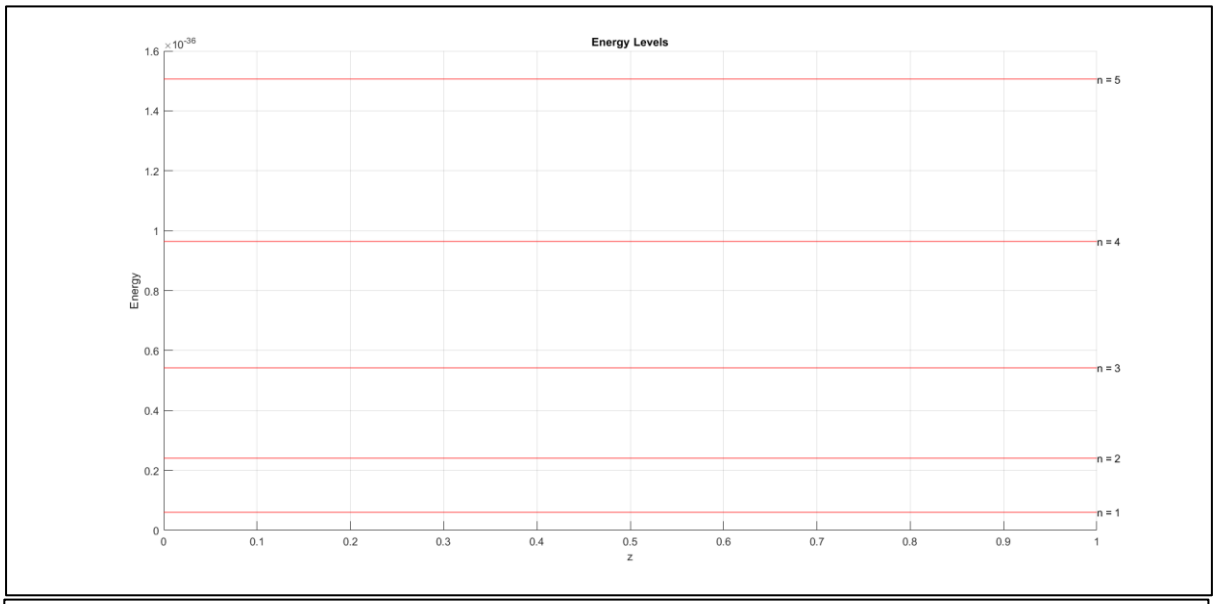
2.1.1 Particle in a One-Dimensional Box (Code - *inf_well_1d.m*)

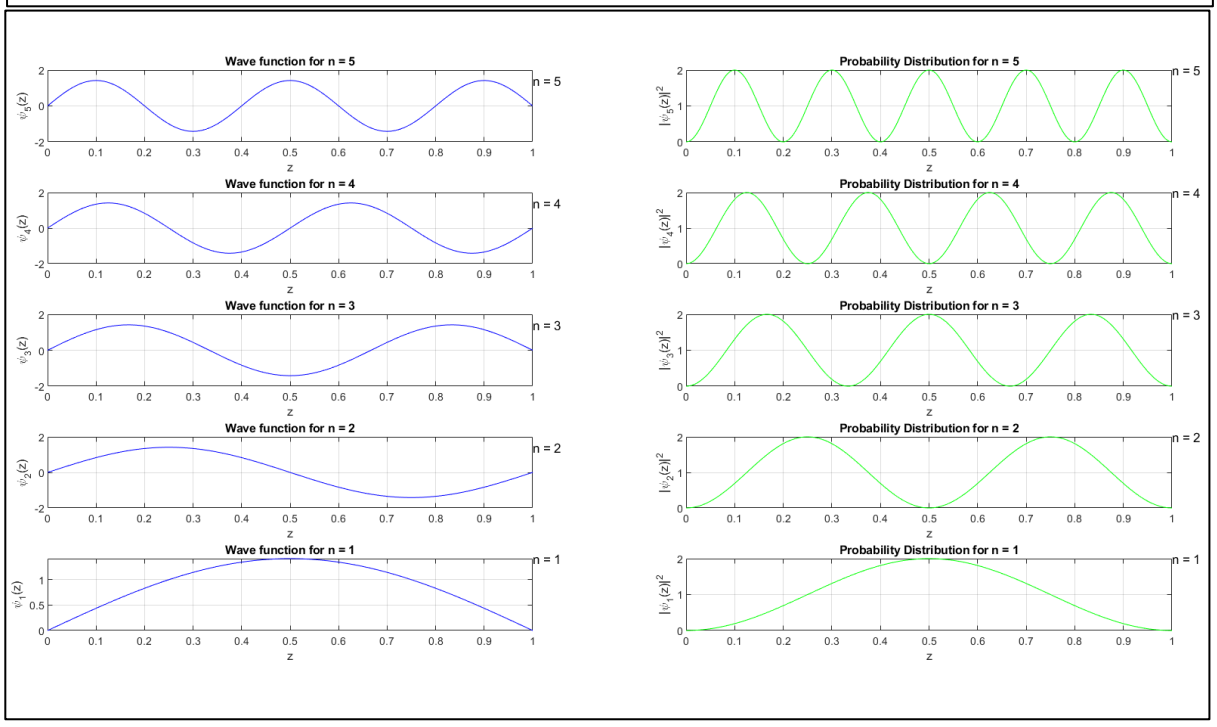
$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L_z}\right)^2$$

$$\psi_n = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right)$$

Where,

$$n = Energy\ level\ (\in \mathbb{N})$$





2.1.2 Particle in a Three-Dimensional Box (Code – *inf_well_3d.m*)

In this case Schrodinger's equation is solved assuming separation of variables.

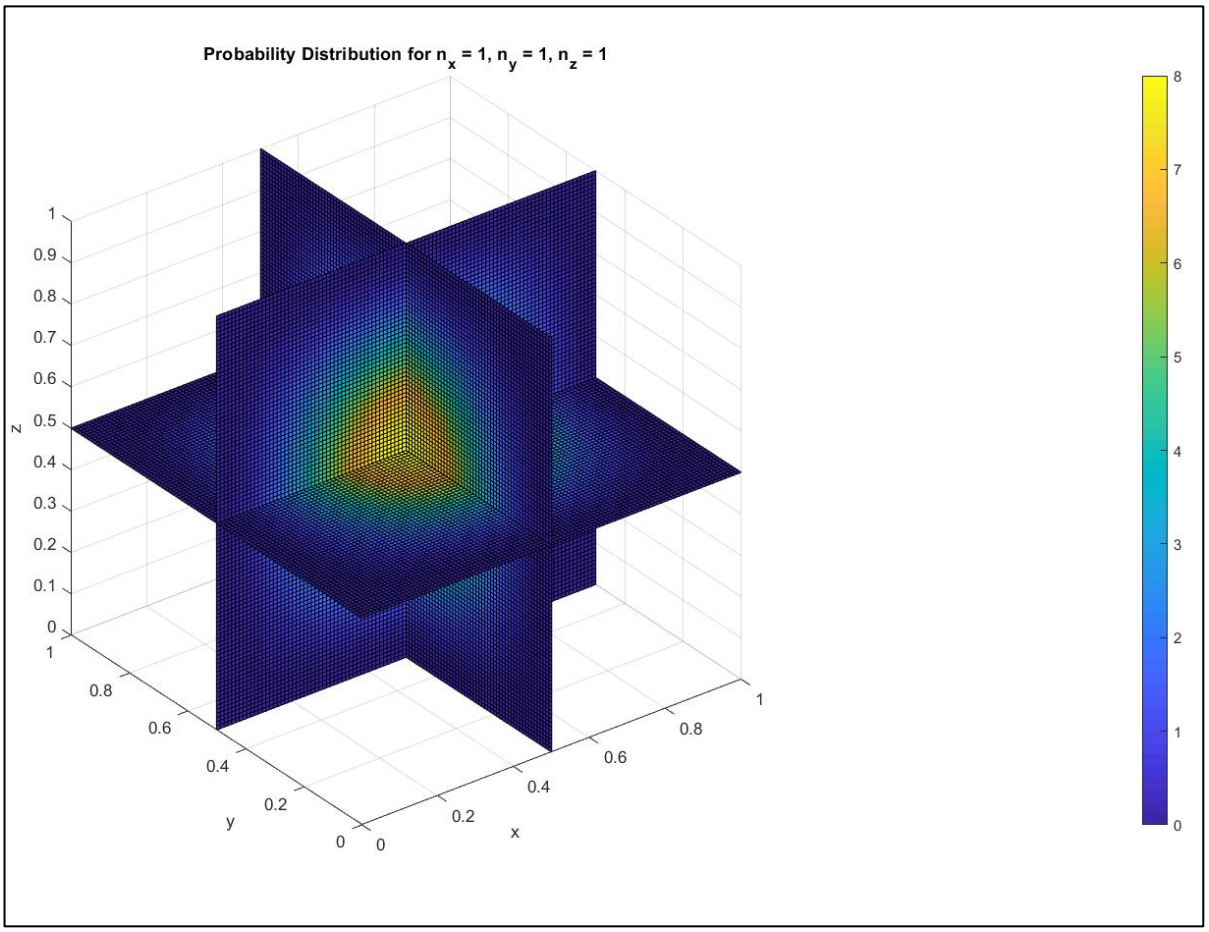
$$\psi(x,y,z) = X(x).Y(y).Z(z)$$

$$E = E_x + E_y + E_z$$

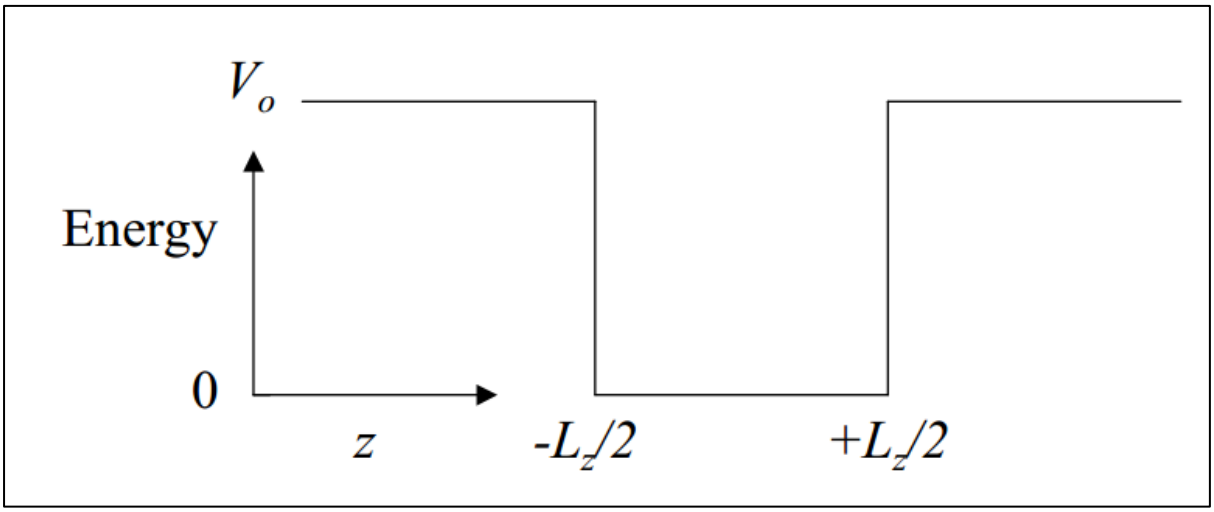
Deducing from 2.1.1,

$$\psi_{n_y n_y n_z}(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right]$$



2.2 Particle in a One-Dimensional Finite Potential Well (Code – *fin_well.m*)



For bound states $E < V_0$ case is considered.

We define,

$$E_1^{\infty} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L_z}\right)^2$$

$$\varepsilon \equiv \frac{E}{E_1^{\infty}}$$

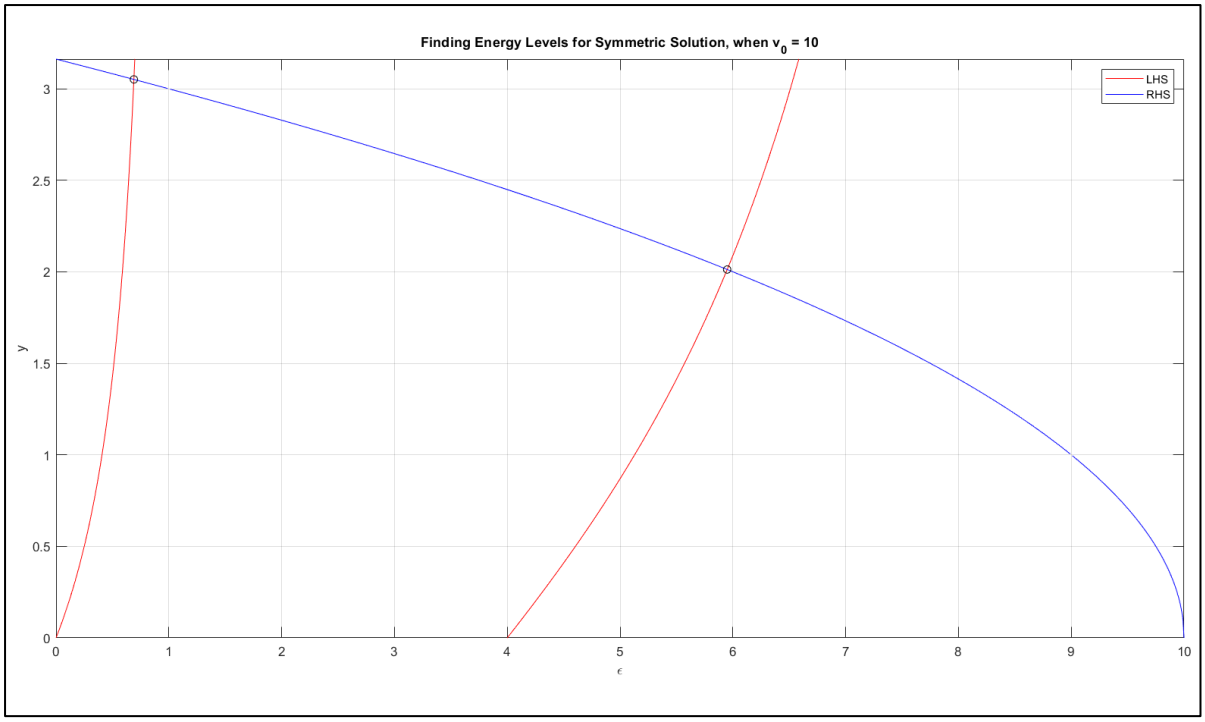
$$v_0 = \frac{V_0}{E_1^{\infty}}$$

2.2.1 Symmetric Solution

The allowed energies satisfy,

$$\sqrt{\varepsilon}\tan\left(\frac{\pi\sqrt{\varepsilon}}{2}\right) = \sqrt{v_0 - \varepsilon}$$

To solve for ε, graphical method is used by plotting LHS (Left Hand Side) and RHS (Right Hand Side) against ε. It was hard to plot correctly and figure out the correct solutions in MATLAB, since MATLAB interpolates and connects discontinuities of tan and cot functions. However, I worked around it by assigning discontinuities as NaN (Not a Number).



The wavefunctions are,

$$\psi(z) = Bc_L \exp\left(\frac{\pi z\sqrt{v_0 - \varepsilon}}{L_z}\right);\ z < \frac{-L_z}{2}$$

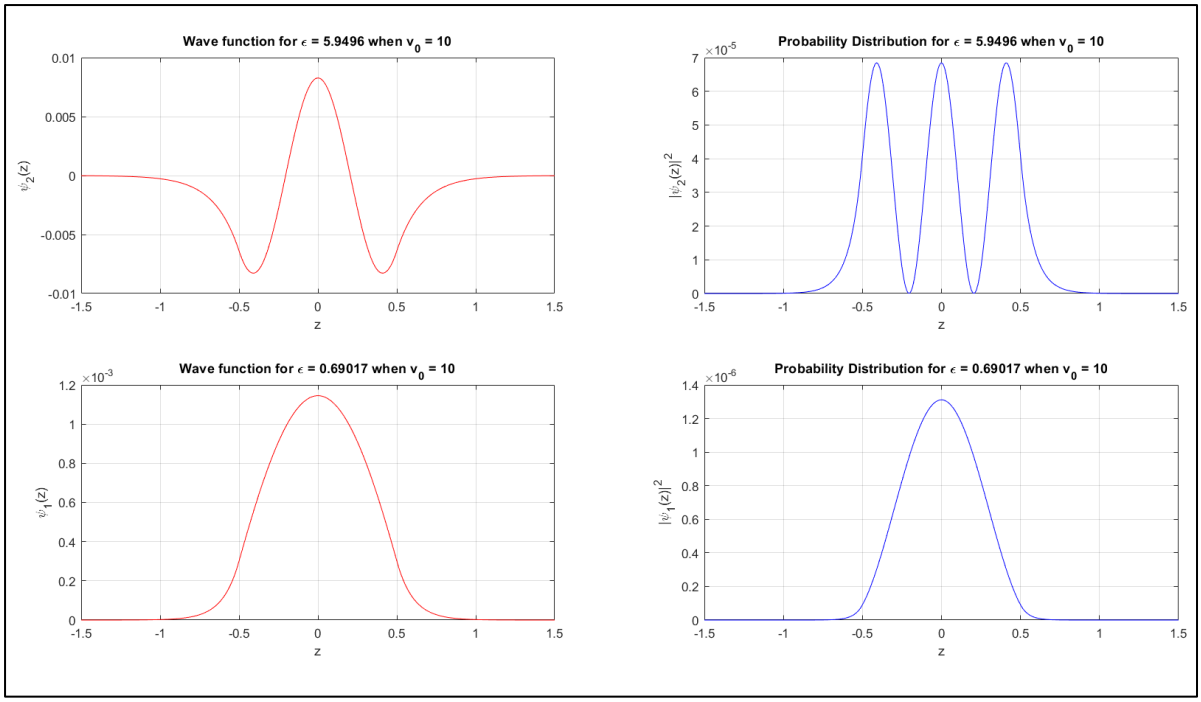
$$\psi(z) = B\cos\left(\frac{\pi z\sqrt{\varepsilon}}{L_z}\right);\ \frac{-L_z}{2} < z < \frac{L_z}{2}$$

$$\psi(z) = Bc_L \exp\left(\frac{-\pi z\sqrt{v_0 - \varepsilon}}{L_z}\right), z > \frac{L_z}{2}$$

Where,

$$B = \sqrt{\frac{2}{1 + \frac{C_L^2}{\pi\sqrt{v_0 - \varepsilon}}\left[\exp\left(\pi\sqrt{v_0 - \varepsilon}\right) + \exp\left(\pi\sqrt{v_0 - \varepsilon}\right)\right] + \frac{\sin(\pi\sqrt{\varepsilon})}{\pi\sqrt{\varepsilon}}}}$$

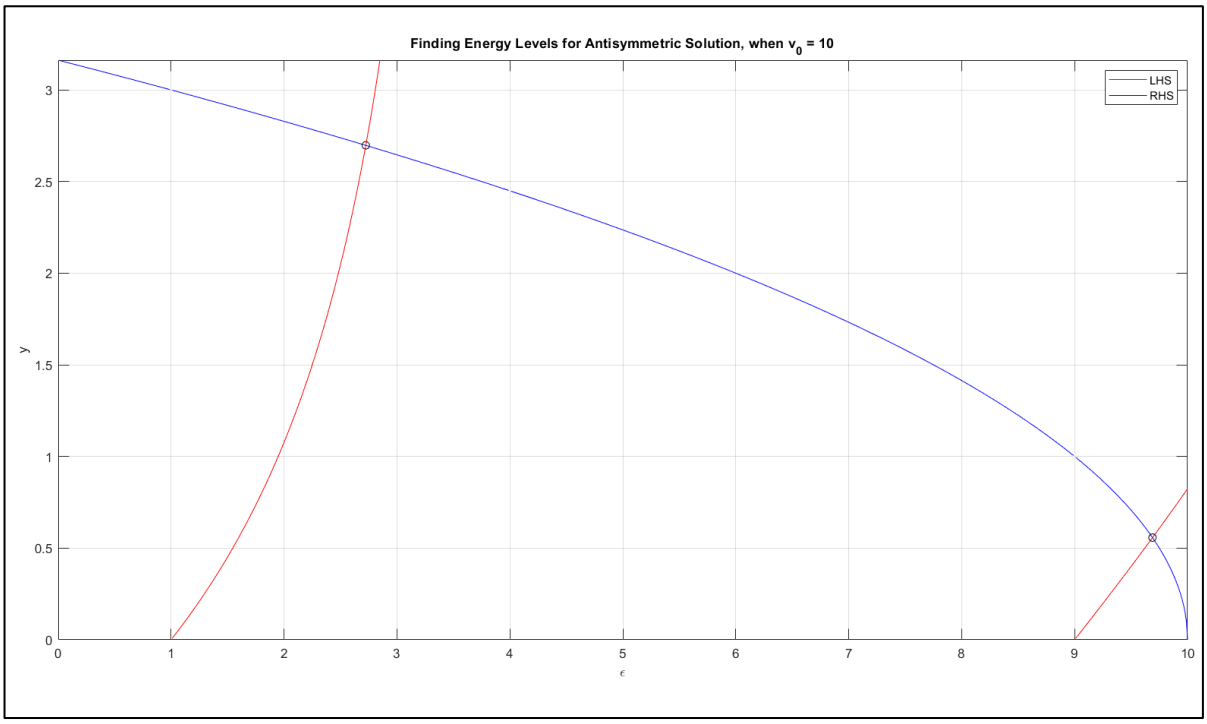
$$c_L = \frac{\cos\left(\frac{\pi\sqrt{\varepsilon}}{2}\right)}{\exp\left(\frac{-\pi\sqrt{v_0 - \varepsilon}}{2}\right)}$$



2.2.2 Antisymmetric Solution

The allowed energies satisfy,

$$-\sqrt{\varepsilon}\cot\left(\frac{\pi\sqrt{\varepsilon}}{2}\right) = \sqrt{v_0 - \varepsilon}$$



The wavefunctions are,

$$\psi(z) = -As_L \exp\left(\frac{\pi z\sqrt{v_0 - \varepsilon}}{L_z}\right);\ z < \frac{-L_z}{2}$$

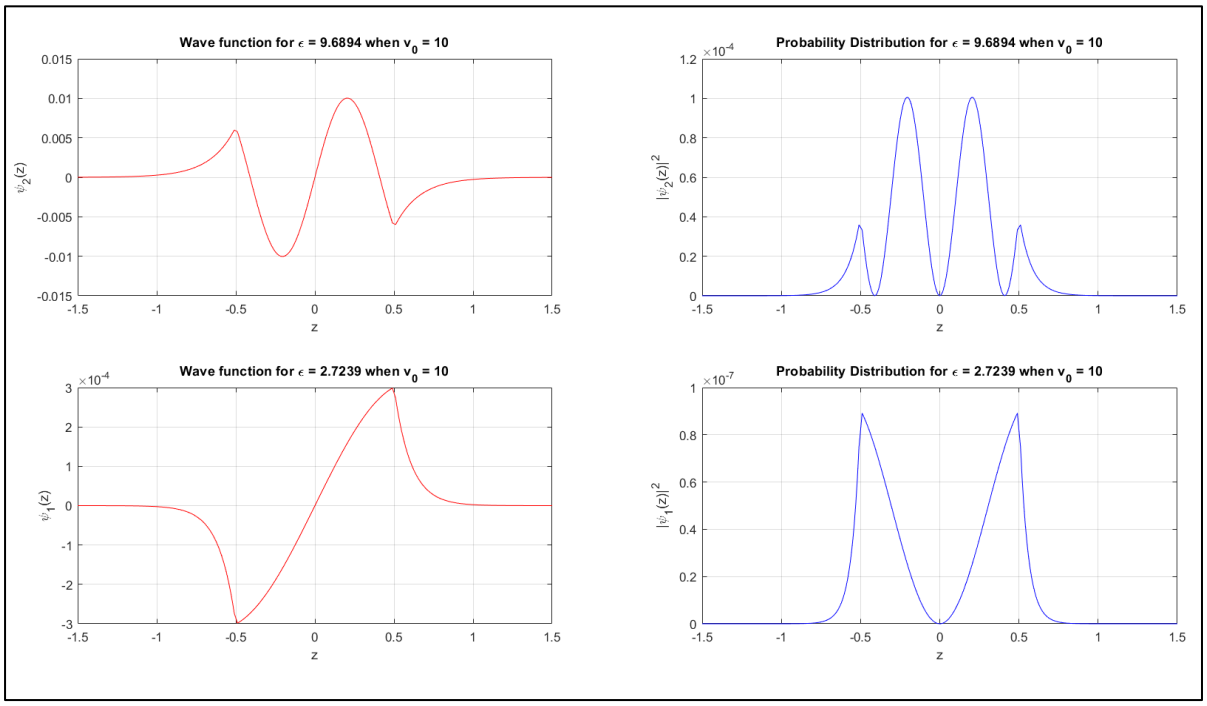
$$\psi(z) = A \sin\left(\frac{\pi z\sqrt{\varepsilon}}{L_z}\right);\ \frac{-L_z}{2} < z < \frac{L_z}{2}$$

$$\psi(z) = As_L \exp\left(\frac{-\pi z\sqrt{v_0 - \varepsilon}}{L_z}\right);\ z > \frac{L_z}{2}$$

Where,

$$A = \sqrt{\frac{2}{1 + \frac{C_L^2}{\pi\sqrt{v_0 - \varepsilon}}\left[\exp\left(\pi\sqrt{v_0 - \varepsilon}\right) + \exp\left(\pi\sqrt{v_0 - \varepsilon}\right)\right] - \frac{\sin(\pi\sqrt{\varepsilon})}{\pi\sqrt{\varepsilon}}}}$$

$$s_L = \frac{\sin\left(\frac{\pi\sqrt{\varepsilon}}{2}\right)}{\exp\left(\frac{-\pi\sqrt{v_0 - \varepsilon}}{2}\right)}$$



2.3 Hydrogen Atom (Code – *H_atom.m*)

The proton is assumed to be fixed at the origin and following parameters were considered.

$$e = magnitude\ of\ the\ charge\ of\ an\ electron = 1.602 \times 10^{-19}\ C$$

$$m_e = mass\ of\ an\ electron = 9.109 \times 10^{-31}\ kg$$

$$m_p = mass\ of\ a\ proton = 1.6726 \times 10^{-27}\ kg$$

$$\mu_e = reduced\ mass = \frac{m_e m_p}{m_e + m_p} = 0.99945 m_e \approx m_e$$

$$\varepsilon_0 = permittivity\ of\ free\ space = 8.854 \times 10^{-12}\ C^2\ J^{-1} m^{-1}$$

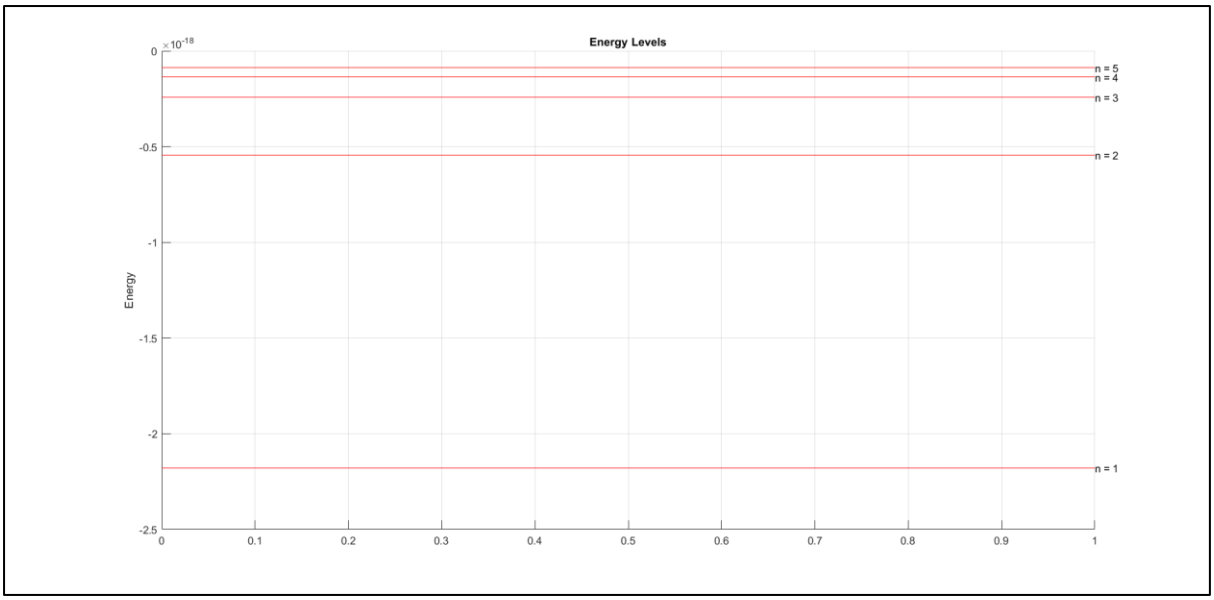
$$a_0 = Bohr\ radius = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}$$

Potential is described by,

$$V(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

Energy levels are given by,

$$E_n = -\frac{m_e e^4}{32(\pi\varepsilon_0 \hbar n)^2}$$



Using separation of variables, wavefunction can be written as,

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

Where,

$$R_{nl}(r) = Radial\ wavefunction$$

$$Y_l^m(\theta,\phi) = Spherical\ harmonics$$

$$\{n,l,m\} \in \mathbb{Z}\,;n \geq 1\,;0 \leq l \leq n-1\,;\ -l \leq m \leq l$$

2.3.1 Radial Wavefunction

$$R_{nl}(r) = \sqrt{\frac{(n-l-1)!}{2n[(n+1)!]^3}}\left(\frac{2}{na_0}\right)^{l+\frac{3}{2}} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right) r^l \exp\left(\frac{-r}{na_0}\right)$$

Where,

$L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$ is given by associated Laguerre Polynomials.

2.3.1.1 Associated Laguerre Polynomials

$$L_a^b(x) = \frac{x^{-b}\exp(x)}{a!}\frac{d^a}{dx^a}[x^{a+b}\exp(-x)]$$

$$\{a,b\} \in \mathbb{Z}\,;\ a \geq 0$$

2.3.2 Spherical Harmonics

$$Y_l^m(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}[\cos(\theta)]\exp(im\phi)$$

Where,

$P_l^{|m|}[\cos(\theta)]$ is given by associated Legendre polynomials.

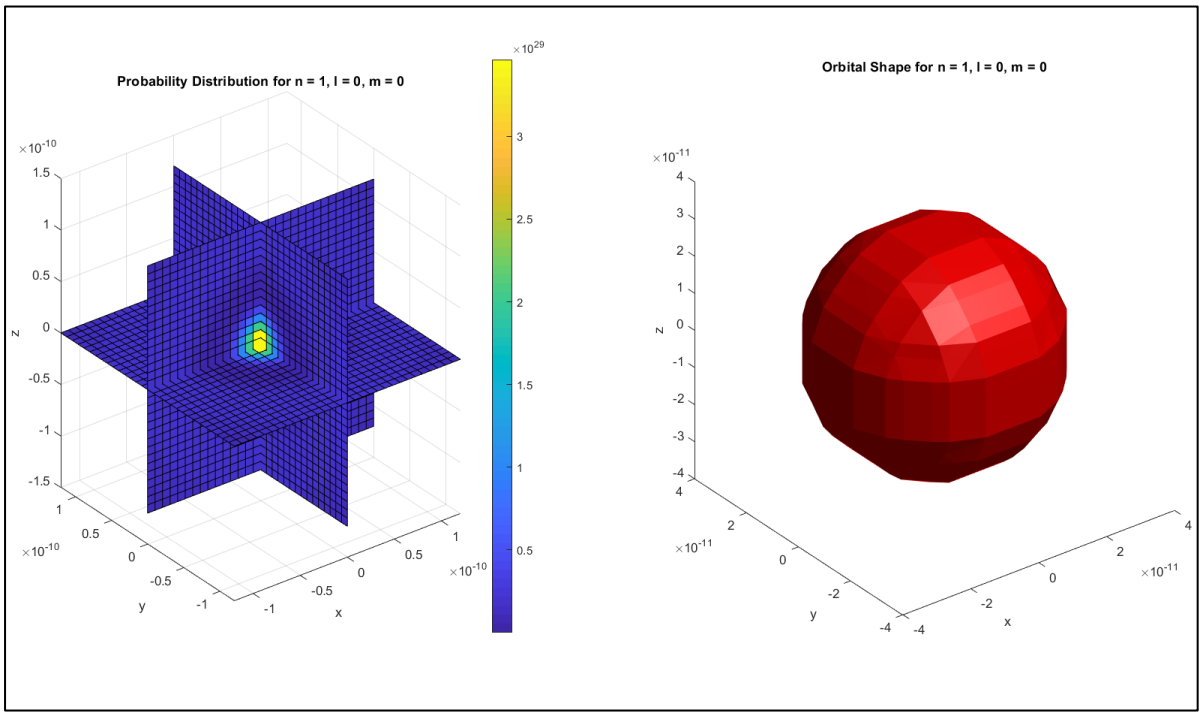
2.3.2.1 Associated Legendre Polynomials

$$P_a^b(x) = \frac{(-1)^b}{2^a a!}(1-x^2)^{\frac{b}{2}}\frac{d^{a+b}}{dx^{a+b}}(x^2-1)^a$$

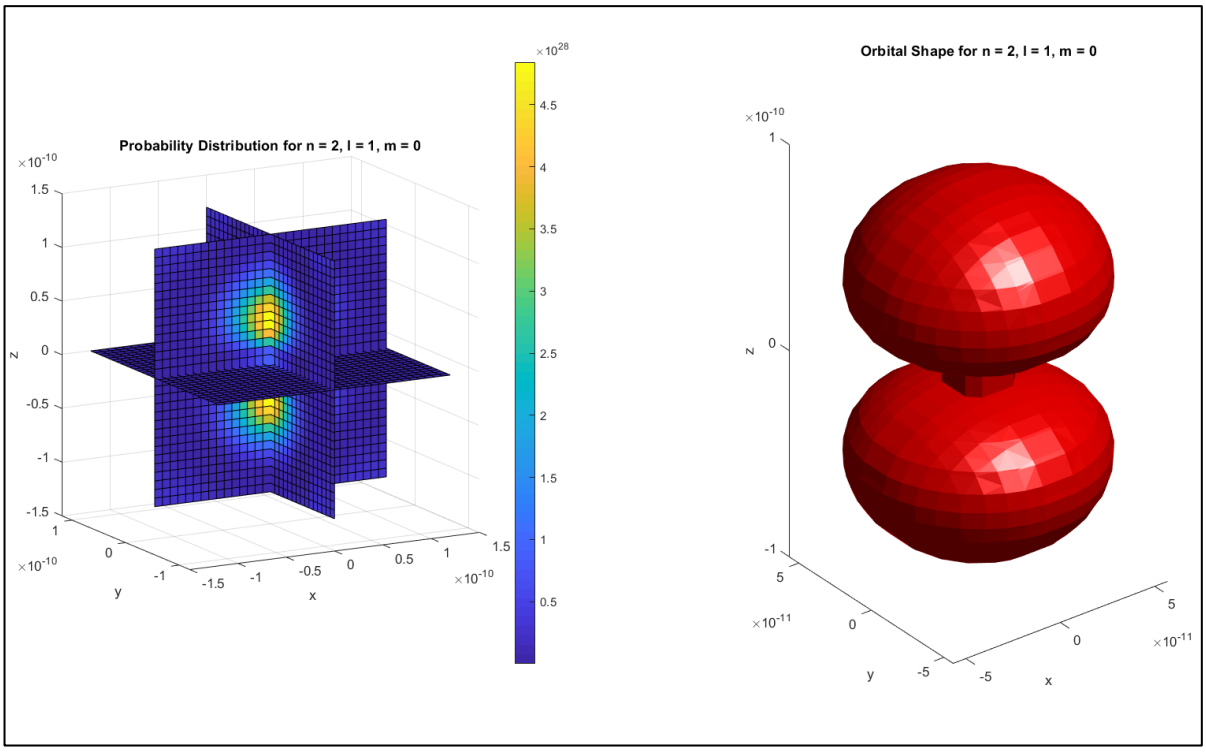
$$\{l,m\} \in \mathbb{Z}\,;1 \leq l\,;\ 0 \leq m \leq l$$

2.3.3 Probability Distributions and Orbital Shapes

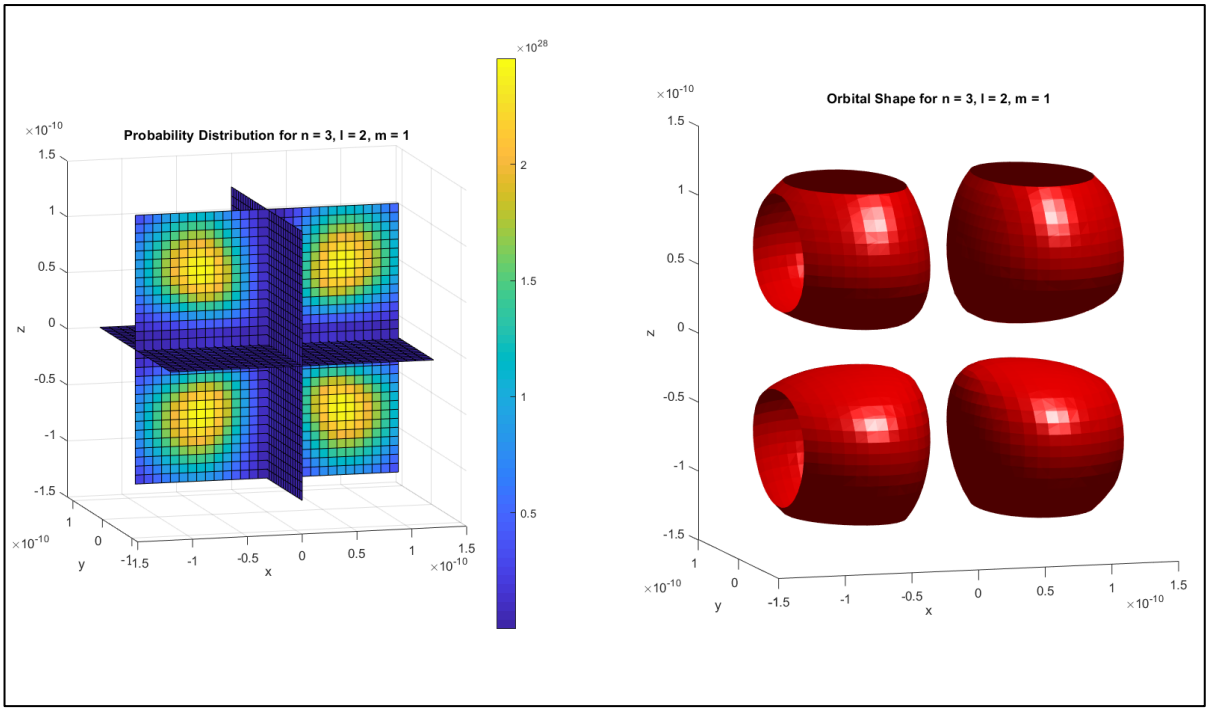
2.3.3.1 s-shell

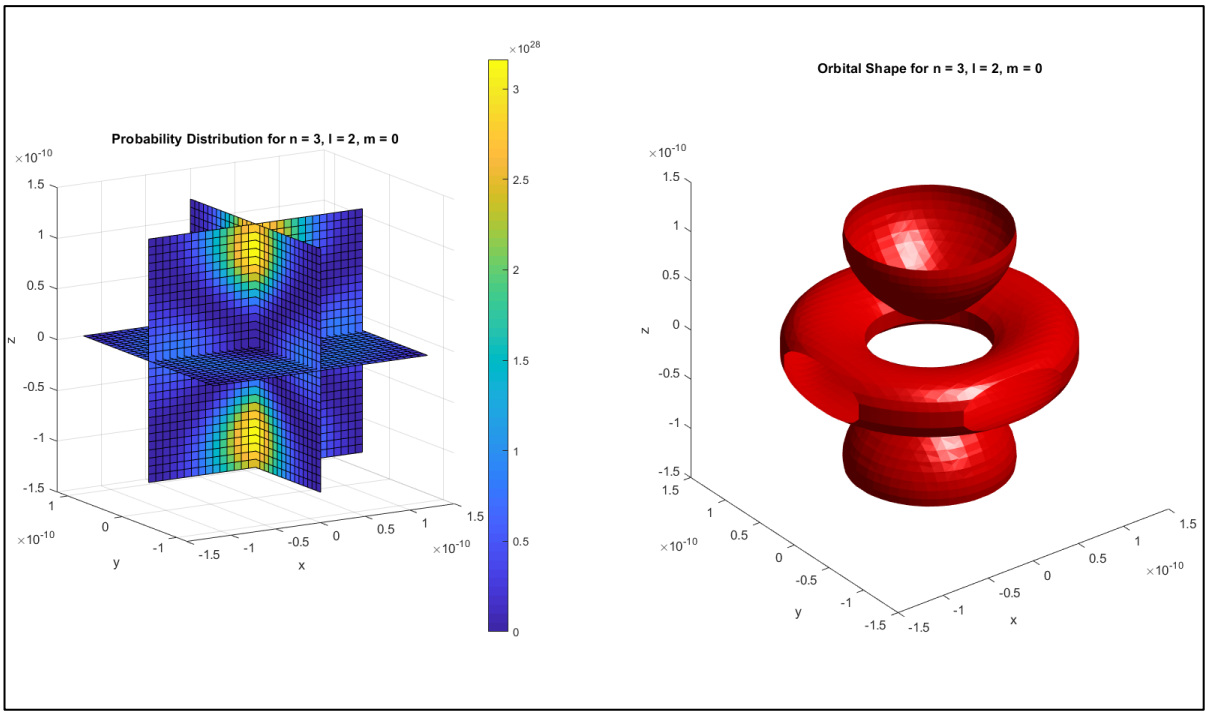


2.3.3.2 p-shell



2.3.3.3 d-shell


Probability Distribution for n = 3, l = 2, m = 1
Orbital Shape for n = 3, l = 2, m = 1


Probability Distribution for n = 3, l = 2, m = 0
Orbital Shape for n = 3, l = 2, m = 0

3. Solving Schrodinger's Equation for Eigenvalues in MATLAB

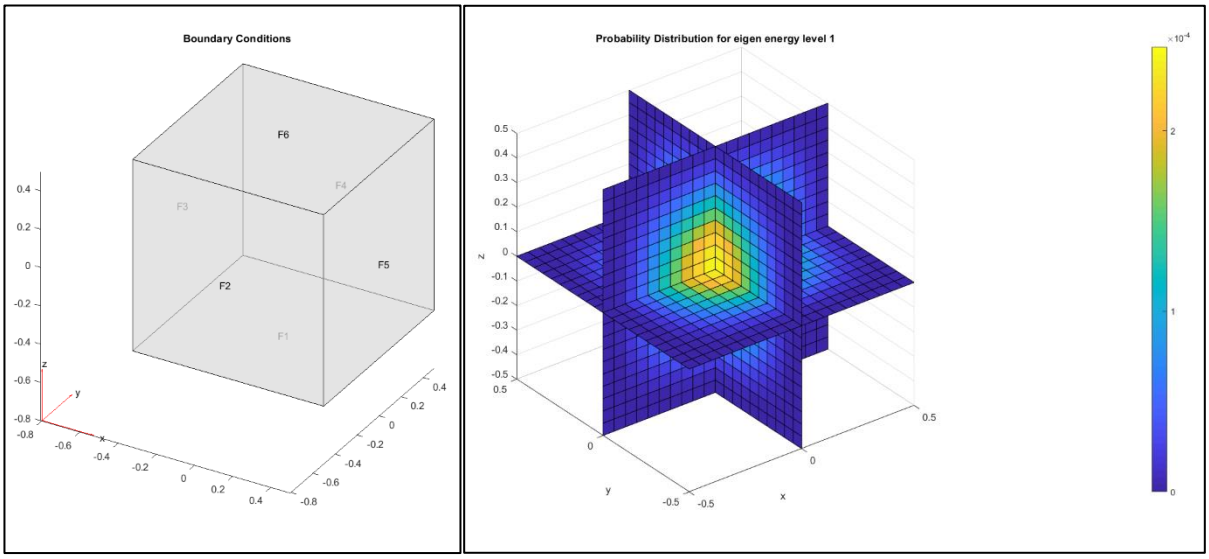
I used *solvepdeeig()* function to solve 3 dimensional Schrodinger's equation. The function, *solvepdeeig()* solves PDE eigenvalue problems of the form,

$$-\nabla.(c\nabla u) + au = \lambda du$$

When, $c = \frac{\hbar^2}{2m}$; $a = V(\vec{r})$; $\lambda = E$; $d = 1$, we can get Schrodinger's equation where $u = \psi$.

3.1 Particle in a Three-Dimensional Box (Code – *eigen_box.m*)

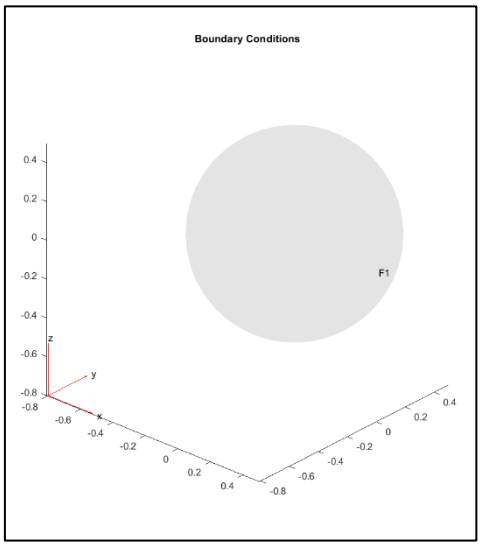
By normalizing $c = 1$, using $a = 0$ and setting boundary conditions to $u = 0$, I could solve the equation for eigenvalues using MATLAB.



When the code is run, one will be asked to input, for which eigen energy level, the probability distribution should be plotted. (One can compare with section 2.1.2 regarding the plots and the quantum numbers n_x, n_y *and* n_z.) Then, I interpolated the solution for the eigenvalue user picked and plotted the probability distribution in 3-dimensional x, y and z planes. This can be extended to other 3-dimensional scenarios as well, by changing the potential function and applying proper boundary conditions. (Please refer to section 3.2)

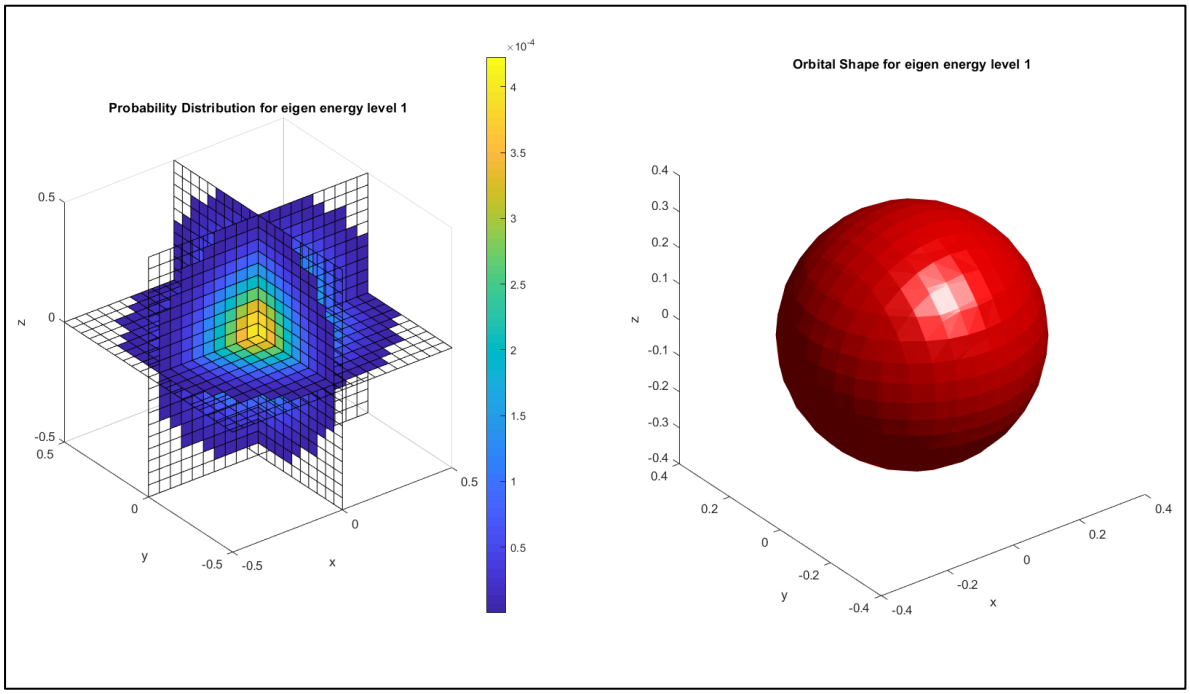
3.2 Hydrogen Atom (Code – *eigen_H.m*)

By normalizing $c = 1$, using $a = \frac{-1}{r}$ as the potential to make numerical calculations computationally less intensive for MATLAB and setting boundary conditions to $u = 0$, I could solve the equation for eigenvalues.

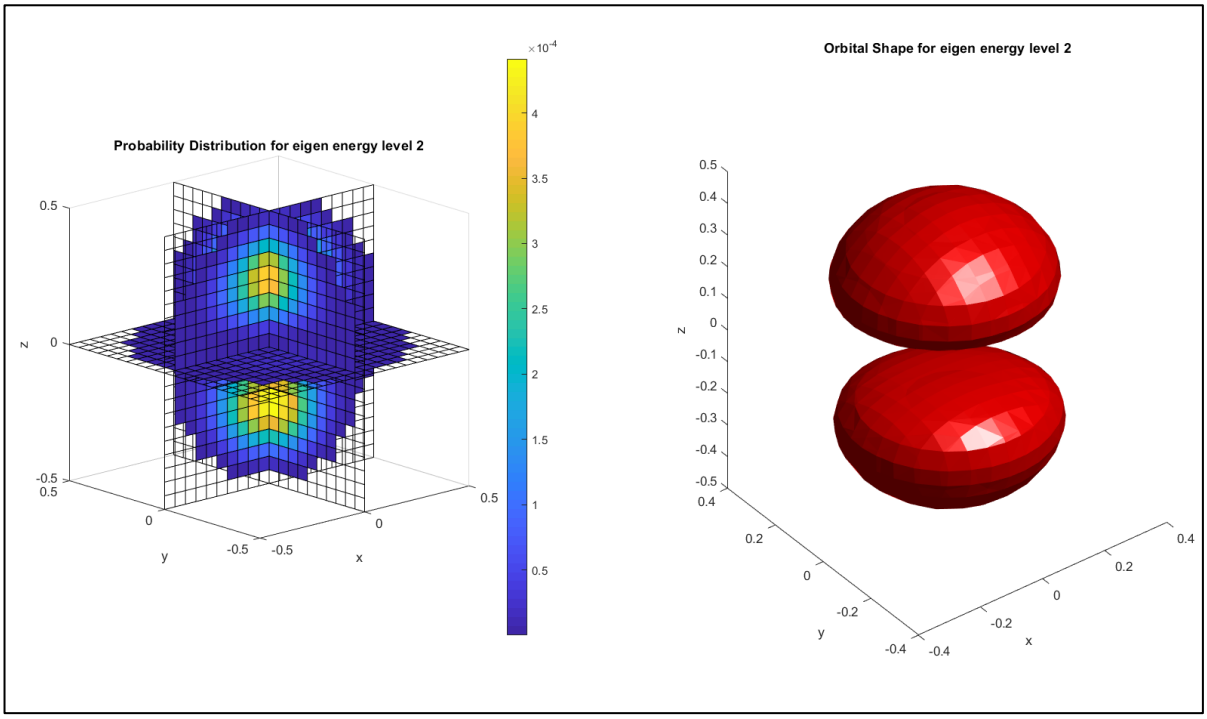


When the code is run, one will be asked to input, for which eigen energy level, the probability distribution should be plotted. (One can compare with section 2.3 regarding the plots and the quantum numbers *n, l and m.*) I also plotted the orbital shape in addition to probability distribution. There may be some minor irregularities in the outputs due to interpolation, using simplified coefficients and applying approximated boundary conditions.

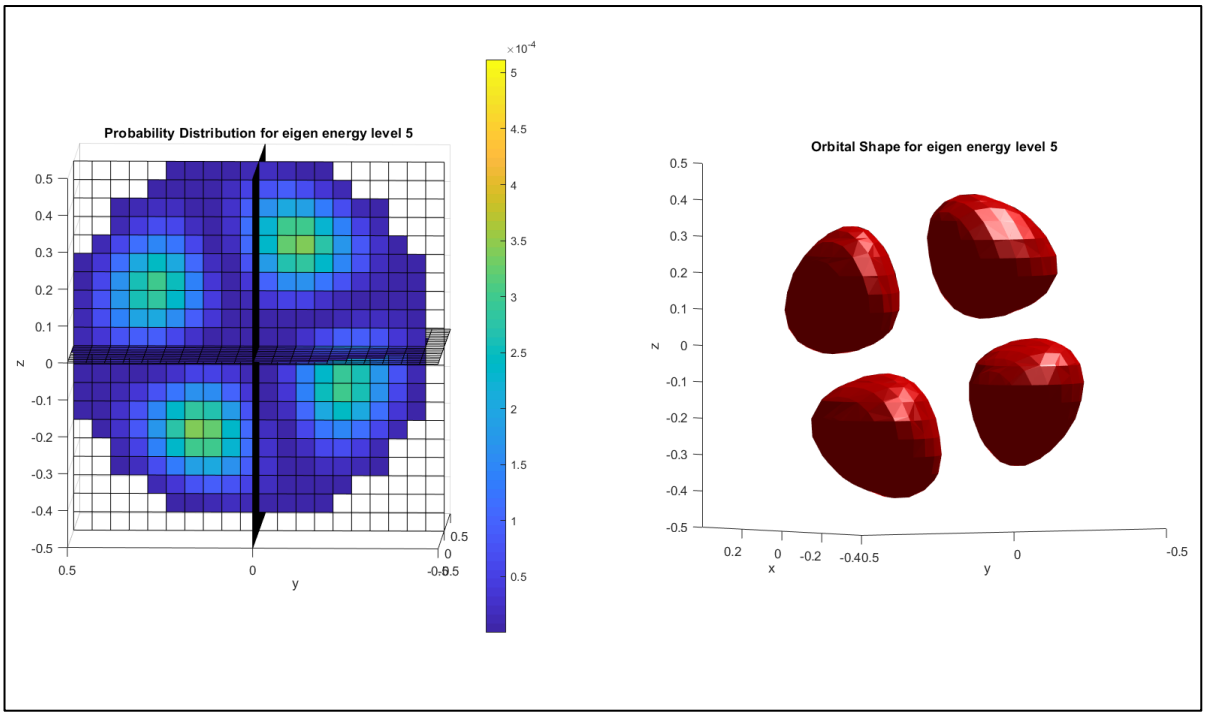
3.2.1 s-shell



3.2.2 p-shell



3.2.3 d-shell



4. Notes

- Schrodinger's equation describes the wavefunction of a quantum mechanical system.
- Probability distribution = $|\psi|^2$
- To visualize three-dimensional probability distributions, I sliced them along x, y and z planes to plot.
- To exaggerate and visualize orbitals of Hydrogen, I plotted an isosurface including the top 85% of the probability distribution.
- I wrote functions to calculate Associated Laguerre polynomial value, Associated Legendre polynomial value and total wavefunction of Hydrogen, so that they can be easily reused.
- Section 3 codes can be extended to solve three-dimensional Schrodinger's equation in other situations as long as the potential function and the proper boundary conditions are given.
- When solving Schrodinger's equation for eigenvalues, due to simplifications done in order to make numerical computations easier for MATLAB, there may be some minor irregularities in the outputs. (e.g.: d-shell is shifted in space)

References

- Lecture slides and notes
- David A.B. Miller. Quantum Mechanics for Scientists and Engineers. ISBN: 978-0-521-89783-9, Cambridge University Press, 2008.
- https://www.youtube.com/playlist?list=PLm8ZSArAXicL3jKr_0nHHs5TwfhdkMFhh
- https://www.mathworks.com/help/pde/ug/pde.pdemodel.specifycoefficients.html
- https://www.mathworks.com/help/pde/ug/pde.pdemodel.solvepdeeig.html