Approximation of a Hydrogen Atom in a Planar, Inversely Dependent Potential

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BACKGROUND

I wanted to find the ground state energy for a hydrogen atom placed in a potential that varies inversely to the distance normal from an infinite planar wall running through space. The wall cannot be thought of as a metal sheet; Gauss's law requires that the electric field produced by an infinitely charged plane not vary in space. This problem has no physical analog but the nature of the potential lends itself to some intuition on how the wavefunction should deform.

The reason that analytic solutions for the hydrogen atom in a field with no potential can be found is the due high symmetry of the system and the separability that symmetry confers to the equation that describes it. Real problems require the discretization of space and this is done by using finite difference methods. Computing the eigenvalues of the Schrodinger equation, even in relatively simple potentials, requires intense computation. Because I am constrained to using my laptop to find my eigenvalue, I decided to make use of the cylindrical symmetry of the problem; this allows me to solve for a slice of the wavefunction and then rotate it around a central axis in space to represent the complete wavefunction. A three-dimensional verification of my solution must still be conducted to determine the validity of my approximation of the wavefunction.

METHODS AND RESULTS

Figures not explicitly specified are plotted using N=500 and a bounding radius (R) of 5Å. The minimized energies obtained for each approximation and the corresponding set of parameters is found in *Table 1*. Constants and equations can be found in the appendix. While the ability of parameters to be logarithmically searched was verified, the actual program linearly searched out the optimal set of parameters for each approximation. This was done because the code constantly changed over time and it was convenient for me to be able to see trends in the energy as the parameter space was searched.

A N by 2N by 3 (X,Y,Z) matrix was created in Matlab. This slice is adjacent to the axis of symmetry and is 'rotated' around it to compute the probability and eigenvalue of solutions. First, a hydrogen atom was generated by evaluating its analytic wavefunction (*Equation 1*) for the 1s orbital across the matrix. The second order central difference of the wavefunction in 3D acted as my Laplacian (*Equation 2*). Together with the potential term (*Equation 3*) in the 3D Schrodinger equation (*Equation 4)* I obtained my expectation values for energy (*Equation 5*) in the central Z plane. To compute values for the total probability and the expected energy of my slice I scaled each element in the central plane by its circumference were it on a circle and added them together. (*Equation 6*) The probability density and the radial energy density for the ground state of the hydrogen atom are found in *Figures 1 and 2*.
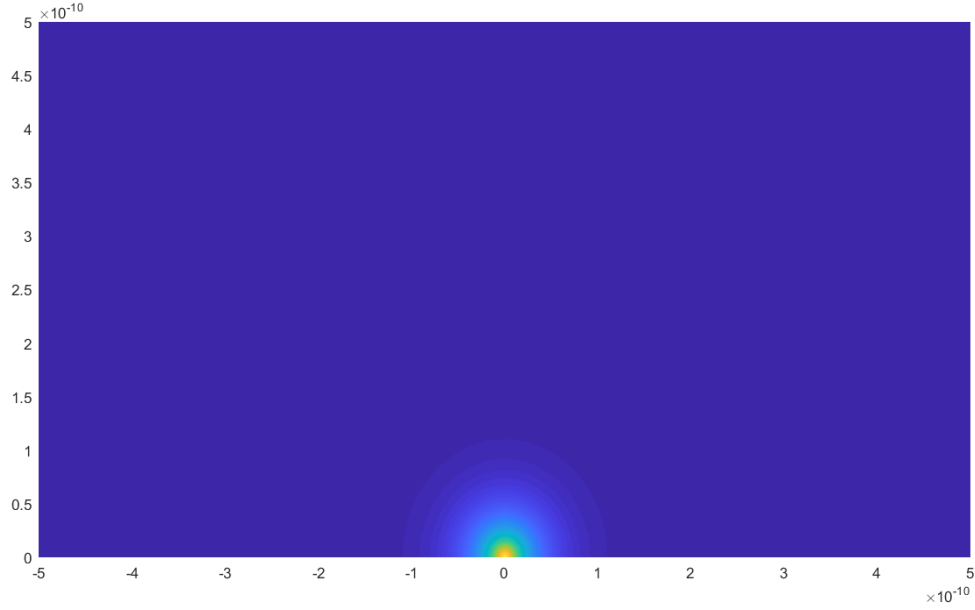
Figure 1. Plot of the probability density in a hydrogen. Units are in angstrom.
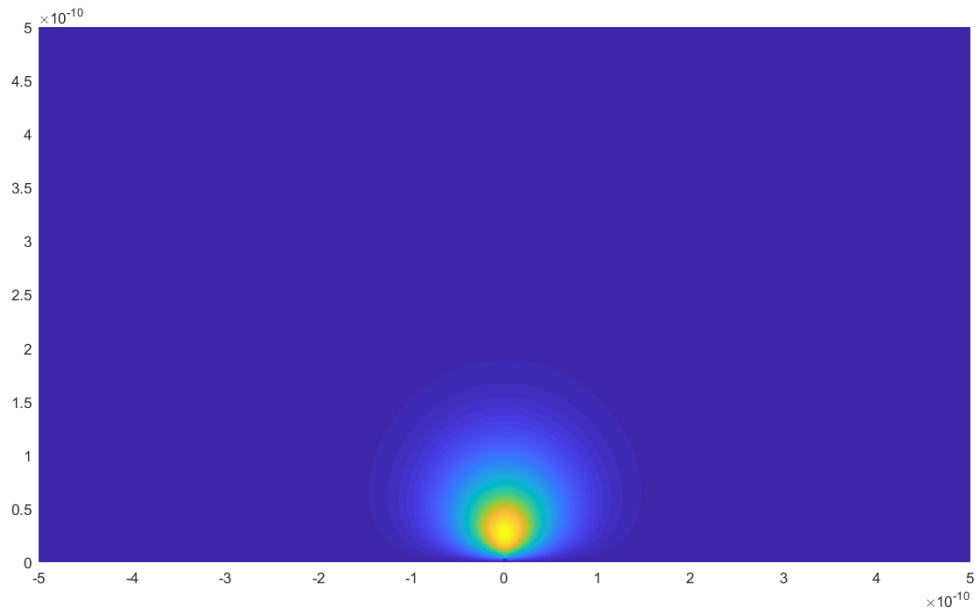

Figure 2. Plot of radial energy density in a hydrogen atom. Units are in angstrom.

With the hydrogen atom reproduced I then adjusted my step size and bounding box until I was satisfied with the result. My initial goal was to find a setting that reproduced the expected probability and energy of the hydrogen atom within 0.1% of the expected values while requiring the least computational cost so that once I varied my parameters in my approximations I could do so efficiently. Since the variation of parameters alters the probability density that is created, a renormalization step was introduced between the generation of the wavefunction and the calculation of the energy. Both the normalized and unnormalized values of probability (*Figure 3*) and energy (*Figure 4*) are plotted. Only the normalized values are subject to the accuracy threshold.
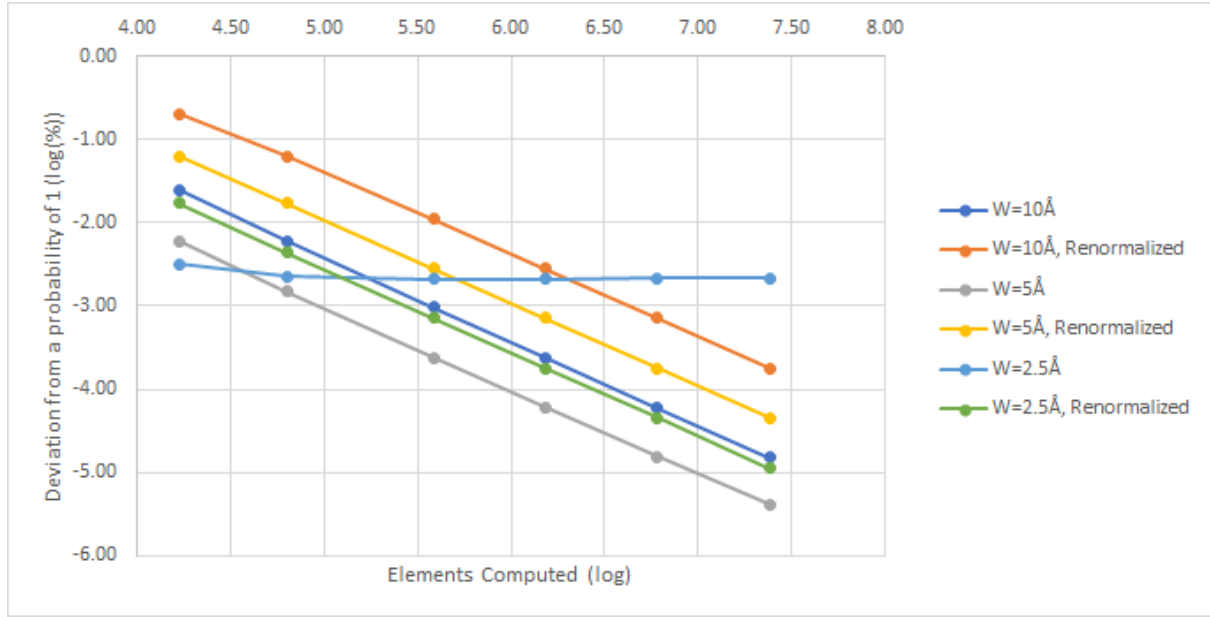
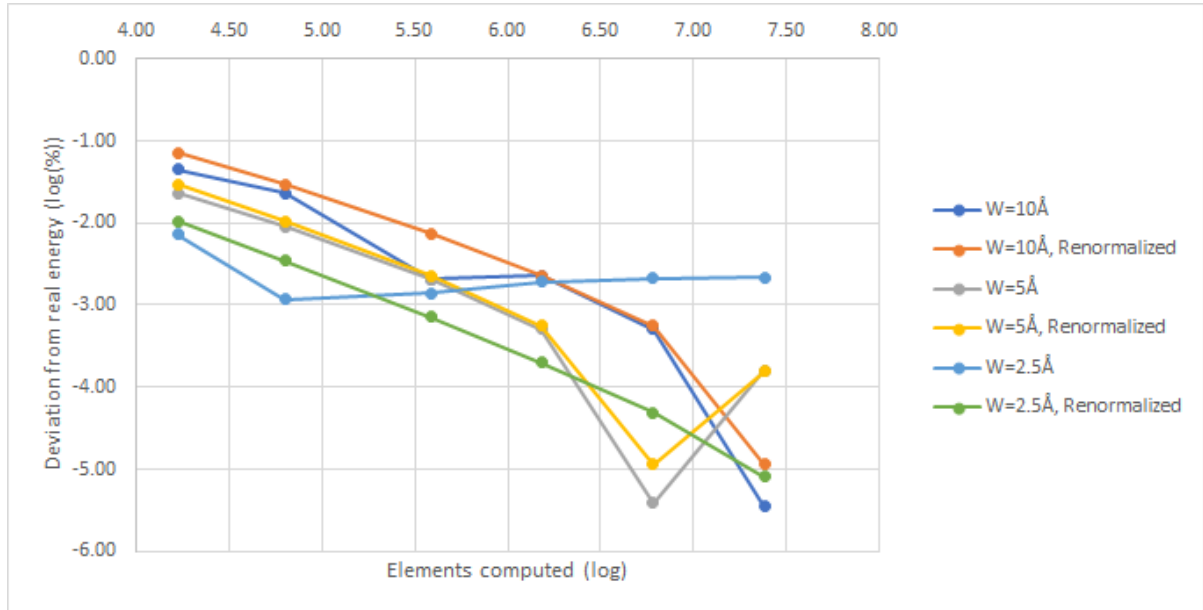*Figure 3*. Log-Log plot of probability vs the number of elements computed at different bounding sizes.

Figure 4. Log-Log plot of energy vs the number of elements computed at different bounding sizes.

The 2.5Å plot appears to plateau because the space is simply too small to fully contain the electron of the hydrogen atom. I believe that the increase in the energy deviation at 5Å in the trial with the most elements is due to my program is converging slightly below the actual value. If I loosen my constraints to an error of 1% then I can scale back to N=100 and W=2.5Å. I believe that the reduction in the elements required by a factor of 25 from the size that meets the 0.1% criteria justifies this decision. All parameter optimizations will hence be conducted using this setting. *Figures 1 and 2* are replicated in *Figures 5 and 6* with N=100 and W=2.5Å to show the space I will be working within.
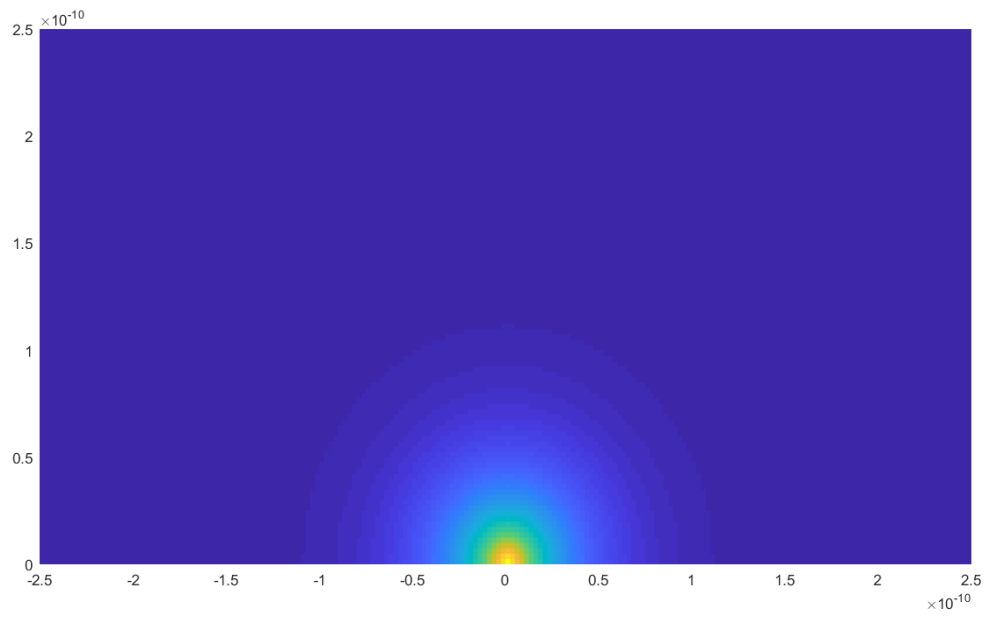
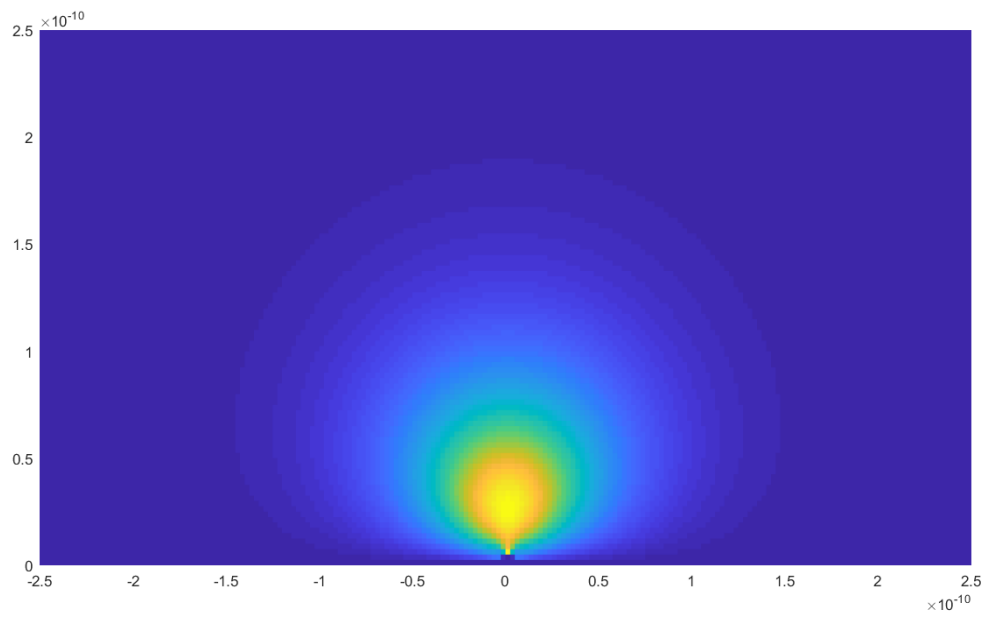*Figure 5*. Plot of the probability density in a hydrogen, N=100, R=2.5.

Figure 6. Plot of radial energy density in a hydrogen atom, N=100, R=2.5.

In all trials involving the planar potential (*Equation 7*), the location of the wall (plane) will be 2Å to the left of the hydrogen atom and act as though it has a charge of 1e. To model the hydrogen atom in a potential I have tried several different approximations. An obvious constraint caused by the infinite potential is that there should be no possibility of finding the hydrogen atom beyond it. It is trivial to set the wave function in this region to zero and then renormalize the remaining wavefunction. A second consequence of the potential is that any probability density near the wall blows up and decreases the energy of the system as may be seen in *Figure 7*.
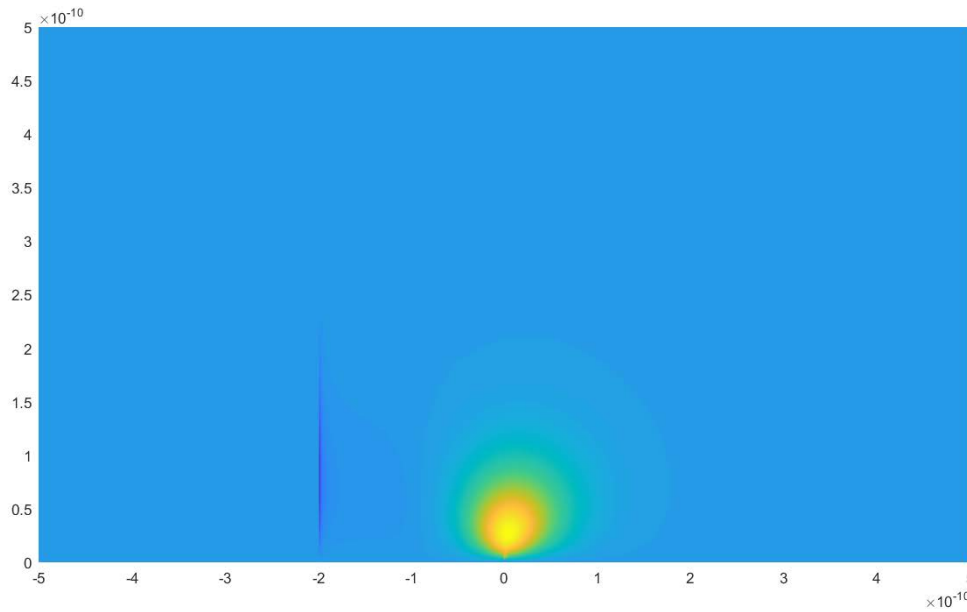

Figure 7. Plot of radial energy density in a hydrogen atom with no probability density beyond the wall and no optimization of its wavefunction.

Due to this I introduce a term called the wall exponential (*Equation 8*). This exponential asymptotically approaches one away from the wall but is zero at it. The exponential factor in this expression is the parameter which can be varied. The searchability of this parameter was verified in *Figure 8* where I simply ran through various values of the exponential factor and plotted its impact on the energy observed. The presence of multiple troughs would imply local minima and would require a non-logarithmic or stochastic search. This was not observed so a logarithmic search can be used to find the minima of this parameter. The effect of introducing an optimized wall exponential on the energy density can be seen in *Figure 9*. This term effectively eliminates the jump in energy density
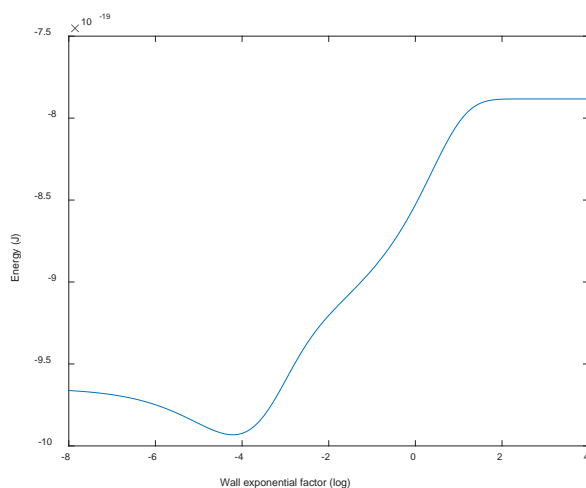

Figure 8. Semi-log plot of the wall exponential factor and the energy of the hydrogen atom in a potential with no probability density beyond the wall.

observed near the wall and significantly lowers the overall energy of the wavefunction. The asymmetry it induces in the probability density can be seen in *Figure 10*.
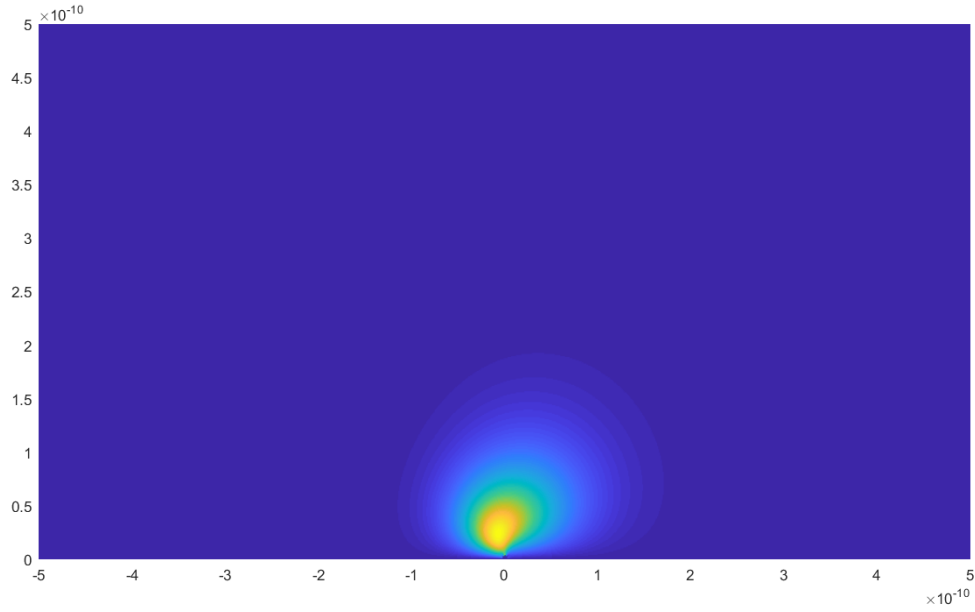

Figure 9. Plot of radial energy density in a hydrogen atom with the optimized wall exponential factor.
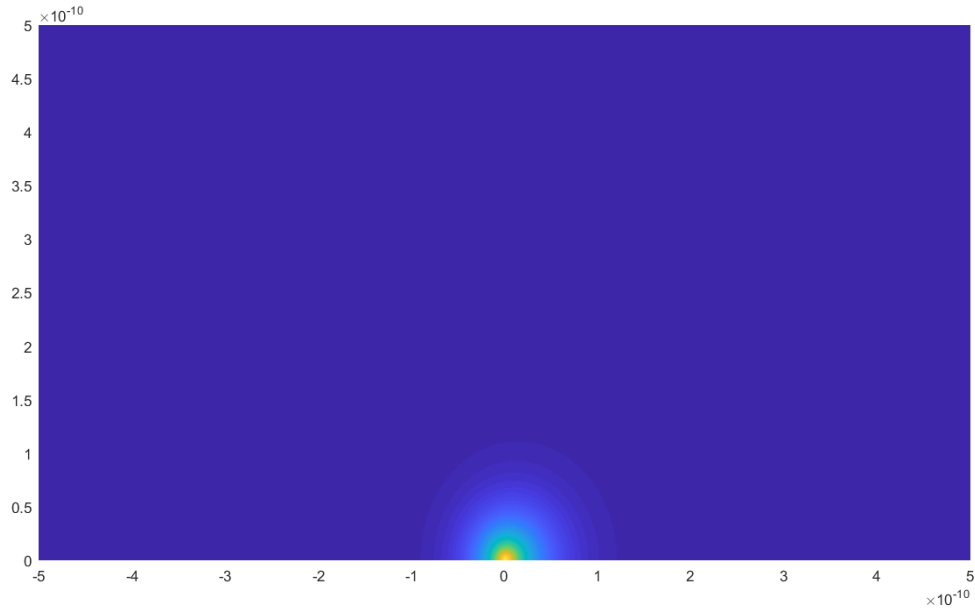

Figure 10. Plot of probability density in a hydrogen atom with the optimized wall exponential factor

The wall potential will be included in all both subsequent approximations. The two I tested were an ellipsoidal exponential representation of the hydrogen atom and a function composed of a summation of cylindrical gaussians.

The ellipsoidal exponential (*Equation 9*) acts to create an ellipsoidal wavefunction for the hydrogen atom with the atom at one of its foci (*Figure 11*). The two parameters that can be varied are the eccentricity of the wavefunction and a radial scalar. Eccentricity acts just as it would on a circle but on a sphere instead. Due to the exponential nature of the ellipsoid, for values of eccentricity greater than 0.45, this approximation appears to break down as the radially changing exponential acts to create a spiral as it is swept from the side of the hydrogen atom facing the potential to the side away from it. The plots optimal produced by this wavefunction are nearly identical to those of *Figures 9 and 10*.
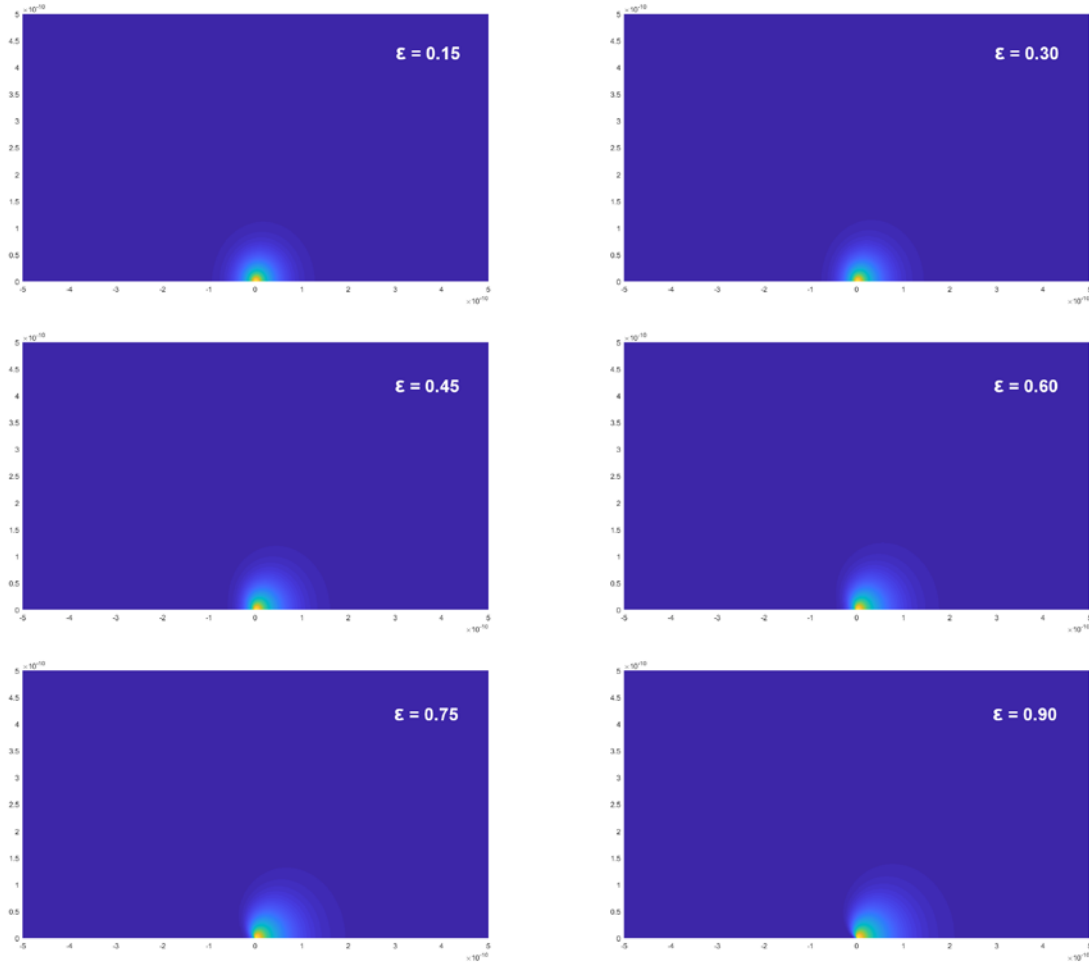

Figure 11. Impact of the eccentricity parameter on the shape of the probability density of the wavefunction.

When the eccentricity is zero the wavefunction converges to that of the hydrogen atom and as it approaches one it elongates it along one axis. The radial scalar changes the rate at which the exponential decays with distance and 'spreads out' the wavefunction more. Their impact on the energy of a hydrogen atom in no potential and the searchability of these parameters in a potential was verified in *Figure 12*. As expected, the ground state energy of the hydrogen atom in no potential was at its lowest when the eccentricity was zero and the radial scalar, one.
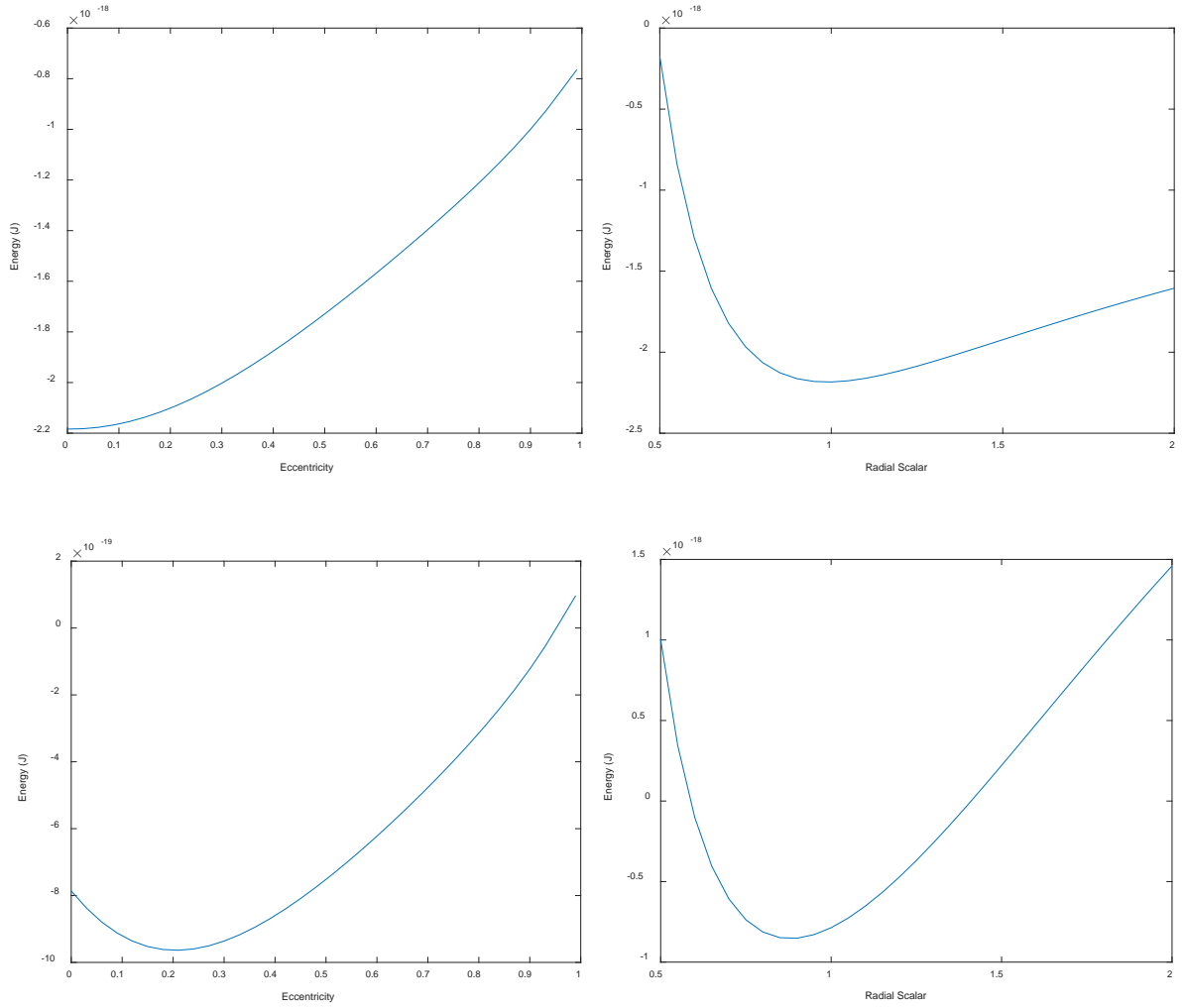
Figure 12. Plot of the eccentricities (left) and the radial scalar (right) on the energy of a hydrogen atom in no potential (top) and in a potential (bottom).

The next approximation uses a sum of cylindrical gaussians (*Equation 10*) to represent the hydrogen wavefunction (*Equation 11*). Each cylindrical gaussian would be the product of three basis gaussians if not for the radial coupling of the X and the Z; the standard deviation of X and Z must be equivalent since they are radially symmetric. As such, the radial mean must be along the axis and can be removed entirely. This leaves only the mean Y position, the standard deviation in Y, and the radial standard deviation. Our search space can be limited by only allowing the mean Y position to fall behind the hydrogen atom.

The summation is created by finding the optimal set of parameters for a gaussian and then adding it to the sum; each subsequent term is evaluated based on its contribution to the sum and will only be added if it decreases the energy. Since the sum is renormalized the sum should theoretically converge to the actual wavefunction and the contribution of each additional term is inversely proportional to the number of terms already in the summation. Because the terms appear in a sum the searchability of their parameters have been evaluated in relation to the first term and on the second term as it is added to the first. Searchability here is evaluated with only one variable parameter; the best approximations that were found for the first and second terms had their other parameters fixed (*Figure 13*). The parameters of the first term can be searched logarithmically but for the second and presumably later terms a

stochastic or linear search will be neccesary. It is unknown whether or not the mean Y position in later terms remains easily searchable as it has a clear trough in the second term.
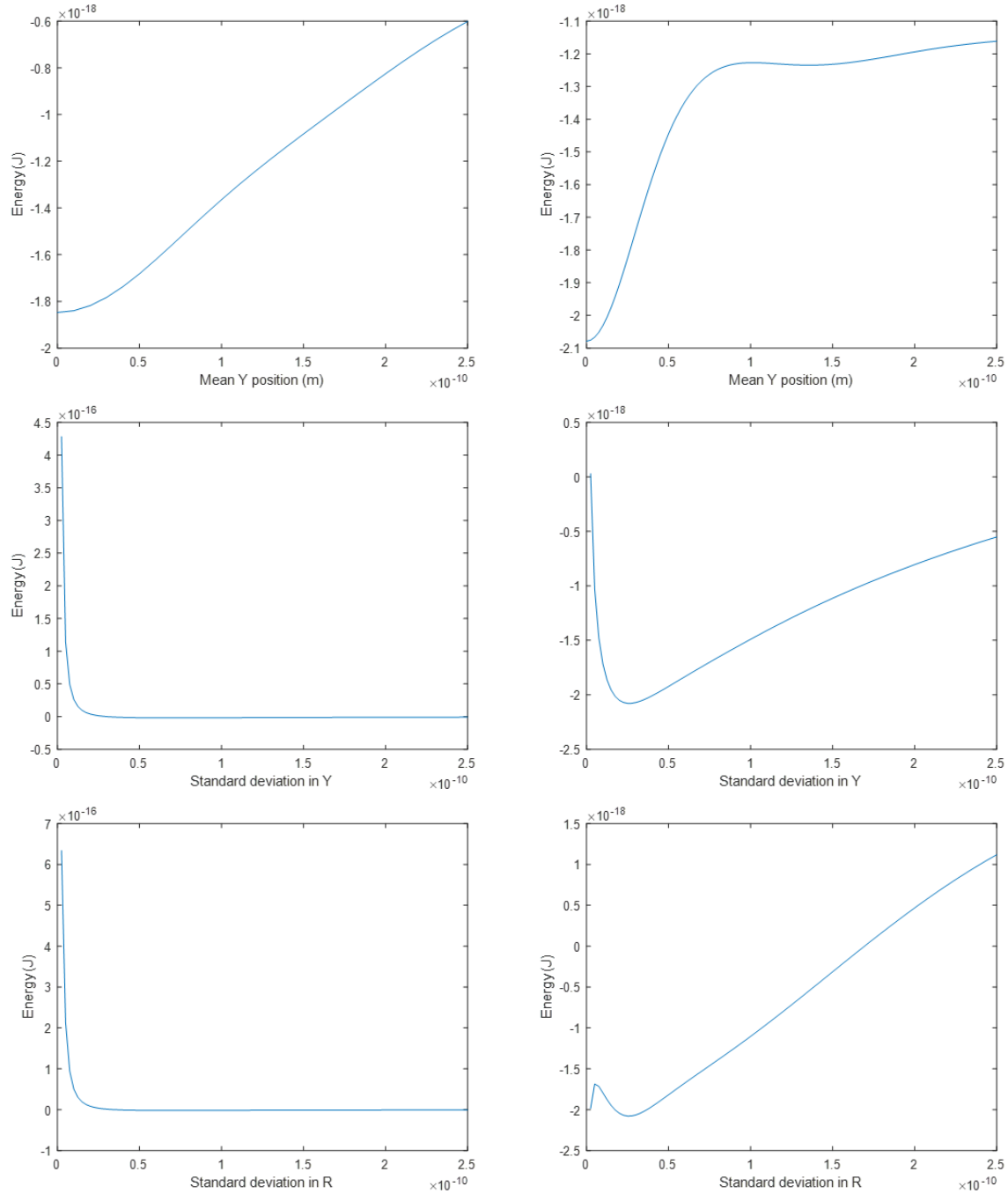

Figure 12. Plot of the effects of varying the mean Y postition (top), the standard deviation in Y (middle), and the standard radial deviation (bottom) on the energy of the one (left) and two (right) term approximation of a hydrogen atom in no potential using cylindrical gaussians.

What I found in my testing is that that terms should have an additional weighting parameter because in an unweighted scenario the third term (and likely beyond) preferentially adds weight to the wavefunction along the axis of symmetry (*Figure 13*). The radial contribution to the total probability here is zero but the added curvature impacts the overall energy of the wavefunction and results in a lower energy than the ground state. This effect can be seen in

the bottom-right plot of *Figure 12* as the radial standard deviation approaches zero. ***This is a key limitation of my choice to use radial weight to reproduce the wavefunction from a slice.***
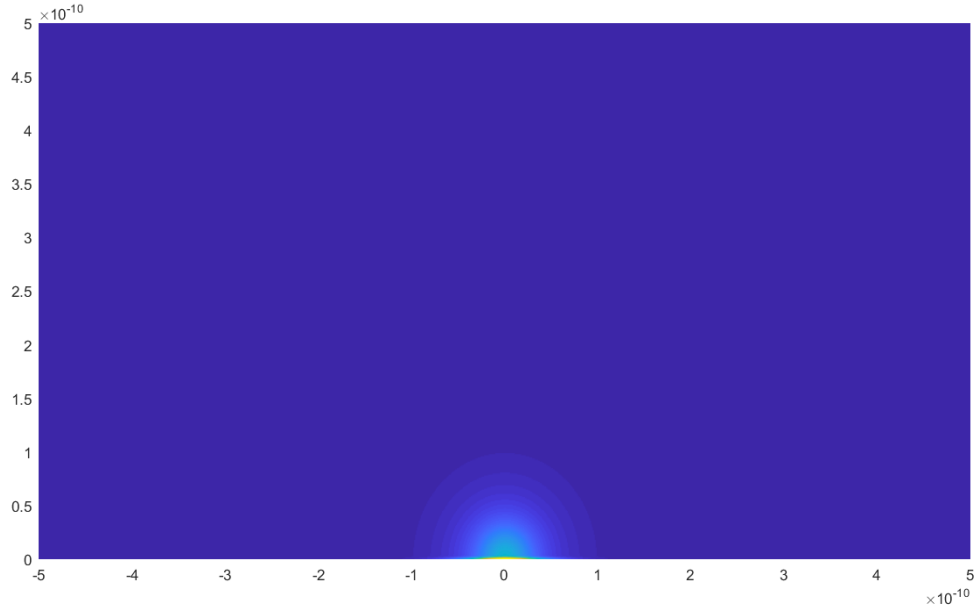

Figure 13. Axial elongation in the third order cylindrical gaussian approximation of the hydrogen atom.

Despite the failure of the third term, just the sum of first and second terms were able to well represent the wavefunction of the hydrogen atom. The first term and the second term act to approximate the tail and the cusp of the wavefunction. This can be clearly seen in the side profiles of the probability densities (*Figure 15*). The radial energy density and the probability density of the sum of the first and second terms may be seen in *Figures 16 and 17*.
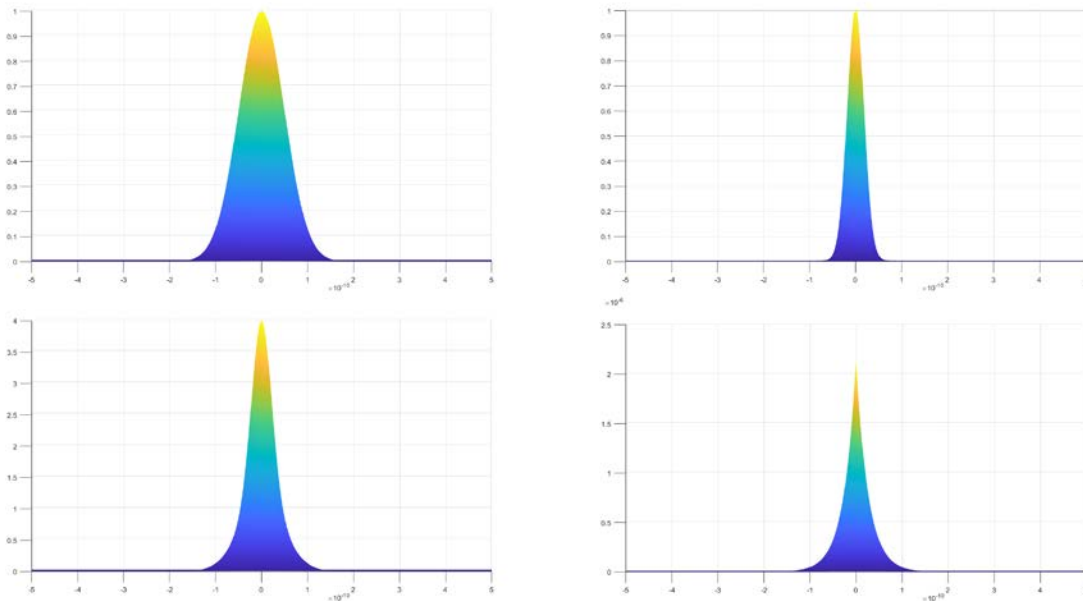

Figure 14. Side profiles of the first term (top-left), the second term (top-right), the sum of terms (bottom-left), and the hydrogen atom (bottom-right).
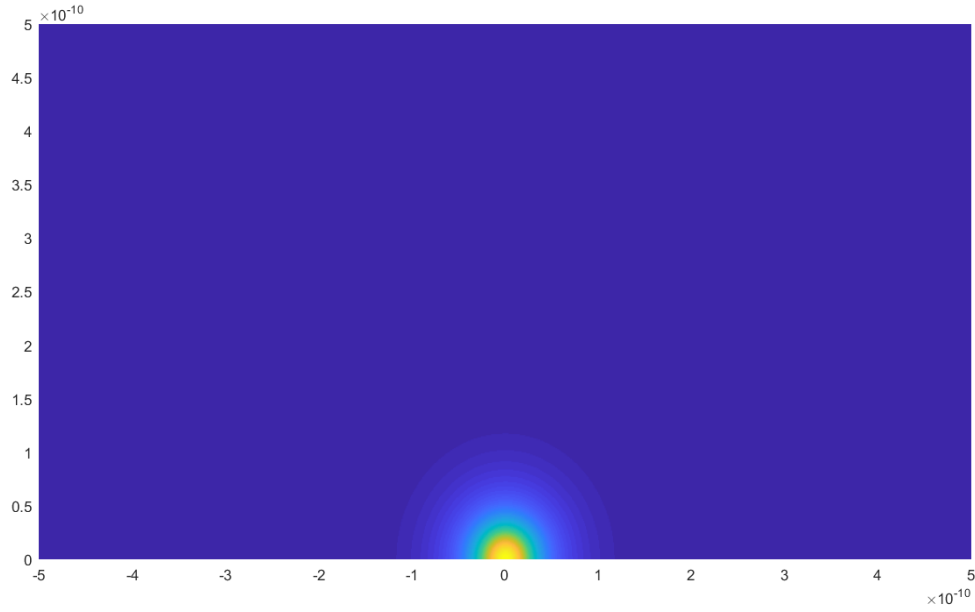
Figure 15. Plot of probability density of the two-term cylindrical gaussian approximation of the hydrogen atom.

Figure 16. Plot of the energy density of the two-term cylindrical gaussian approximation of the hydrogen atom.

In a potential the unweighted approximation was again limited to only two terms. The expected asymmetry in the wavefunction did indeed appear (*Figures 17 and 18*). I do not know why the energy density plots of the cylindrical gaussian approximations differs so starkly from those of the others. I believe that part of it is that the terms which represent the cusp and the tails are poor at representing the region in between. Additionally, homogeneity is represented poorly on color plots and the area with the most curvature is simply smaller.

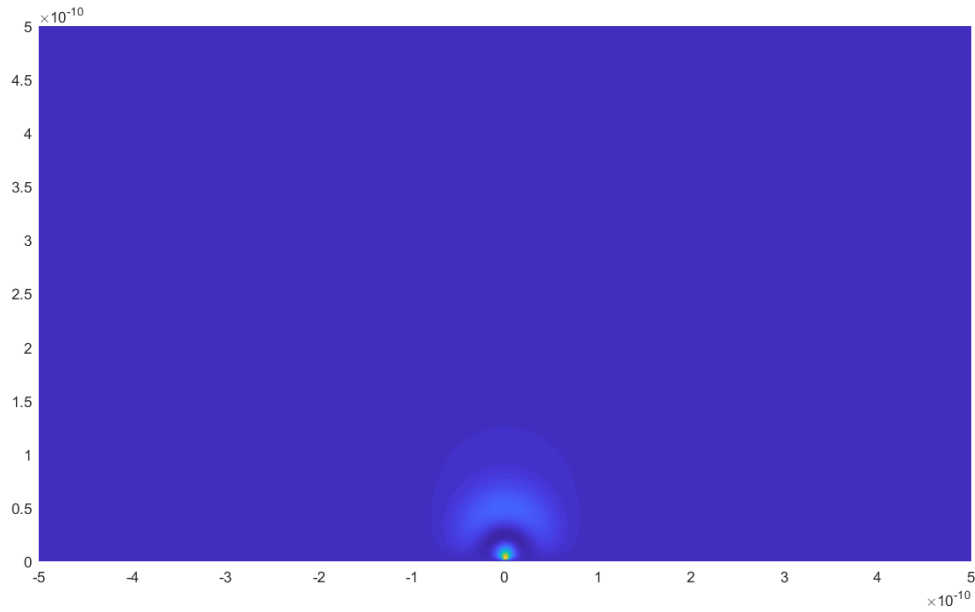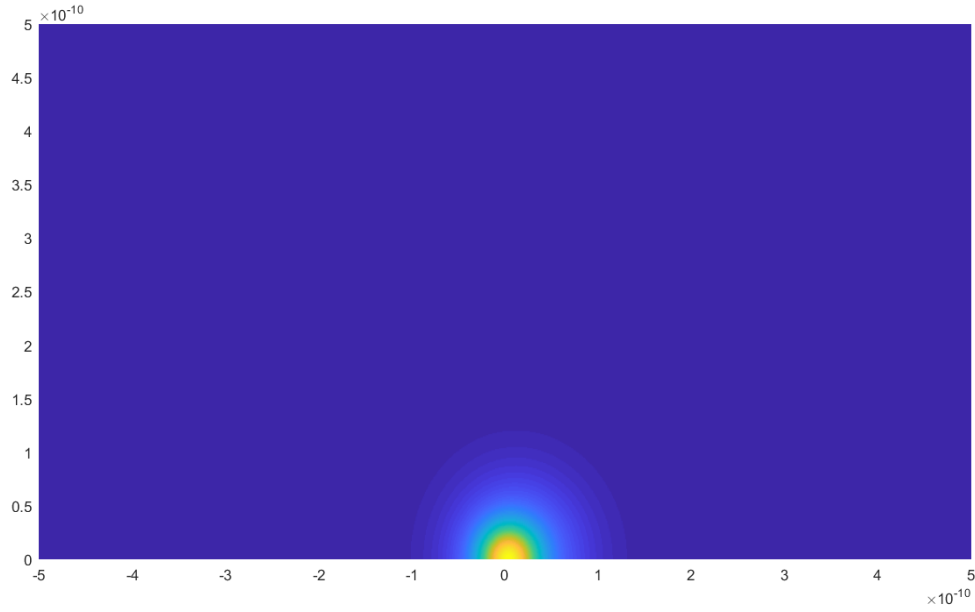*Figure 16.* Plot of probability density of the two-term cylindrical gaussian approximation of the hydrogen atom in a potential.
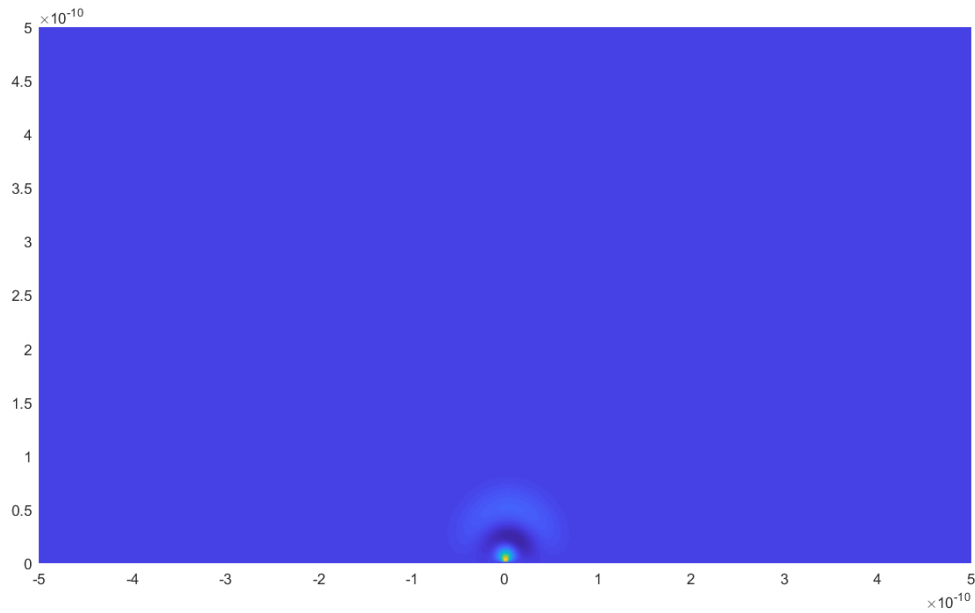
Figure 17. Plot of the energy density of the two-term cylindrical gaussian approximation of the hydrogen atom in a potential.

To verify the ground state energy of the wavefunction in the potential I turned to a pre-existing solver, NuSol. This program iteratively solves a 3D matrix until it converges. There are a variety of matrix representations and solvers available in the program with the default using a discrete variable representation matrix and the FEAST algorithm. I left these settings as is. Computing a grid size of N=101 appears to be the limit of my laptop. NuSol requires a much larger grid size than the slice method to converge to the energy of the hydrogen atom and significantly more resources.

CONCLUSIONS

I tried a variety of methods to calculate the energy of the hydrogen atom in a potential while trying to minimize the number of parameters needed to represent it. To both ends I believe that I was reasonably successful.

The single most effective term I created was the wall exponential as it both induced asymmetry in the wavefunction and eliminated probability density near the wall. The ellipsoidal exponential approximation is natively better than the analytic 1s representation (9.428E-19 vs 6.164E-19) but once the wall exponential was introduced the resulting wavefunctions became nearly identical (9.885E-19 vs 9.873E-19). With the wall exponential, the ellipsoid results in a slightly lower ground state energy but the computational cost that searching through three parameters incurs far outweigh the marginal benefits of using a more complex approximation.

The sum of gaussians approach appeared to be converging toward the energy of the hydrogen atom in no potential until the quirk caused by my radial weighting resulted in a large error. With appropriate weighting, I believe that this approach offers the greatest chance of beating the record set by the wall exponential and the ellipsoid. The downside of this is that each term would have five parameters to optimize and this does not account for the need to iteratively reoptimize earlier terms based on the latter terms added. I believe that the only way to reasonably approach this is to add in some clever way to mutate and evolve the set of basis wavefunctions that make up the sum. I attempted something like this early on but at that time I was treating the gaussians as factors to be multiplied together instead of terms in a sum.

The NuSol program appears to be converging towards the ground state energy of the hydrogen atom in no potential but it does so very slowly as the grid size is increased. This is very problematic as the memory and computational cost are proportion to the number of elements and scales with N^3. Despite how costly it is, it does provide a valuable check on the results I have obtained using simpler methods. The value obtained from NuSol for N=101 was 7.111E-19 which verifies the value of 9.885E-19 J that I have obtained is in the neighborhood of the real value. Based on the energies returned by the different grid sizes that I tried, NuSol had yet to begin asymptotically converging to a specific value of energy for the hydrogen atom in a potential.

Table 1. Minimized energies obtained in attempts to the numerical representation of the hydrogen wavefunction in no potential and in the potential, slice results evaluated at N=500 and R=5Å.

No probability beyond wall = NPBW, wall exponential = WE

Potential (Y/N)	Methods	Parameters	Energy (J)
N	Expected		2.179E-18
N	Analytic 1s		2.180E-18
N	Ellipsoid exponential (converged to analytic 1s)	$\varepsilon = 0$ $p = 1$	2.180E-18
N	First cylindrical gaussian	$\bar{y}_1 = 0$ $\sigma_{y1} = 7.03\text{E-}11$ $\sigma_{r1} = 7.03\text{E-}11$	1.848E-18
N	Sum of first two cylindrical gaussians	$\bar{y}_2 = 0$ $\sigma_{y2} = 7.03\text{E-}11$ $\sigma_{r2} = 7.03\text{E-}11$	**2.083E-18**
N	Sum of first three cylindrical gaussians	$\bar{y}_3 = 0$ $\sigma_{y3} = 5.00\text{E-}11$ $\sigma_{r3} = 0.10\text{E-}11$	2.422E-18
N	NuSol	N=63 R=2.5Å	1.806E-18
N	NuSol	N=81 R=2.5Å	1.869E-18
N	NuSol	N=101 R=2.5Å	1.917E-18
Y	Analytic 1s, NPBW		6.164E-19
Y	Analytic 1s, NPBW, WE	$\omega = 5.10$	9.873E-19
Y	Ellipsoid exponential, NPBW	$\varepsilon = 0.218$ $p = 0.960$	9.428E-19
Y	Ellipsoid exponential, NPBW, WE	$\varepsilon = 0.218$ $p = 0.960$ $\omega = 6.10\text{E-}3$	**9.885E-19**
Y	First cylindrical gaussian	$\bar{y}_1 = 0$ $\sigma_{y1} = 7.22\text{E-}11$ $\sigma_{r1} = 7.05\text{E-}11$ $\omega = 6.41\text{E-}3$	6.549E-19
Y	Sum of first two cylindrical gaussians	$\bar{y}_1 = 0$ $\sigma_{y1} = 2.62\text{E-}11$ $\sigma_{r1} = 2.61\text{E-}11$ $\omega = 5.25\text{E-}3$	8.922E-19
N	NuSol	N=63 R=2.5Å	6.525E-19
N	NuSol	N=81 R=2.5Å	6.721E-19
N	NuSol	N=101 R=2.5Å	7.111E-19

APPENDIX A – VARIABLES AND EQUATIONS

a_0 = Bohr radius

ε = Eccentricity

e = Electron charge

N = Grid points

R = Grid size (m)

s = Grid spacing (m)

ϵ_0 = Permittivity of free space

p = Radial scalar

r = Radius from axis of symmetry

μ = Reduced mass

ℏ = Reduced Planck constant

ω = Wall exponential factor

y_w = Wall position

Equation 1. Analytic representation of the 1s hydrogen wavefunction

$$\psi_{x,y,z} = \frac{1}{\sqrt{a_0^3 \pi}} e^{-\frac{\sqrt{x^2+y^2+z^2}}{a_0}}$$

Equation 2. Finite difference representation of the Laplacian in cartesian coordinates

$$\nabla\psi_{x,y,z} = (\psi_{xx} + \psi_{yy} + \psi_{zz}) =$$

$$\frac{1}{s^2}(\psi_{x+1,y,z} + \psi_{x-1,y,z} + \psi_{x,y+1,z} + \psi_{x,y-1,z} + \psi_{x,y,z+1} + \psi_{x,y,z-1} - 6\psi_{x+1,y,z})$$

Equation 3. Potential of the hydrogen atom

$$V_{x,y,z} = -\frac{e^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}$$

Equation 4. Schrodinger equation

$$\nabla\psi + V\psi = E\psi$$

Equation 5. Energy density

$$E_{x,y,z} = s^3\psi_{x,y,z}\left(-\frac{\hbar^2}{2\mu}\nabla\psi_{x,y,z} + V_{x,y,z}\psi_{x,y,z}\right)$$

Equation 6. Finite cylindrical approximation to the expectation energy

$$E = \iiint_{-\infty}^{-\infty} \psi(\nabla\psi + V\psi)\, dxdydz \approx \sum_{y=-N}^{N}\sum_{x=0}^{N} 2\pi x E_{x,y,z}$$

Equation 7. Hydrogen atom potential with the wall

$$V_{w\,x,y,z} = \frac{e^2}{4\pi\epsilon_0}\left(-\frac{1}{\sqrt{x^2+y^2+z^2}} + \frac{1}{y-y_w}\right)$$

Equation 8. Wall exponential term

$$L_{y,\omega} = 1 - e^{-\omega\left(\frac{y-y_w}{s}\right)}$$

Equation 9. Ellipsoid exponential approximation of the hydrogen wavefunction in a potential

$$\psi_{x,y,z,p,\varepsilon,\omega} = L_{y,\omega}\frac{1}{\sqrt{a_0^3\pi}}e^{-\frac{\sqrt{x^2+y^2+z^2}}{a_0 p\left[1-\varepsilon\sin\left(\tan^{-1}\left(-\frac{y}{\sqrt{x^2+z^2}}\right)\right)\right]}}$$

Equation 10. Cylindrical gaussian

$$G_{x,y,z,\bar{y},\sigma_r,\sigma_y} = e^{-\frac{(\bar{y}-y)^2}{2\sigma_y^2}-\frac{x^2+z^2}{2\sigma_r^2}}$$

Equation 11. Nth order cylindrical gaussian representation of the hydrogen wavefunction in a potential

$$\psi_{x,y,z\,M} = \sum_{m=1}^{M} L_{y,\omega m}G_{x,y,z,\bar{y}_m,\sigma_{rm},\sigma_{ym}}$$