Comparing the Accuracy and Runtime of Variational Monte Carlo to the
Direct Eigensolver Method to Find the Ground State Energy of Various
Physical Quantum Systems

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# 1 Abstract

Analytic methods of solving the time independent Schrödinger equation rely heavily on approximations. Computational methods increase accuracy relative to an analytic solution in finding ground state energies of various involved quantum potentials. Two algorithms, variational Monte Carlo and the direct eigensolver, are programmed and their accuracy and runtime in solving for the ground state of a given potential is determined.

# 2 Executive Summary

Nearly every problem in the field of quantum mechanics comes down to solving the Schrödinger equation to determine the quantum state of a system known as the wavefunction. The interesting aspect of the wavefunction is that when it is squared, it becomes a probability distribution which relays information regarding the most likely state of the system. A real-life example of this is the following. For a significant amount of time, the science community believed that electrons moved in determinable paths around the center of the atom, the nucleus, similar to how planets move around the sun. Eventually, Erwin Schrödinger hypothesized that it is impossible to know where the electron is in an atom because the electron behaves as a wave opposed to a particle with a definitive position. In this case, the Schrödinger equation can be solved for this system to determine the wavefunction for the electron. The square of the wavefunction determines the probability distribution for the electron, or where it is most likely located.

The time independent Schrödinger equation always has the same form of the sum of the kinetic and potential energies of a system; however, depending on the potential, the Schrödinger equation changes, which will give us different wavefunctions for different systems. For stationary states (or states that do not depend on time, which simplify our solutions), the solution to the Schrödinger equation give information about the stationary state wavefunction as well as the energy of the system. The total energy of a quantum system is the sum of the kinetic and potential energies. Kinetic energy is the energy associated with motion; for instance, a moving baseball has a high kinetic energy compared to a stationary baseball. Potential energy is energy measured in relation to a fixed value. Potential energy is less intuitive; however, it can be understood by discussing gravitational potential energy. Imagine holding a ball on the top of the hill. This ball has a high amount of gravitational potential in relation to the ground because as the ball is released, this potential energy will transfer into kinetic energy, and the ball will speed up towards the ground.

The goal becomes solving the Schrödinger equation for a system after inputting the kinetic and potential energies into our Hamiltonian in units of electron volts. The kinetic energy is generally the same for each system; however, the inter-

esting difference between wavefunctions for different systems comes from their potentials. For example, for the hydrogen atom, we want to determine the wavefunction for the electron orbiting the nucleus by noting that there is a particular potential energy between the electron and the nucleus depending on the inverse distance between them. By this, the electron has a lower potential closer to the nucleus, which makes intuitive sense due to the fact that the nucleus applies an attractive force on the electron.

In general, it can be very onerous to solve the Schrödinger equation due to the fact that the nature of the equation can be interpreted either as a second order partial differential equation or an eigenvalue equation, both of which can be difficult to solve. It is always beneficial to apply the use of a computer to find approximate solutions for the wavefunctions for these challenging potentials. In this project, two algorithms are created and tested with various potentials, each increasing in complexity. With these algorithms, we attempt to calculate the ground state, or lowest energy state, of a system, which has many important real-life implications.

We first develop an algorithm based on the variational principle of quantum mechanics using the Monte Carlo computational method. To understand the algorithm, we discuss what the variational principle is, as well as how to use the Monte Carlo method

An observable in quantum mechanics is any quantity that can observed via an experiment. The particular observable we are interested in is approximating is the energy which is found through the Hamiltonian of the system. Solving the Schrödinger equation determines what are known as the eigenfunctions, or potential states of the system, depending on the various energies. To simplify this prescription, imagine an atom with various energy levels. Each energy level corresponds to a different eigenfunction describing the state of the electron at this energy level. While finding these eigenfunctions are difficult, we instead try to go in the other direction: we guess what the eigenfunction is and then calculate the energy. The variational principle states that the expected value of the energy, or what energy you expect to get if you perform an experiment, will be greater than, or equal to, the ground state energy of the system. From this principle, we see that if we guess what the state is, calculate the energy, and then slightly alter the guess made for the wavefunction, we can determine if this wavefunction is a more accurate representation of the true, physical ground state. If the guess we make decreases the energy, then we know that this new wavefunction is a better guess for what the wavefunction of the ground state is. We then repeat this process with this new wavefunction as our current state. The benefit of using a computer is that it can quickly alter the wavefunction and calculate the energy.

The Monte Carlo method allows us to perform the variational principle computationally. The Monte Carlo method is an algorithm that repeatedly performs

random samples to obtain a numerical result. In our case, we can repeatedly randomly sample the wavefunction and alter a very small portion of it to determine if this lowers our energy. With this method, we can choose a very simple wavefunction, write code to calculate the energy given this input, and use our Monte Carlo algorithm to vary the wavefunction until we are constantly getting roughly the same energy for many iterations in succession. In this case, we say this is the ground state energy of the system for the particular potential.

Another algorithm that can be used to determine the ground state energy is a direct eigensolver. Quantum mechanics can be completely described in the language of linear algebra, and hence, the Schrödinger equation can be written as what is known as an eigenvalue equation.

Linear algebra is a branch of mathematics that gives us a neat formalism for solving systems of linear equations. When we have many linear equations of the form $a_1 x_1 + a_2 x_2 + ... + a_n x_n = c$ where each $a_i$ is a constant (as well as $c$) and our variables are the $x_i$'s, linear algebra allows us to find every $x_i$ such that each of our equations will be solved with the same variables. This solution can be represented as a list of numbers, known as a vector; the coefficients (the $a_i$'s) for each equation are represented in a matrix. While not particularly intuitive, we can represent our wavefunction in Hilbert space (a vector space) as a vector and operate the Hamiltonian (which is the matrix corresponding to the total energy of the system) on it, we get back the energy of the vector. The formalism of quantum mechanics allows us to represent our Hamiltonian as a matrix, which we can use an algorithm to find the energy of the system, called the eigenvalue.

Once we have these algorithms, we can program the energies for the following potentials: the hydrogen atom, the helium atom, and the hydrogen molecule ion($H_2^+$). The important question to ask is which algorithm converges the fastest and gives the most accurate energies in relation to theoretical and experimental observations. The final chapter will dive into determining runtime of both sets of code as well as accuracy compared to experimental results.

A real-life use of these codes is to find the ground state energies for much more complicated potentials. A lot of information can be discovered from studying the form of the wavefunction, and a computer, after verifying our ground state energy matches experimental results, allows us to determine the wavefunction without using convoluted analytic approximations.

# Contents

# 3   Discretizing the Wavefunction

A wavefunction, discussed in the executive summary, is a representation of the quantum state of the system (The wavefunction is represented by the Greek letter psi: $\psi$). Its interpretation can be extended mathematically to representing a probability distribution, and thus the most likely state of a system. Physically, the wavefunction is a continuous function defined in all space. For example, the function $f(x) = x^2$ is continuous and defined in all space because for any value of $x \in \mathbb{R}$ has a mapping to its value, $f(x)$. The wavefunction works in the same manner.

A problem emerges, however, when trying to model a wavefunction using a computer. The computer cannot represent a continuous function defined over all space because it cannot store that much information (it cannot store an infinite amount of information). Because of this, we have to limit our representation of the wavefunction. For instance, we model our wavefunction as discrete points, instead of a continuous line. The spacing between points we represent as $dr$ and as we shrink $dr$, we expect to receive a more accurate answer. The problem is that when we shrink $dr$, it takes the computer a longer time to run.

Another stipulation is that we have to determine "how far" out in space we will go. By this, we mean that we have to choose the number of points (maybe 1,000, maybe 10,000...) that will allow us to get accurate answers. The problem again is that if we choose a very large number of points, the computer will again take a longer time to run.

The fundamental problem of these algorithms is choosing $N$ (the total number of points) and $dr$ (the distance between the discrete points) such that our

computer converges to an answer quickly and the answer is accurate. The computational cost is dependent on both $dr$ and $N$ and we must determine what is more valuable in our programs, a large volume, or a fine resolution.

For the entirety of this thesis, we invoke natural units by setting $\hbar = c = \epsilon_0 = 1$ so that length (e.g. $dr$) is measured in $1/eV$ and mass (e.g. $m_e$) is measured in $eV$.

# 4    Chapter 1: Variational Monte Carlo

## 4.1    The Variational Principle

### 4.1.1    Overview of the Variational Principle

The most general form of the Schrödinger equation for a given potential, $V(\vec{r})$, is written as:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = -i\hbar\frac{\partial\Psi}{\partial t} \tag{4.1}$$

or written in Dirac notation as the time independent Schrödinger equation, (TISE):

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle \tag{4.2}$$

The variational principle of quantum mechanics allows for the ground state energy of a given potential to be approximated when standard analytic methods are insufficient or too complex. For a given Hamiltonian, $\hat{H}$, the variational principle gives an upper bound approximation to the ground state energy, $E_{gs}$. The variational principle is stated as:

$$E_{gs} \leq \langle\Psi|\hat{H}|\Psi\rangle = \langle H\rangle \tag{4.3}$$

The proof of this principle hinges on the facts that $\Psi$ can be written as a linear combination of the Hamiltonian's eigenvectors, $\Psi = \Sigma c_n\psi_n$ and that $\Psi$ is normalized, $\langle\Psi|\Psi\rangle = 1$. Intuitively, this principle states that the ground state energy of the wavefunction for a given potential must be less than or equal to

the expectation, or average, total energy of any arbitrary state. To put this principle to use analytically, a viable trial wavefunction can be used with the only stipulation that it is normalized. Next, $\langle H \rangle$ is calculated with this trial wavefunction to yield an upper bound on the ground state energy. As the trial wavefunction is perturbed by means of changing various parameters or by choosing a completely new trial wavefunction, a more accurate upper bound can be computed. If the trial wavefunction selected happens to be the ground state wavefunction for the given potential, The variational principle will yield $E_{gs} = \langle H \rangle$.

### 4.1.2 Analytic Solution to the Hydrogen Atom Potential using the Variational Principle

A common example of using the variational principle analytically is in solving the TISE for the hydrogen atom potential,

$$V(\vec{r}) = \frac{-e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}$$

but for the ground state, we know $n = 1$, thus $l = 0$, so the second part of the potential term vanishes. Although the ground state wavefunction is well known, allow us to guess a trial wavefunction in the form of a Gaussian with variable parameters for the width and height of the Gaussian: $\psi(r) = Ae^{-br^2}$. Using Dirac notation, we know that

$$\langle H \rangle = \langle \psi | H | \psi \rangle = \int \psi^* \hat{H} \psi dV$$

After $\psi$ is normalized and $\langle H \rangle$ is calculated, in terms of our variable parameter b, we obtain that the expectation of the total energy is $\langle H \rangle = \frac{3\hbar^2 b}{2m_e} - \frac{e^2}{\sqrt{2}\pi^{3/2}\epsilon_0}b^{1/2}$. This tells us that as we vary b, the expectation of $H$ can fluctuate. Therefore, if

we find the minimum of $H$ as a function of $b$, we will known which $b$ value gives the best approximation to $E_{gs}$. To do this, we will differentiate $\langle H \rangle$ with respect to $b$, set it equal to zero and find which $b$ gives us the best approximation. After doing so, we find that $b_{min} = \frac{m_e^2 e^4}{18\hbar^4 \pi^3 \epsilon_0^2}$. Plugging in this value of $b_{min}$ into $\langle H \rangle$ will give us the upper bound for the ground state energy: $\langle H \rangle_{min} = \frac{-m_e e^4}{12\pi^3 \epsilon_0^2 \hbar^2} \approx -11.5eV$. As we know, the true ground state for this potential is $-13.6eV$ which gives us a roughly 15.4% error. As a sanity check, using the true ground state of the hydrogen atom,

$$\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

gives us $-13.6eV$, which is the analytic form as we would expect.

This is the basis of variational Monte Carlo which allows us to use the Monte Carlo algorithm to find an approximation to the ground state for a given potential which will be discussed in the following section.

## 4.2 Variational Monte Carlo Method

### 4.2.1 Overview of Variational Monte Carlo

Variational Monte Carlo utilizes the Metropolis algorithm to optimize the wavefunction and obtain the best possible approximation to the ground state energy. We use this algorithm to find the wavefunction that gives the lowest possible energy. In summary, the Metropolis algorithm is as follows:

1. Begin with the initial state of the system

2. Perturb the system slightly

3. Calculate the energy of the system after the small perturbation

4. If this suggested move decreases the energy, accept this move unequivocally and allow this new state to be the current state of the system

5. Otherwise, if the suggested move increases the energy, accept the move based on the Boltzmann probability: $P(s) = e^{-\Delta E_s/kT}$

This Boltzmann probability gives us a variable parameter to make sure that our code does not get stuck in a local minimum, opposed to the global minimum. If we allow the system to 'wiggle' by allowing an increase in energy to be a potential new state of the system, we allow our code to find its way out of local minima. Variational Monte Carlo uses this algorithm by taking a trial wavefunction, adjusting the wavefunction by a specific suggested move, re-calculating the energy of the wavefunction, and accepting/rejecting based on the above rules.

The following graph shows how the system may accidentally get stuck in a false minimum:
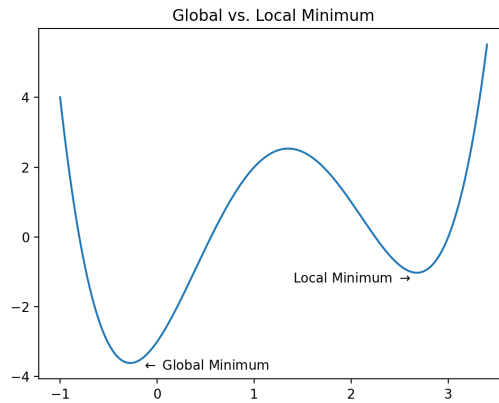


Figure 1: Local vs. Global Minimum

By adding in the Boltzmann probability,

$$P(s) = e^{-\Delta E_s / kT}$$

and choosing an appropriate simulation temperature $(kT)$, we allow an increase in energy to let the system rise up along these parabolas and potentially "escape" so that we do not get stuck in a false minimum. It is important to reiterate that the temperature has no physical meaning; it is purely part of our minimizing algorithm.

The first test of the VMC algorithm is done using the hydrogen potential above with a linear initial trial wavefunction of a decreasing linear function: $\psi(r) = N - r$ (We choose the number of points N to ensure the wavefunction tends towards zero at the boundary). Also, this choice of wavefunction is spherically symmetric, which it must be as we know ground state wavefunctions are of this form.
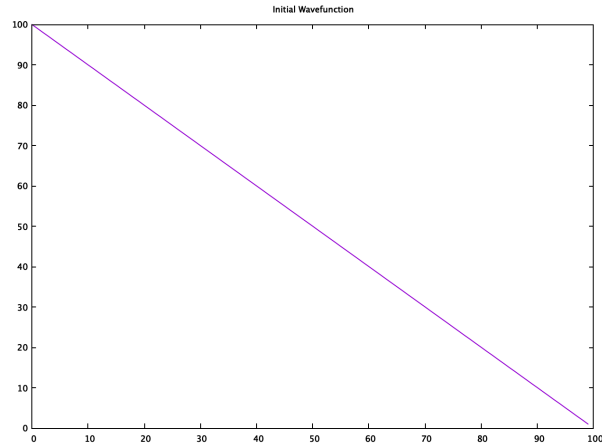


Figure 2: Initial Wavefunction

The suggest algorithm that was implemented is to invoke a Gaussian 'bump' about a random point in the wavefunction which yields a smooth perturbation in the wavefunction. The smoothness of this suggestion is important because the Hamiltonian is dependent on the second derivative in the kinetic term and a sharpness in the wavefunction will yield a discontinuity in the second derivative, yielding no solutions to the Schrödinger equation. After one suggested move, the wavefunction appears as:
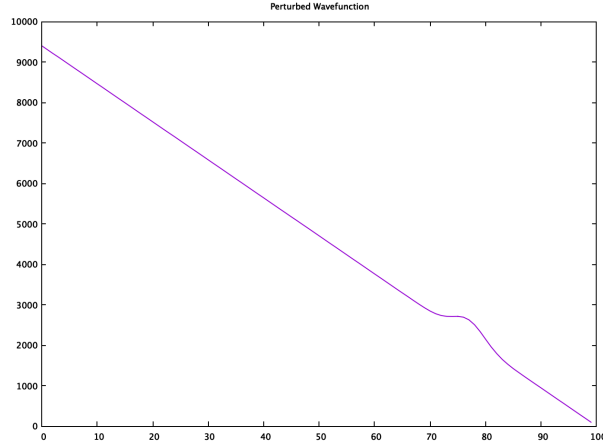


Figure 3: Perturbed Wavefunction

It is important to note that the y-axis has undergone a scale shift due to the perturbed wavefunction being normalized.

After this new wavefunction is normalized and the energy is calculated, the Metropolis algorithm is utilized:

```
diffH = expH_prime − expH
if expH_prime < expH:
        expH = expH_prime
if expH < expH_prime:
        Boltz_Prob = exp(−diff_H / kT)
        u = random(0, 1)
        if P < u:
                current_psi = initial_psi
        else if u < P:
                expH = expH_prime
                current_psi = psi_new
```

where `expH` is the current energy of the system, `random()` is a uniform random probability distribution between that picks a value for $u$ between 0 and 1, `expH_prime` is the energy of the suggested wavefunction, `inital_psi` is the wavefunction before the perturbation, and `kT` $\approx 1.0 \times 10^{-5}$ (this simulation temperature gives accurate results for $E_{gs}$).

### 4.2.2   Boundary Conditions

There are two important boundary conditions to take care of in order to output the proper ground state wavefunction of our potential: what happens as $\lim_{r\to\infty} \psi(r)$ and $\lim_{r\to 0} \psi(r)$. These boundaries must be considered separately as they require different stipulations of the wavefunction for each:

$i$) Large $r$ Behavior ($\lim_{r\to\infty} \psi(r)$): For the variational principle to be a viable method, the wavefunction must conform to the normalizability rule for all wavefunctions. For the wavefunction to be normalizable, it must tend towards zero as $r$ grows large. For our algorithm, a restriction on the righthand 'tail' of the wavefunction has been imposed to mandate our wavefunction to tend to zero as $r$ grows large. This restricts the wavefunction by mandating the last element of $\psi$ to be zero and the two subsequent values to be half of the value before it. This will ensure a smooth decrease to zero for large $r$ values.

15

*ii*) Small $r$ Behavior($\lim_{r \to 0} \psi(r)$): The cusp condition [4, 5] is put into the algorithm due to the fact that the VMC optimizer realizes that if it sends all values of $\psi$ besides $\psi(0)$ to 0 and allows $\psi(0)$ to increase to $+\infty$, this will minimize the energy to $-\infty$. Clearly, this is not what should be happening as the hydrogen atom has a finite value for its ground state energy. The cusp condition restricts the value of $\psi(0)$ and makes it dependent on $\psi(1)$. Known as the Kato Theorem, the cusp must cancel the $1/r$ term from the potential at the origin to ensure the energy does not diverge here. (Note: Due to the use of natural units, $\hbar = \epsilon_0 = 1$)

$$\frac{1}{\psi}\frac{\partial \psi}{\partial r} = -\frac{Ze^2 m_e}{4\pi} \tag{4.4}$$

This equation tells us that the slope of the wavefunction for small $r$ is proportional to the value of the wavefunction. Therefore, $\psi(0)$ can be determined based on $\psi(1)$ through the finite forward difference approximation between these points:

$$\psi' \approx \frac{\psi(1) - \psi(0)}{2h} = \frac{-Ze^2 m_e}{4\pi}\psi(0)$$
$$\psi(0) = \frac{\psi(1)}{1 - [e^2 m_e (dr)]/4\pi} \tag{4.5}$$

where $dr$ is the computational spacing between elements. This formula tells us that we can perturb any element of $\psi$ besides 0 and $\psi(0)$ will be automatically determined by the value of $\psi(1)$.

There is also an important consideration that must be taken into account regarding the energy in the first bin. Due to the $1/r$ behavior of the Hamiltonian,

16

at the origin, the energy must be calculated analytically, opposed to numerically for every other bin. This is done by using a Taylor expansion of the wavefunction up to $\mathcal{O}(r^2)$:

$$\psi(r) \approx A + Br + Cr^2$$

Analytically, solving for $\langle H \rangle$ in this first bin through $\langle T \rangle + \langle V \rangle$ is done by computing integrals over the range from $0 \to dr$. $\langle H \rangle$ will therefore be a function of $A, B, C$, and $dr$. Determining what the coefficients are is done by requiring the wavefunction to both pass through the first three points as well as using the finite differences (first and second derivative) formulae. This yields:

$$A = \psi(0)$$
$$B = \frac{\psi(2) - \psi(0) - 2\psi(1)}{2(dr)}$$
$$C = \frac{\psi(2) + \psi(0) - 2\psi(1)}{2(dr)^2}$$

Using this, the energy in the first bin is calculated and added to the standard energy calculation for the remaining bins giving a value for $\langle H \rangle$. The total energy for this bin is calculated by the integrals:

$$\langle V \rangle_{r \approx 0} = \int_0^{dr} \psi^*(r) V(r) \psi(r) dV$$

and

$$\langle T \rangle_{r \approx 0} = \int_0^{dr} \psi^*(r) \hat{T} \psi(r) dV$$

with $\psi(r)$ as the Taylor expansion above, $V(r)$ as the hydrogen potential, and $\hat{T} = \frac{-\hbar^2}{2m_e} \nabla^2$ (where $\nabla^2$ (the Laplacian) is in spherical coordinates). After ana-

17

lytically solving this integral, the energy in the first bin is obtained:

$$\langle H \rangle = -\frac{e^2}{\epsilon_0}[\frac{1}{2}A^2 dr^2 + \frac{2}{3}AB dr^3 + \frac{1}{2}AC dr^4 + \frac{1}{4}B^2 dr^4 + \frac{2}{5}BC dr^5 + \frac{1}{6}C^2 dr^6]$$
$$- \frac{2\hbar^2 \pi}{m_e}[AB dr^2 + 2AC dr^3 + \frac{2}{3}B^2 dr^3 + \frac{2}{3}BC dr^4 + \frac{1}{2}CB dr^4 + \frac{6}{5}C^2 dr^5]$$

Together, this expression for $\langle H \rangle$ in the first bin, as well as the cusp condition, fix the singularity problem at the origin by giving an analytic solution to the energy as well as verifying that our program does not bias towards raising $\psi(0)$ too strongly.

This is an important example of using analytic methods to assist when numeric methods fall short.

### 4.2.3    VMC Algorithm Results for Hydrogen Atom Potential

For this part we are using a resolution $dr = 3 \times 10^{-5}$ (which is arbitrary for now. We use a more methodical $dr$ later) and a volume of a sphere with radius: $N * dr = 100 * dr$.

After the VMC optimizer has run for many iterations, it outputs the proper ground state wavefunction for the given potential for the hydrogen atom. We know from the analytical solution to the hydrogen atom potential that the true wavefunction is given as

$$\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

which is a decreasing exponential with a decay length of $a_0$ where $a_0$ is the Bohr radius.

The variational Monte Carlo algorithm for the hydrogen atom potential yields the following wavefunction:
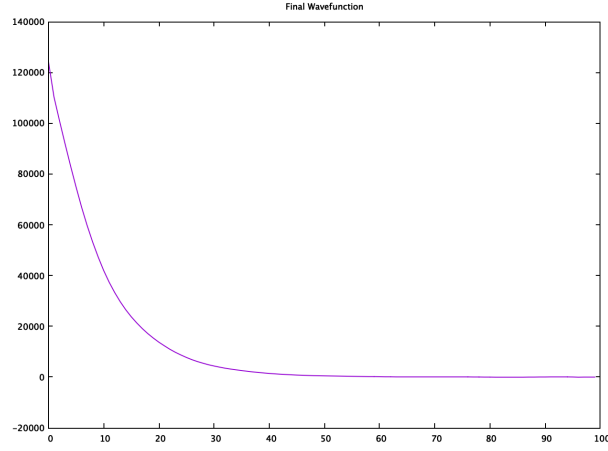


Figure 4: Final Wavefunction

which is in fact a decreasing exponential matching the analytic form and where the y-axis is arbitrary and the x-axis is in units of step-size.

After, the difference in analytic energy and numeric energy vs. iterations is plotted in order to get an average $E_{gs}$ for this potential:
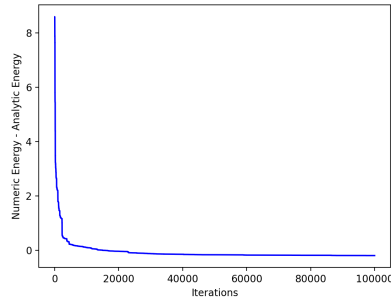


Figure 5: Change of Energy During the VMC Alg.

Clearly, the system is converging to an energy value. If we calculate the average of these energy values after the system has 'thermalized' yields an average ground state energy of: $E_{gs} = -13.7349 \, eV$. Compared to the true analytic value of $E_{gs} = -13.6 \, eV$, this gives a percent error of 0.9823%. From this, we see that this method yields quite an accurate value for the ground state energy.

A question now needs to be posed: If the variational principle can only be as accurate as the true ground state energy, how is the energy of this VMC optimizer giving an energy less than $-13.6 \, eV$ when the lowest possible energy for the potential is that of the ground state? This can be accounted for due to the finite site spacing $dr$ between bins. The true ground state energy is done by computing an integral of which the bin spacing is infinitely small. Using a finite $dr$ value allows for inaccuracy in the $E_{gs}$ calculation while using the VMC optimizer. Also note that in Chapter 5, when we alter $dr$ and $N$ more methodically (make $dr$ dependent on the total length of space we are sampling, as well as $N$), we find an energy greater than $-13.6eV$. This will be a more valuable insight into the nature of the VMC code: we can find an energy less than the ground state in our program; however, it is just a numerical construct, opposed to a physical one.

# 5    Chapter 2: The Direct Eigensolver Algorithm

## 5.1    Analytic Eigensolver

Although the essence of the Schrödinger equation is a second order partial differential equation, the time independent Schrödinger equation (T.I.S.E) can be written as an eigenvector equation:

$$\hat{H} \left| \Psi \right\rangle = E \left| \Psi \right\rangle \tag{5.1}$$

Solving this eigenvalue equation by standard methods ($det(\hat{H} - \lambda E) = 0$) yields the energy eigenvalues of the given potential. The smallest eigenvalue is defined as the ground state energy. However, due to the arduousness of this process for large wavefunction matrices, it can be solved easily via numerical methods. An example of how to solve this equation analytically can be seen by the generic Hamiltonian:

$$\hat{H} = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

Solving for the eigenvectors of this matrix yields: $det(\hat{H} - \lambda E) = 0 \Rightarrow (a - \lambda)(d - \lambda) - b * c = 0 \Rightarrow \lambda^2 - (a + d)\lambda + (ad - bc) = 0$ The roots of this equation are the eigenvalues of this $\hat{H}$ matrix and the eigenvectors are solved by finding a vector such that when it is multiplied by $\hat{H}$, it outputs the same vector times one of the eigenvalues found above.

## 5.2    The Eigensolver Algorithm

An eigensolver algorithm can be implemented by prescribing a Hamiltonian matrix determined by the potential and coordinates of the system and using the scipy module function `eigsh()` to find the corresponding eigenvectors and eigenvalues of a given matrix.

### 5.2.1 Infinite Square Well and Harmonic Oscillator Potentials

The simplest potential to solve is the infinite square well which is also the easiest to create a Hamiltonian matrix for. This potential is given by:

$$V(\vec{r}) = \begin{cases} 0 & \text{if } 0 \leq x \leq a \\ \infty & \text{else} \end{cases}$$

Thus, in our box from 0 to a, our Hamiltonian is only a kinetic term. In cartesian coordinates, the kinetic piece is: $\frac{-\hbar^2}{2m_e}\frac{d^2}{dx^2}$ Since we have to use a finite difference equation for the second derivative due to the impossibility to yield infinite spacing between points on a computer, the second order difference being used is:

$$\psi_i'' \approx \frac{\psi_{i+1} - 2\psi_i + \psi_{i-1}}{(dr)^2}$$

This shows that the $i^{th}$ component of the kinetic term is dependent on the terms around it, or the $j^{th}$ term such that $j = i \pm 1$. This yields a kinetic energy matrix of[6]:

$$\hat{T} = \begin{bmatrix} -2 & 1 & 0 & \dots & & & \\ 1 & -2 & 1 & 0 & \dots & & \\ 0 & 1 & -2 & 1 & 0 & \dots & \\ 0 & 0 & 1 & -2 & 1 & 0 & \dots \\ \vdots & & & & & & \ddots \end{bmatrix}$$

Now, since $\hat{H} = \hat{T}$ (by definition of the infinite potential well, the potential in the region of interest is zero), the eigenvectors and eigenvalues of the Hamiltonian are found using the sparse matrices eigenvalue solver from the module Scipy. A sparse matrix is a matrix with mostly zero elements and some non-zero elements. These types of matrices allow the `eigsh()` function to quickly find the eigenvalues and eigenvectors due to the barren nature of the matrices. We

know that the general form for the eigenvectors of this potential are given by

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right); \forall n \in \mathbb{Z}$$

When we plot the eigenvectors, we see they do in fact yield the first few solutions to the infinite square well potential:
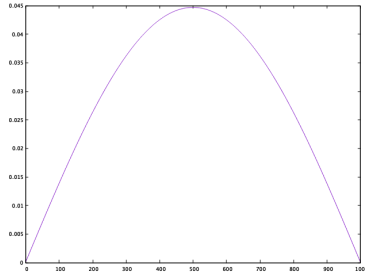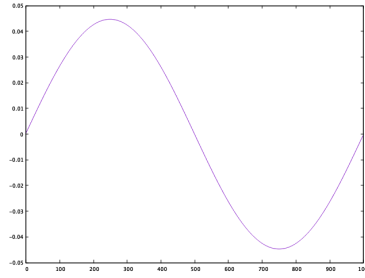


Figure 6: Infinite 1D Well: $\psi_0$



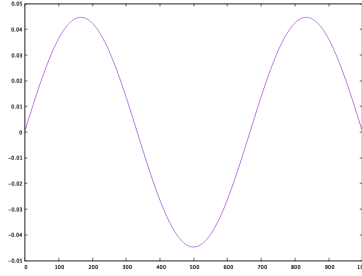Figure 7: Infinite 1D Well: $\psi_1$



Figure 8: Infinite 1D Well: $\psi_2$

These do in fact match the theoretical wavefunctions generated completely analytically in any quantum mechanics textbook.

The simplest nonzero potential that can be used is the one-dimensional harmonic oscillator potential:

$$\hat{V}(x) = \frac{1}{2}m\omega^2 x^2$$

which is symmetric about the origin. Generating a potential energy matrix can be done using the same logic as above. The matrix elements of $V$ can be given

23

by:

$$V_{ij} = \langle i | V | j \rangle = \int \psi_i V \psi_j \, dx$$

Since $\hat{V}$ only connects sites $i, j$ to themselves (unlike how $\hat{T}$ connects adjacent sites through the derivative), we can 'pull' $\hat{V}$ out of the inner product:

$$V_{i,j} = V \langle i | j \rangle = V(x_i) \delta_{ij}$$

Thus,

$$V_{ij} = V(x_i)$$

only if $i = j$ (i.e. only diagonal elements of the matrix are utilized only). For the harmonic oscillator potential, for an odd N value, the $i = j = (N-1)/2$ value is the origin and the diagonal values around it are proportional to $x^2$. An example for N $= 5$ is:

$$\hat{V} = \begin{bmatrix} 4 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 4 \end{bmatrix}$$

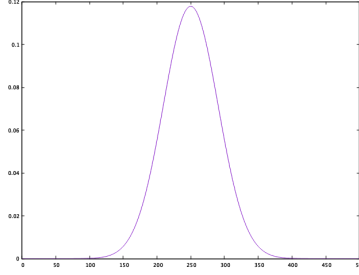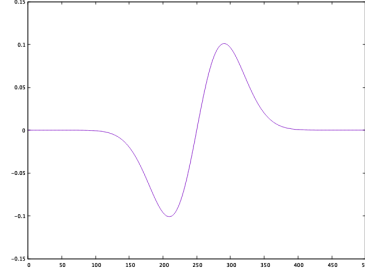When a larger N value is used, the eigenvectors are found and given by:



Figure 9: SHO: $\psi_0$
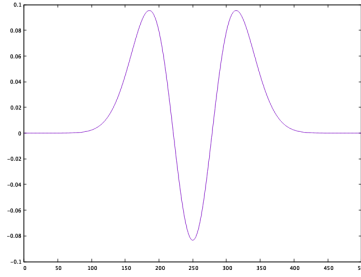


Figure 10: SHO: $\psi_1$



Figure 11: SHO: $\psi_2$

which match the first three analytic wavefunctions for the harmonic oscillator potential having the form:

$$\psi_n = \frac{1}{\sqrt{2^n n!}}\pi^{-1/4}e^{-x^2/2}H_n(x); \forall n \in \mathbb{Z}$$

where $H_n(x)$ is the $n^{th}$ Hermite polynomial given by:

$$H_n(x) = (-1)^n e^{x^2}\frac{d^n}{dx^n}e^{-x^2}$$

### 5.2.2 The Hydrogen Atom Potential

The hydrogen atom potential again is:

$$V(\vec{r}) = \frac{-e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2} \tag{5.2}$$

but for the ground state, $l = 0$ so the potential can be written simply as: $V(\vec{r}) = \frac{-e^2}{4\pi\epsilon_0 r}$. The coordinate system best used for this central potential is spherical coordinates with the Schrödinger equation:

$$\frac{-\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi$$

It is known that the ground state wavefunction, $\psi_{100}(r,\theta,\phi)$, is spherically symmetric so by the separation of variables, $\psi(r,\theta,\phi) = \sqrt{\frac{1}{4\pi}}R_{10}(r)$ where $Y_0^0(\theta,\phi) = \sqrt{\frac{1}{4\pi}}$(the spherical solution). We define a change of variables which makes the Schrödinger equation easier to solve. Let $u(r) = rR(r)$. Plugging $\frac{u(r)}{r}$ as $\psi$ into the Schrödinger equation, we obtain[7]:

$$\frac{-\hbar^2}{2m_e}\frac{d^2u}{dr^2} - \frac{e^2}{4\pi\epsilon_0 r}u = Eu$$

The form of this differential equation is much easier to solve with our eigensolver because now our Laplacian term is just a second derivative, which is solved just as it was for the 1-D potentials above (infinite square well, harmonic oscillator). The potential matrix is diagonal just as before which each $V_{ii} \propto \frac{1}{r}$. The $V_{00}$ element presents an issue as $\frac{1}{0}$ clearly yields an asymptote. To fix this, the potential is taylor expanded about a point close to zero. We can Taylor expand $\frac{1}{r}$ by:

$$\frac{1}{r} \approx -\frac{1}{r_0} + \frac{1}{r_0^2}(r - r_0) - \frac{1}{2}\cdot\frac{1}{r_0^3}(r - r_0)^2 + \dots$$

Now, with $r_0 = 10^{-6}$, $V_{00} = V(0) \propto -\frac{1}{r_0} + \frac{1}{r_0^2}(0 - r_0) - \frac{1}{2} \cdot \frac{1}{r_0^3}(0 - r_0)^2$ (where terms of $\mathcal{O}(r_0^3)$ are neglected)

Now, with kinetic and potential matrices defined, the eigensolver finds the ground state for the function $u(r)$. $\psi_{100}$ is found by undoing the original radial equation substitution:

$$\psi_{100}(r, \theta, \phi) = \sqrt{\frac{1}{4\pi}} \frac{u(r)}{r} \tag{5.3}$$

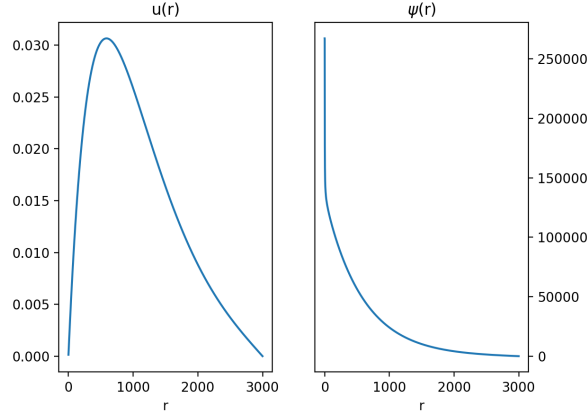$u(r)$ and the subsequent eigenfunction for $\psi$ are shown here (after $\psi$ has been normalized):



Figure 12: u(r); $\psi(r)$

(Note: $\psi(r)$ appears linear at the beginning due to the compact nature of subplots in the matplotlib python module. This is not the wavefunction diverging at the origin as $\psi(0)$ is defined via the Kato theorem (equation 4.4)). Here we are using $N = 5 \times 10^3$ and $dr = 1.0 \times 10^{-6}$

27

### 5.2.3 Energy of the Hydrogen Wavefunction from the Eigensolver

After the eigensolver finds $u(r)$ which eventually becomes $\psi_{100}(r, \theta, \phi)$ after adding the $Y_0^0$ and $\frac{1}{r}$ term, and normalizing, the energy can be calculated. This energy for this normalized wavefunction is calculated as $-13.47eV$ which is roughly a $0.96\%$ error from the true experimental value of $-13.6eV$. This is about two times less accurate than the Metropolis algorithm which gave a ground state energy of $-13.7eV$. Subsequent sections will discuss accuracy vs. runtime of these methods.

# 6 Chapter 3: The Helium Atom

## 6.1 Helium with the VMC Algorithm

### 6.1.1 Theory

We begin with the Hamiltonian for the helium atom which presents a new challenge:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r_1} - \vec{r_2}|} \qquad (6.1)$$

We lose linearity due to the electron-electron interaction between the two electrons in the helium atom. We are therefore unable to write the Hamiltonian as a sum of two independent Hamiltonians which is rather easy to find the eigenvalues of. We first propose an initial wavefunction as a tensor product of two hydrogenic wavefunctions, each one representing an electron: $\psi = \psi_0(r_1)\psi_0(r_2)$. From here, the Coulomb potential term that gives rise to a problem will have to be dealt with separately. However, the wavefunction can be normalized, and a energy without a perturbation from the Coulomb potential ($V_c$) can be calculated.

To start, we neglect the electron-electron interaction term. Two individual wavefunctions are created where one wavefunction corresponds to the nucleus and one electron and the other wavefunction corresponds to the nucleus and the other electron. Indivually, we are able to perturb these wavefunctions and implement a VMC code. These wavefunctions can be normalized individually since their inner product over all space is 1 (therefore the integrals can be separated). From there, the same energy code from the hydrogen VMC algorithm can be used, with the change from $Z = 1 \rightarrow Z = 2$ in the potential terms.

Without $V_c$, the eigenvalue problem becomes:

$$(\hat{H}_1 + \hat{H}_2)\psi(r_1)\psi(r_2) = \hat{H}_1\psi(r_1)\psi(r_2) + \hat{H}_2\psi(r_1)\psi(r_2) = (E_1 + E_2)\psi(r_1)\psi(r_2)$$

Thus, the energy is a sum of the two electron energies. Just looking at this part of the Hamiltonian (and completely disregarding the electron-electron repulsion) gives $E = -106.797eV$ for hydrogenic wavefunctions, $\psi(r_1), \psi(r_2)$. Note that this is not exactly $8 * -13.6eV$ (this comes from the fact that the nuclear charge is now equal to $+2$ so $E_{tot} = (4E_0 + 4E_0)$ due to the approximations made in the VMC code. Compared with the experimental value ($E = -78.95eV$), this is far too negative. It is clear why this is: the Coulomb interaction was disregarded and its contribution is not negligable. To deal with this part of the wavefunction, an approximation must be performed. The approximation being used is known as the Hartree-Fock approximation for the helium atom.

### 6.1.2   The Hartree-Fock Approximation

The Hartree-Fock approximation is a estimation of the effective field felt by one electron due to the other electron and the neucleus together. Imagine a system of a nucleus and two electrons (for the case of helium) where 1 electron has a greater distance to the nucleus than the first electron. To use the Hartree-Fock approximation, we group the inner electron with the nucleus and propose a hydrogenic wavefunction. From here, we calculate the effective field of this hydrogenic system of the first electron for any point in space and determine the Coulombic field that the second electron feels in any point in space. This is essentially Gauss' law: for a spherically symmetric potential, we can say that the field due to the first electron is proportional to the charge enclosed in some volume.

To use the Hartree-Fock approximation method[8, 9, 10], the Coulomb potential must first be Taylor expanded to become what is known as the Hartree pseudo-potential:

$$V_H(r) = \int \frac{4\pi}{\epsilon_0} \frac{n(\vec{r'})r'^2}{r_>} dr'$$  (6.2)

Where $n(r')$ is the electron density $i.e.$ $n(r') = e^2 \sum_i |\psi|^2$ and $Y_0^0 = \sqrt{\frac{1}{4\pi}}$. We then use this Hartree potential as the approximation to the more complicated Coulomb potential to determine $\langle V_c \rangle$. This potential can be graphed in the same way the Coulomb potential can be since it is a indefinite integral which outputs a function after integrating. This function, which represents the average field that the second electron feels as a result of assuming the first electron emits a charge density of that of a hydrogenic wavefunction appears as:
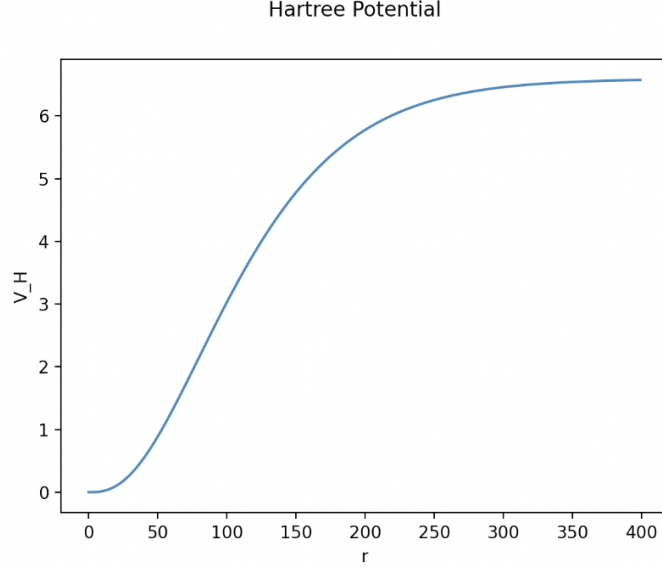
Figure 13: The Hartree Potential

To understand the trends of this graph, we have to study small $r$ and large $r$ behavior (where $r$ is the distance from the inner electron which is held constant, to the further electron). When the electrons are near the same radial distance, our Gaussian sphere encloses a total charge of zero, leading to a potential of zero, which we see in the graph. Conversely, at large radial distance, the potential falls off as the standard $-1/r$ Coulombic interaction, again, as expected.

Now that we have an analytical form of the electron-electron interaction potential that is easy to use, the Hartree-Fock approximation method can commence: A random electron is chosen to be perturbed, the unperturbed electron's energy is calculated followed by the Hartree Potential's contribution. This is done in the same way via:

$$\langle V_c \rangle = \int |\psi|^2 V_H dr'$$

where $V_H$ is defined in equation 6.2. Last, the standard accept/rejection of this

new energy in the standard Metropolis algorithm is done.

### 6.1.3   VMC Results for the Helium Atom

We initialize the composite wavefunction as the tensor product of two hydrogenic wavefunctions with the decay constant changed to $2/a_0$ since $Z = 2$. Since this time, our initial wavefunction is very close to the true wavefunction of helium, the convergence time is much quicker. After 10,000 iterations, the final wavefunctions are given by[11]:
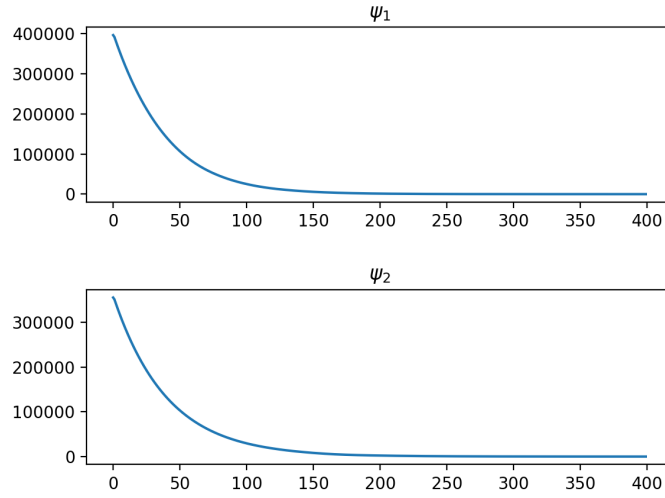


Figure 14: Helium Two Electron Wavefunctions

We can also look at the energy per iterations, find off when it "thermalizes" and determine the average ground state energy:
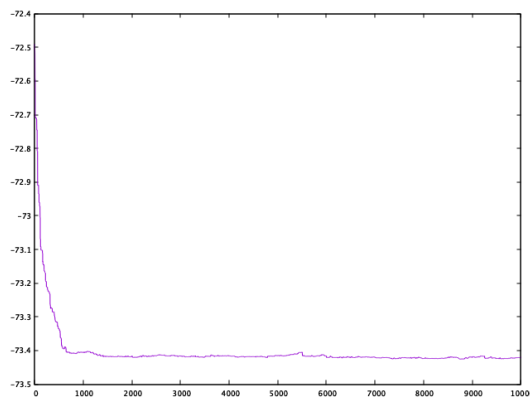
Figure 15: Helium Energy vs. Iterations

When we cut off around 1500 iterations, we determine the ground state energy to be $-73.419eV$. The experimental value of the ground state of helium is roughly $-79.0eV$. The percent error that we obtain is $\approx 7.09\%$. This is not a great approximation but due to the nature of the Hartree-Fock approximation for the Coulomb term, we cannot get exactly $-79eV$.

## 6.2  Helium with the Eigensolver Algorithm

### 6.2.1  Theory and Method

As with the VMC algorithm, the Coulomb term is challenging to represent via matrices. We perform a "zeroeth" order approximation to the Coulomb term by completely disregarding it. We do this approximation because the eigenvalues of the Hartree matrix are produced based on the wavefunctions of one of the electrons. Since we are trying to determine both wavefunctions simultaneously, we must use an approximation. This is the nature of perturbation theory. We disregard the term that creates a problem in our calculation and then use the solutions to the easily calculable part to determine first order corrections to our wavefunctions. How this applies to our eigensolver is we will solve for the

eigenfunctions (wavefunctions) of the unperturbed Hamiltonian:

$$\hat{H}_0 = \hat{H}_1 + \hat{H}_2 \tag{6.3}$$

where $\hat{H}_1, \hat{H}_2$ are the Hamiltonians for the individual electrons (without electron-electron interaction). We determine $\psi_0(r_1)$ and $\psi_0(r_2)$ from this Hamiltonian which gives us an energy that we expect to be roughly equal to that we would receive from the VMC algorithm before adding in the $U_{eff}$ term. With the eigensolver algorithm, we determine the wavefunctions for the unperturbed potential, $\hat{H}_0$ give an energy of $E_0 = -106.06eV$. We now take the hydrogenic eigenfunctions we have produced, $\psi_0(r_1)$ and $\psi_0(r_2)$, and plug them into our $U_{eff}$ code that we produced for the VMC algorithm. (Note that the eigenfunctions again are technically $u(r_1)$ and $u(r_2)$ that was discussed above that need to be transformed into the wavefunctions)

### 6.2.2   Results of *He* with the Eigensolver

After plugging our new eigenvectors into our $U_{eff}$ code to determine the first order perturbation to the energy, we find that the expectation value of the Coulomb interaction. The full results of our *He* eigensolver are:

$$E_0 = -106.06eV$$
$$U_{eff} = 34.05eV$$
$$E_{Tot} = -72.01eV$$

which is roughly the same energy we get from the VMC code. We notice that our $U_{eff}$ is what causes our major source of error, which is to be expected as this is an approximation of the true coulombic repulsion. From this eigensolver, we receive an error of $\approx 8.8\%$.

# 7 Chapter 4: Hydrogen Molecule Ion $(H_2^+)$

## 7.1 VMC for $H_2^+$

### 7.1.1 Theory

The hydrogen molecule ion consists of two protons separated by a distance R with 1 electron a distance $r_1$ and $r_2$ from proton 1 and 2 respectively. The Hamiltonian for this system is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_{p_1}}\nabla_{p_1}^2 - \frac{\hbar^2}{2m_{p_2}}\nabla_{p_2}^2 - \frac{e^2}{4\pi\epsilon_0}(\frac{1}{r_1} + \frac{1}{r_2}) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{R} \quad (7.1)$$

where the first term represents the kinetic energy of the electron, followed by the kinetic energy of protons 1 and 2 respectively. Subsequently, we have the potential energy between proton 1 and the electron as well as proton 2 and the electron. Lastly, we have the proton-proton repulsion potential term.

In order to simplify the calculation quite drastically, we will take the following two approximations:

1) *The Born-Oppenheimer Approximation*: This approximation says that the wavefunctions of this Hamiltonian can be approximated by neglecting the proton's kinetic energy piece. This is due to the fact that the mass of the proton is so much larger than the mass of the electron. Because of this, since the kinetic energy of the proton is inversely proportional to it's mass, the kinetic energy will be very small compared to the kinetic energy of the electron. With this approximation, we can set $T_{p_1} = T_{p_2} = 0$

2) *The Fixed Proton Approximation*: We assume at first that the protons are "glued down" so that R does not vary. While this is not a perfectly physical representation (each proton will produce a repulsive force on the other), we can find $\langle H \rangle_{min}$ for a given $R$ value and then repeat this for many different $R$ values in order to find the true ground state. This simplifies the Hamiltonian to (excluding the constant proton-proton repulsion piece):

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0}(\frac{1}{r_1} + \frac{1}{r_2}) \tag{7.2}$$

Since the electron can be viewed as a hydrogenic wavefunction with either of the two protons, we can assume a linear superposition of hydrogenic wavefunctions, each associated with one proton($r_1$ represents the distance from proton 1 to the electron while $r_2$ represents the distance from proton 2 to the electron):

$$\psi = A[\psi(r_1) + \psi(r_2)] \tag{7.3}$$

Our first challenge is to normalize this wavefunction which presents a new integral that must be taken into account:

$$1 = A^2 \langle \psi | \psi \rangle = A^2[\langle \psi_1 | \psi_1 \rangle + \langle \psi_2 | \psi_2 \rangle + 2 \langle \psi_1 | \psi_2 \rangle] = A^2[2 + 2S]$$

The new term is $S = \langle \psi_1 | \psi_2 \rangle$ which at first glimpse appears to be zero (orthogonality of wavefunctions) but since these represent hydrogenic wavefunctions on two different protons, this is actually a measure of the overlap of these two wavefunctions. In order to find the normalization integral, we must first calculate

37

the overlap integral:

$$S = \int \psi(r_1)\psi(r_2) \, d^3\vec{r} \tag{7.4}$$

Clearly, this integral will span values between 0 and 1 and will depend on the wavefunctions. It is not as evident by looking at the integral, but this overlap will also depend on R, the distance between the protons. The following diagram represents how the type of orbital (wavefunction) as well as R can alter the value of the overlap[12]:
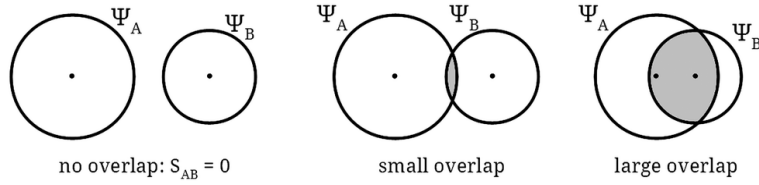


Figure 16: Overlap of Orbitals

To compute $S$ numerically, we have to write $r_2$ in terms of $r_1$. If we define $\theta$ as the angle between $r_1$ and $R$, then we can write $r_2$ in terms of $r_1$, $R$, and $\theta$. First, let $r_1 = r$. From there, $r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$ by the law of cosines. (We define our coordinate system by 'pinning' one proton to the origin). Now our integral becomes

$$S = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \psi(r)\psi(\sqrt{r^2 + R^2 - 2rR\cos\theta}) \, r^2 \sin\theta dr d\theta d\phi$$

It is now clear that S depends on both the wavefunctions as well as R. This integral can now easily be computed analytically with a double for loop (since the $\phi$ integral just equals $2\pi$). To test that we have programmed this correctly, we can choose 1$s$ orbitals ($\psi_0$) and vary R to see how S changes:
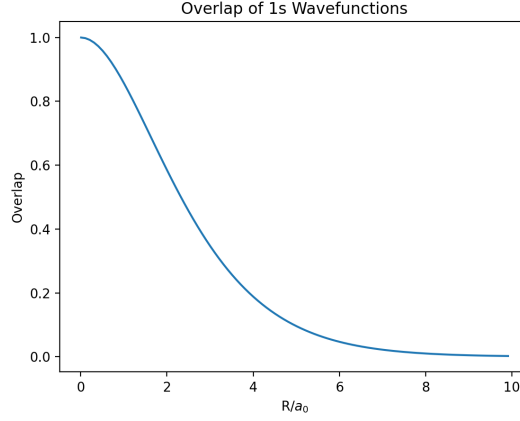
38

Figure 17: Overlap of $1s$ Wavefunctions

If the 1s wavefunctions are very close, they can be treated as on top of one another so the inner product is the same as a normalization integral which equals one. As $R/a_0$ increases, the overlap tends towards zero. Physically, this says that if R is very large, the wavefunctions do not affect one another. To find $\langle H \rangle$ easily, we can rearrange the eigenvalue equation and exploit the fact that $\hat{H}_0 \psi_0 = E_0 \psi_0$ where $\hat{H}_0$ is the hydrogen Hamiltonian. (Let $E_1$ be the energy of $\psi_0(r_1)$ and $E_2$ be the energy for $\psi_0(r_2)$. In this case, we aren't calling $E_1$ and $E_2$ to be $E_0 = -13.6eV$ because as we perturb $\psi(r_1), \psi(r_2)$, the energies will change)

$$\langle H \rangle = \frac{E_1 + E_2}{2} - 2|A|^2 (\frac{e^2}{4\pi\epsilon_0}) [\, \langle \psi_0(r_1)| \frac{1}{r_2} |\psi_0(r_1)\rangle + \langle \psi_0(r_1)| \frac{1}{r_1} |\psi_0(r_2)\rangle ] \ (7.5)$$

This derivation is written explicitly in Griffith's text where the only addition here is to change $E_0$ in the text to $\frac{E_1+E_2}{2}$ since we are perturbing and changing the individual hydrogenic wavefunction's energies.

We use the energy code from the hydrogen VMC algorithm to find $E_1$ and $E_2$. We also have two new integrals to compute, the direct integral $D$ and the exchange integral $X$:

$$D = \langle \psi_0(r_1)|\frac{1}{r_2}|\psi_0(r_1)\rangle \tag{7.6}$$

$$X = \langle \psi_0(r_1)|\frac{1}{r_1}|\psi_0(r_2)\rangle \tag{7.7}$$

The direct (Coulomb) integral physically represents the classical electrostatic repulsion between the two charge distributions corresponding to $\psi(r_1)$ and $\psi(r_2)$. The exchange integral has no classical correspondence; it is purely quantum mechanical. The integral results from the fact that the wavefunctions must be anti-symmetric due to the Pauli exclusion principle.

To see how these integrals behave, we have plotted $D$ and $X$ in the states $1s$ for both wavefunctions:
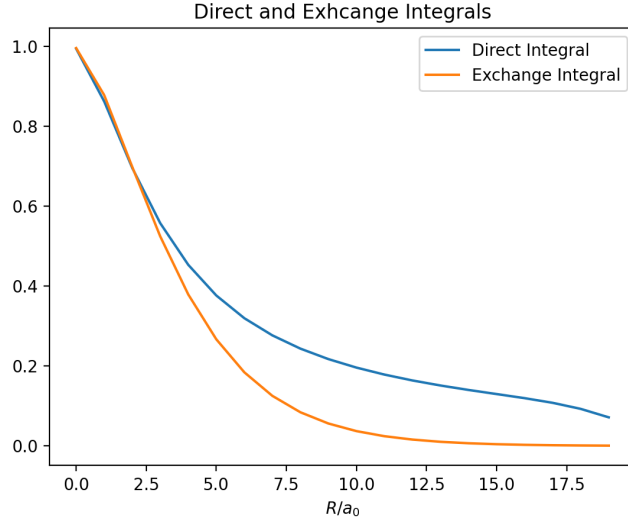


Figure 18: Direct and Exchange Integrals

These integrals can be computed in the same manner as the overlap integral as above by treating $r_2$ as being dependent on $r_1$ by $r$, $R$, and $\theta$. After these integrals are programmed, any wavefunction for $\psi(r_1)$ and $\psi(r_2)$ can have its energy computed via equation 7.5.

### 7.1.2 Results of VMC for $H_2^+$

After allowing the VMC algorithm to run for an appropriate amount of time for each value of R, and adding in the constant proton-proton repulsion piece, the following graph displays the computed ground state energy value for each value of R:
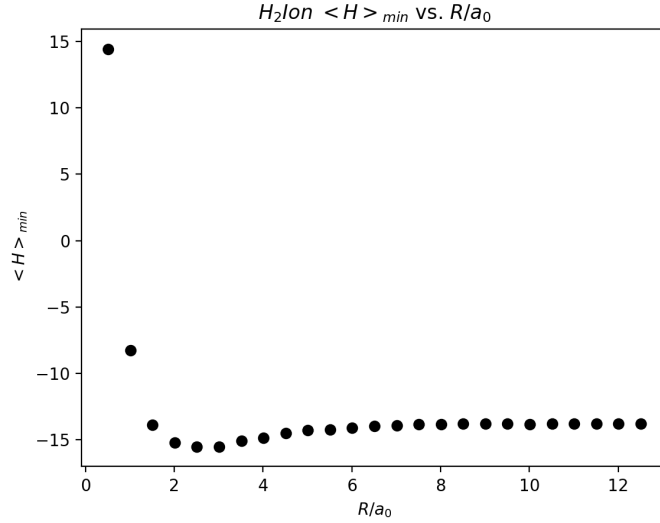


Figure 19: Energy of the $H_2^+$ Ion vs. $R/a_0$

There is a ground state energy value at $R \approx 2.4 * a_0$. This value determined by the VMC code turns out to be $-15.5eV$. The experimental ground state value for this molecule is $-16.25eV$. This gives a percent error of 4.6%. It is also important to recognize that the graph tends to $E_0$ as $R/a_0 \to \infty$ which is what

makes physical sense as you could look at this molecule as a hydrogen atom and a proton infinitely far away. The graph also tends to $\infty$ as $R/a_0 \to 0$ which shows that it takes infinite energy to push the protons close to each other.

## 7.2 $H_2^+$ Eigensolver

To program our Hamiltonian matrix for the $H_2$ ion, we can take the $T$ and $V$ matrices from the hydrogen eigensolver, and add a matrix corresponding to the potential term between the electron and the second proton. In the basis we have been using, $|r\rangle$, we receive a problem in coding this matrix. We have lost spherical symmetry so working in this basis will not be sufficient. We again have to write $r_2$ in terms of $r_1$ by the law of cosines. For each $r_1$ value, we have to calculate the average potential energy in this sphere of space from the second proton, where the sphere of space has radius $r_1$. We then obtain the formula for the $ij^{th}$ element of the $V_2$ matrix by:

$$V_{2_{ij}} = \frac{-e^2}{4\pi\epsilon_0} \int_0^\infty \frac{r_{1_i}^2 sin(\theta_i)}{\sqrt{r_{1_i}^2 + R^2 - 2r_{1_i}Rsin(\theta)}} d\theta * \frac{1}{4\pi r_{1_i}^2} \qquad (7.8)$$

This, in turn, gives the average energy in sphere from the second proton about a sphere around the first proton. We are dividing by $4\pi r_{1_i}^2$ in the equation to find the average. We anticipate that this will be a very mediocre approximation at best because for some $\theta$ values, $V_2$ will be large at a given $r_1$ but as $\theta$ is changing $V_2$ will begin to change. As we change the distance between protons, $R$, we calculate the energy determined by the eigensolver and then graph:
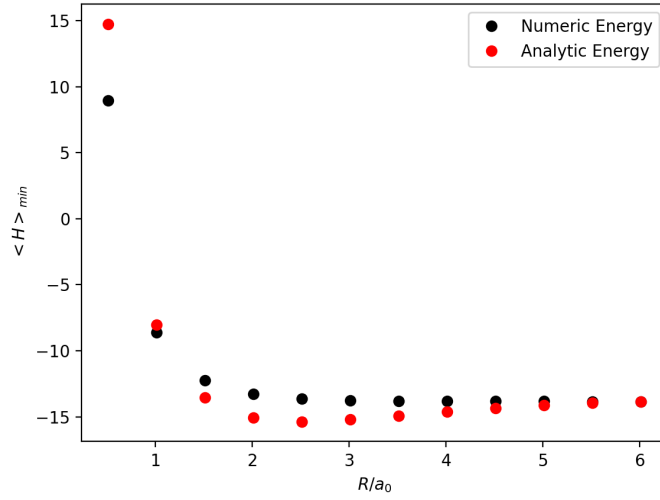
Figure 20: Energy of the $H_2^+$ Ion vs. $R/a_0$

It is evident that the numeric form does not perfectly match the analytic form. In fact, the eigensolver does not even show a bound state. While small $R$ and long term behavior tends to match, the important area is not as precise. This is due to the fact that the eigensolver has no way to determine the overlap of the wavefunctions, $S$ which is a purely quantum effect. Due to this, we don't see this system bonding unless we encapsulate the interaction between the two wavefunctions through the overlap. A method to fix the lack of a bound state in the above graph is discussed in the future developments chapter at the end. In short, we discuss a proposal to change our basis to be $|r, \theta\rangle$ so that our basis encapsulates the impact that varying $\theta$ has on the $V_2$ potential.

# 8 Chapter 5: Comparing the Accuracy and Runtime of The VMC and The Eigensolver Algorithms

The basis of the VMC code is the python module `numpy` and the eigensolver algorithm uses the Scipy module's package `eigsh()`. To determine the superiority of one of the two algorithms, we must test both runtime as well as accuracy. Each code is now re-run so that the run time and energy can be re-calculated and noted in order to determine our analysis of the superior algorithm. The results are listed (Note: accuracy $= 100 - $ error; values are not exactly as shown above due to different values of $N$ and $dr$ used):

Table 1: Accuracy, Runtime for the Hydrogen Atom

|         | VMC            | Eigensolver    |
|---------|----------------|----------------|
| dr      | $(5a_0)/(N-1)$ | $(5a_0)/(N-1)$ |
| N       | 1,000          | 3,000          |
| Runtime | 1.22 min       | 3.06 min       |
| Energy  | -13.49 $eV$    | -13.64 $eV$    |
| Error   | 0.8%           | 0.03%          |

Table 2: Accuracy, Runtime for the Helium Atom

|         | VMC            | Eigensolver    |
|---------|----------------|----------------|
| dr      | $(5a_0)/(N-1)$ | $(5a_0)/(N-1)$ |
| N       | 4,000          | 3,000          |
| Runtime | 9.48 min       | 16.05 min      |
| Energy  | -73.47 $eV$    | -73.16 $eV$    |
| Error   | 7.0%           | 7.58%          |

Table 3: Accuracy, Runtime for the $H_2^+$ Ion (with $R/a_0 = 2.4$)

| | VMC | Eigensolver |
|---|---|---|
| dr | $(10a_0)/(N-1)$ | $(10a_0)/(N-1)$ |
| N | 1,000 | 3,000 |
| Runtime | 2.47 min | 2.50 min |
| Energy | -15.39 $eV$ | -13.59 $eV$ |
| Error | 5.3% | 16.3% |

The VMC algorithm has three sources of error: finite $dr$, finite $N$, and finite convergence time, while the eigensolver algorithm has two sources of error: finite $dr$ and finite $N$. As we increase the complexity of the potentials, we begin to invoke physical error as well (using the Hartree-Fock approximation, overlap effects) which add on to the error that we see in the results. It is evident that error increases as complexity increases. For simple potentials, or potentials with very accurate approximations, both the VMC algorithm as well as the eigensolver algorithm can be utilized to quickly and accurately converge to the ground state energy of these systems.

# 9    Chapter 6: Further Developments

Further development that arise from this project have begun but lack significant testing and polishing to warrant being written in previous chapters. The overview of these are described below.

## 9.1    $|r, \theta\rangle$ Basis for the $H_2^+$ Eigensolver Algorithm

We propose an upgrade to our eigensolver in order to encapsulate the effect that varying $\theta$ has on the energy eigenvalues. To do this, we must use 2D polar coordinates and a basis of $|r, \theta\rangle$. From this, each point in our matrix will represent, not just a radial value, but also an azimuthal value, $(r_i, \theta_i)$. We now must discuss how the Laplacian piece of the kinetic operator changes as well as
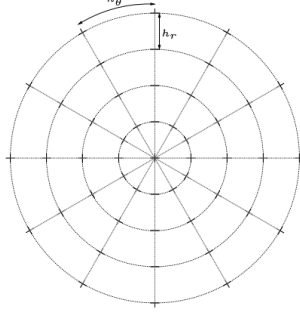
Figure 21: Polar Grid

the diagonal elements of the potential operator. Let us begin with the kinetic operator and how the 2D polar Laplacian behaves[15, 16].

We begin with the polar grid where $h_r = L/N$, where L is the total length of space we are sampling over, and $N$ is the number of pieces we are cutting our radial space into, and $h_\theta = 2\pi/M$, where M is the number of pieces we are cutting the circle into. The polar Laplacian is:

$$\nabla^2 \equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}$$

Using the finite differences, as discussed above, as well as defining $r = i * h_r$ and $\theta = m * h_\theta$, we can write this Laplacian as a finite difference operator:

$$\nabla^2 u_{i,m} \equiv \frac{u_{i+1,m} - 2u_{i,m} + u_{i-1,m}}{h_r^2} + \frac{1}{i * h_r}\frac{u_{i+1,m} - u_{i-1,m}}{h_r}$$
$$+ \frac{1}{(i * h_r)^2}\frac{u_{i,m+1} - 2u_{i,m} + u_{i,m-1}}{h_\theta^2} \tag{9.1}$$

From this definition, we can produce our Laplacian matrix where instead of each row or column being represented by points, $r_i$, we have two values, $(r_i, \theta_i)$.

Thus, the rows (and therefore columns) have values: $(0,0)$, $(r_1,\theta_0)$, $(r_1,\theta_1)$, ..., $(r_1,\theta_{M-1})$, $(r_2,\theta_0)$, ..., $(r_{N-1},\theta_{M-1})$. This gives $M*(N-1)+1$ rows and columns in our matrix. Now, for a given row, $(r_i,\theta_i)$, the row effects columns, $(r_{i-1},\theta_i)$, $(r_i,\theta_i)$, $(r_{i+1},\theta_i)$, $(r_i,\theta_{i-1})$, and $(r_i,\theta_{i+1})$ of the Laplacian matrix depending on Equation 8.1 above. We have a singularity for $r=0$ which needs a special form:

$$\nabla^2 u_{0,0} = \frac{4}{Nh_r^2} \sum_{m=0}^{m-1} (u_{1,m} - u_{0,0}) \tag{9.2}$$

Which allows us to easily define the first row of our matrix. From here, once we have the Laplacian matrix, we define the kinetic operator as before:

$$\hat{T}_{i,j} = \frac{\hbar^2}{2m_e} \nabla^2 u_{i,j} \tag{9.3}$$

Now, for our potential matrix, we again see that it is diagonal with respect to our new basis:

$$\hat{V}_{1\,i,j} = \langle r_i,\theta_i| V_1 |r_j,\theta_j\rangle = \frac{-e^2}{4\pi\epsilon_0 r_{1_i}} \langle r_i,\theta_i|r_j,\theta_j\rangle \tag{9.4}$$

Which is only non-zero when $r_i = r_j$ and $\theta_i = \theta_j$. $\hat{V}_2$ has the same diagonal form but we represent $r_{2_i}$ in terms of $r_{1_i}$ again by the law of cosines in order to introduce dependence of the proton distance:

$$\hat{V}_{2\,i,j} = \frac{-e^2}{4\pi\epsilon_0 \sqrt{r_{1_i}^2 + R^2 - 2r_{1_i}R\sin(\theta_i)}} \langle r_i,\theta_i|r_j,\theta_j\rangle \tag{9.5}$$

Using the $|r,\theta\rangle$ basis, we now can define our Hamiltonian matrix and find the energy eigenvalues. The problem that pops up is the Hamiltonian is much larger and by using finite differences, it is challenging to compute accurate eigenvalues while keeping a reasonable runtime. For instance, if we take $N = M = 1,000$,

we will get very accurate eigenvalues; however, the Hamiltonian will have dimension $999,001 \times 999,001$ which will either take far to long to converge to an answer, or will take up too much memory to ever converge. Because of this, it is important to maximize $N$ and $M$ such that we receive a finite runtime with an accurate energy value. This has yet to be accomplished, but it is still informative to view the shape of the wavefunction for moderate $N, M$:
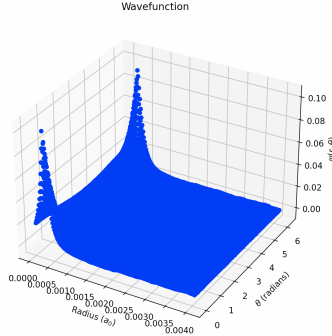


Figure 22: Eigenfunction for $H_2^+$ ion with basis $|r, \theta\rangle$; $R/a_0 = 2.4$

We see exponential decay as $r$ increases, as well as the wraparound of the wavefunction matching at $\theta = 0 = 2\pi$. The peak we examine is at the location of the second proton. Another problem that causes concern is the lack of a peak at $r = 0$, the location of the first proton. While this is a good beginning, it is far from complete and must be left out of the previous analysis.

## 9.2 $H_2$ VMC Code

The analysis for the $H_2$ molecule has begun, but the lack of the code for the $|r, \theta\rangle$ basis causes no $H_2$ eigensolver. Thus, the $H_2$ molecule is left out of the above analysis; however, it's VMC results are interesting, nonetheless. For the

$H_2$ molecule, we have two nuclei separated by a distance $R$, and two electrons free to move around the system. The Hamiltonian for this system is:

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + \frac{-e^2}{4\pi\epsilon_0}(\frac{1}{|\vec{r_1} - \vec{r_2}|} + \frac{1}{R} - \frac{1}{r_1} - \frac{1}{r_1'} - \frac{1}{r_2} - \frac{1}{r_2'}) \quad (9.6)$$

where we invoke the Born-Oppenheimer and fixed proton approximations to simplify the Hamilton. We guess a wavefunction that associates one electron with each proton. This is known as the Heitler-London approximation:

$$\psi(r_1, r_2) = A[\psi_0(r_1)\psi_0(r_2') + \psi_0(r_1')\psi_0(r_2)] \quad (9.7)$$

where $\psi_0$ is a hydrogenic wavefunction. We then normalize:

$$1 = \int\int |\psi(r_1, r_2)|^2 d^3\vec{r_1} d^3\vec{r_2} = A^2[\int \psi_0(r_1)^2 d^3\vec{r_1} \int \psi_0(r_2')^2 d^3\vec{r_2}$$
$$+ \int \psi_0(r_1')^2 d^3\vec{r_1} \int \psi_0(r_2)^2 d^3\vec{r_2} + 2\int \psi_0(r_1)\psi_0(r_1')d^3\vec{r_1} \int \psi_0(r_2)\psi_0(r_2')d^3\vec{r_2}]$$

Since each wavefunction is individually normalized, we can simplify this normalization equation. (Also note that as we perturb each wavefunction, the individual wavefunctions will lose normalization equal to 1, but since the perturbations are small, we approximate these to be still normalized to speed up the algorithm). Let $I_1 = \langle\psi_0(r_1)|\psi_0(r_1')\rangle$ and $I_2 = \langle\psi_0(r_2)|\psi_0(r_2')\rangle$ and we see:

$$A = \frac{1}{\sqrt{2(1 + I_1 I_2)}} \quad (9.8)$$

By the same method for the $H_2^+$ ion, we find expressions for $\langle T_1 \rangle$, $\langle T_2 \rangle$, $\langle V_1 \rangle$, $\langle V_1' \rangle$, $\langle V_2 \rangle$, $\langle V_2' \rangle$. We write the expressions here and leave the Griffith's text for a more in-depth derivation. Note that $E_i$ is given by calculating the energy of

49

one of the wavefunctions in $\psi(r_1, r_2)$ in our initial hydrogen atom VMC code. Also, since we have four degrees of freedom (4 wavefunctions we can perturb), we call these $\psi_i$ for $i = 1, ..., 4$.

$$\langle T_1 \rangle = A^2 [(E_1 + E_1')(1 + I_1 I_2) + \frac{e^2}{4\pi\epsilon_0}(\langle\psi_1| \frac{1}{r_1} |\psi_1\rangle)$$
$$+ \langle\psi_1| \frac{1}{r_1'} |\psi_1'\rangle I_2 + \langle\psi_1'| \frac{1}{r_1'} |\psi_1\rangle I_2 + \langle\psi_1'| \frac{1}{r_1'} |\psi_1'\rangle] \tag{9.9}$$

By symmetry, $\langle T_2 \rangle$ is the same with each subscript 1 replaced with a subscript 2 referencing a different wavefunction. Now, for the potentials:

$$\langle V_1 \rangle = \frac{-e^2}{4\pi\epsilon_0}[\langle\psi_1| \frac{1}{r_1} |\psi_1\rangle + \langle\psi_1| \frac{1}{r_1} |\psi_1'\rangle I_2 + \langle\psi_1'| \frac{1}{r_1} |\psi_1\rangle I_2$$
$$+ \langle\psi_1'| \frac{1}{r_1} |\psi_1'\rangle] \tag{9.10}$$

Where the other potential expectation values have similar expressions. Finally, we need an expression for the expectation of the electron-electron repulsion potential. We simplify the expression by letting $\frac{1}{|\vec{r_1} - \vec{r_2}|} = \frac{1}{r_{12}}$:

$$\langle V_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \int \int |\psi(r_1, r_2)|^2 \frac{1}{r_{12}} d^3\vec{r_1} d^3\vec{r_2}$$
$$= \frac{e^2}{4\pi\epsilon_0} A^2 [2D_2 + 2X_2] \tag{9.11}$$

where

$$D_2 = \int \int |\psi(r_1)|^2 \frac{1}{r_{12}} |\psi(r_2)|^2 d^3\vec{r_1} d^3\vec{r_2} \tag{9.12}$$

and

$$X_2 = \int \int \psi(r_1)\psi(r_1')\frac{1}{r_{12}}\psi(r_2)\psi(r_2')d^3\vec{r_1}d^3\vec{r_2} \tag{9.13}$$

These integrals are numerically calculated by the method outlined in Griffith's text. Once we have all of these expectation values in terms that can be integrated numerically, we can calculate $\langle H \rangle$ given our input arrays, $\psi_1, \psi_2, \psi_3, \psi_4$. From here, we use the VMC algorithm to perturb each of these input arrays, calculate $\langle H \rangle$ for this state, and accept/reject accordingly. Since we are computing many integrals numerically, our code begins to slow down considerably. Each iteration of the VMC code takes roughly 7 minutes to run. Because of this, we see very long runtimes for running multiple VMC iterations. The energy versus proton distance we observe is as expected:
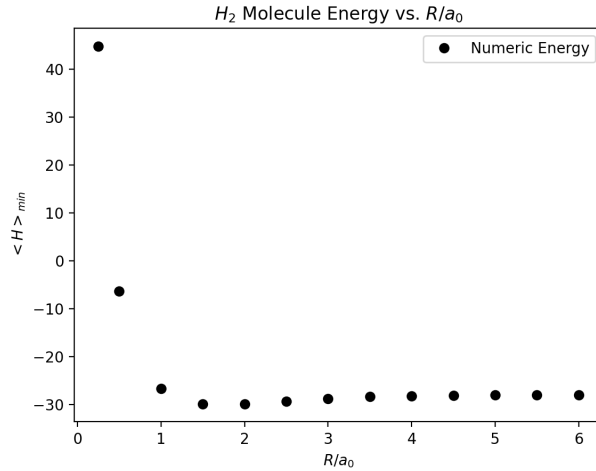


Figure 23: $\langle H \rangle$ vs. $R/a_0$ for the Hydrogen Molecule

Again, we are seeing a bound state at roughly $R/a_0 = 1.5$ which is close to the true bond length of the hydrogen molecule of $R/a_0 = 1.4$. Our ground state energy is $-29eV$ which is a 5.2% error from the true ground state energy of $-30.6eV$.

# 10    Conclusion

There are clearly positives and negatives of both of these two algorithms, VMC and the eigensolver. When complexity of molecules increase, runtimes grow very large for both of these algorithms in order to encapsulate the true nature of the quantum system. Further testing is necessary in order to determine how efficient we can tune these algorithms; however, for simpler potentials, the accuracy and speed of these algorithms makes them very useful in corroborating theoretical predictions or experimental results.

# 11    Works Cited

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# 12    Appendix

# List of Figures

## List of Tables