

Quantum Monte Carlo calculation of the Hydrogen molecule ground state energy

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May 2023

Abstract

In this project, we go through some examples of Monte Carlo integration and give examples for each of them. We determine a trial wavefunction for a H_2 molecule to calculate its ground state energy through a metropolis Monte Carlo method. We then use variational methods to minimize the trial wavefunction. We do an imaginary time evolution to the ground state energy. We find a binding energy of $E_b = 4.711 \pm 0.088 \text{ eV}$ and a proton separation of $S = 0.77 \pm 0.03 \text{ \AA}$. Finally we find the local energy of a helium atom changing the proton separation to $S = 0 \text{ \AA}$. For the helium atom we find a local energy of $E = -78.32 \pm 0.11 \text{ eV}$

Key words: Monte Carlo, Metropolis, Hydrogen molecule ground state

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1 Introduction

The project's objective is to calculate the ground energy state of a H_2 molecule using the Born-Oppenheimer approximation (Born & Oppenheimer (1927), Encyclopedia (2022)). For that aim, we employ a Monte Carlo or probabilistic method. There are many Monte Carlo integration techniques with varying degrees of complexity. In this report we will present different methods, namely Basic Monte Carlo integration, importance sampling and Metropolis methods, and work out the complications that each of them bring.

We determine the ground state energy in two steps. Firstly, we will determine a trial function for the energy eigenstate and use the metropolis and variational methods to calculate and fix the variables. That is, we will fix a β parameter that will be part of the trial function and the proton separation. The second step involves exploiting the mapping of the Schrödinger Equation for imaginary time to a diffusion equation, to then evolve the approximate state onto the exact ground state and find its energy. The project follows the steps from Koonin (1986).

2 Monte Carlo Integration and useful mathematical methods

Monte Carlo uses large amounts of random numbers to determine the probabilities of finding different solutions to problems that are more difficult or impossible to calculate algebraically. These solutions are approximations of the answer rather than exact solutions, so error rates must be taken into account. Nevertheless, as you increase the number of random numbers, the error rate decreases.

2.1 Basic Method

The mean of a function is given by

$$\bar{f} = \frac{\sum_{i=1}^N f(x_i)}{N} = \frac{\sum_{i=1}^N f_i}{N} \quad (1)$$

where N is the number of iterations, and $f_i \equiv f(x_i)$. The expectation value of our mean is equivalent to the true value $\langle \bar{f} \rangle = \mu$. The variance (var or σ^2) is given by

$$\begin{aligned} \text{var}(f_i) &= \langle (f_i - \mu)^2 \rangle = \\ \langle f_i^2 \rangle - \mu^2 &= \langle f_i^2 \rangle - \langle f_i \rangle^2 = \sigma^2 \end{aligned} \quad (2)$$

We calculate the total uncertainty by finding the standard error of the mean

$$\sigma_{\bar{f}}^2 = \text{var}(\bar{f}) = \langle \bar{f}^2 \rangle - \langle \bar{f} \rangle^2 = \frac{1}{N} (\langle f_i^2 \rangle - \langle f_i \rangle^2) = \frac{\sigma^2}{N} \quad (3)$$

and, therefore

$$\sigma_{\bar{f}} = \frac{\sigma}{\sqrt{N}} \quad (4)$$

$N \rightarrow N - 1$ when we must estimate μ using the sampled data. The key to this method is the fact that it has a conversion rate proportional to $\frac{1}{\sqrt{N}}$. It does not increase when adding dimensions so, while other methods like the trapezoidal or Simpson's method have a much faster conversion rate at lower dimensions, at higher dimensions the Monte Carlo method takes the lead and performs much faster calculations. Given

$$I = \int_a^b f(x) dx \quad (5)$$

The Basic Monte Carlo method follows the formula:

$$\hat{I} = (b - a) \bar{f} = \frac{(b - a)}{N} \sum_{i=1}^N f_i \quad (6)$$

where \hat{I} is the approximation of I . It always has a convergence of $\frac{1}{\sqrt{N}}$ towards the exact solution (Caffisch 1998), where N is the number of points selected.

2.1.1 Example

We have calculated an example using this method. The integral

$$I = \int_0^1 \frac{1}{1+x^2} dx \quad (7)$$

has the exact solution $\frac{\pi}{4}$. The convergence towards the exact solution is shown in figure 1. This example could be easily extended to a two-dimensional, three-dimensional, or even a higher-dimensional problem by randomizing points $[x,y,z]$ in an equation such as

$$I = \oint_0^1 \frac{1}{1+x^2+y^2+z^2} dx dy dz \quad (8)$$

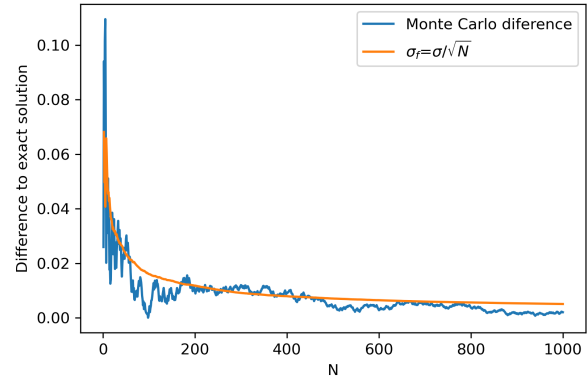


Figure 1: Convergence rate of the Monte Carlo method (shown in orange) compared to the difference to the exact solution (shown in blue). This result was produced by running the code once, and does not prove the absolute correctness of our method. Nevertheless, it does suggest that we are on the right path.

2.2 Importance sampling and rejection method.

This is a brief explanation of importance sampling technique or the von Neumann method (von Neumann 1951).

The expectation value of a function f with respect to a normalized probability density $p(x)$ is given by

$$\langle f \rangle = \int f(x) p(x) dx \quad (9)$$

We can make use of this property to increase the efficiency of the previous method by altering the equation. If we redefine our initial equation to be

$$\int_a^b f(x) dx = \int_a^b w(x) \frac{f(x)}{w(x)} = \int_a^b w(x) g(x) dx \quad (10)$$

we get a better convergence. This method employs a known probability density function $g(x)$. It is also required that $\int g(x) = 1$ in the range we are calculating (since probability distributions must equal 1). With a

good choice of $w(x)$, more precisely, if $\frac{f(x)}{w(x)} \approx 1$, the convergence should improve. This is because very few points are discarded, and the function $w(x)$ already gives us a close approximation to the solution. We calculate the function $w(x)$ with a probability distribution $g(x)$. The last step would be to apply equation 1. Suppose that our choice of $g(x)$ is not invertible so we can not use it directly as our probability distribution. We would then use the rejection method to sample from a distribution $\rho(x)$ to get a probability $g(x)$. In that case, the function $\rho(x)$ must be invertible to get a probability distribution or be a known probability distribution such as the Gaussian distribution or a linear distribution. The steps (Feiguin 2009b) to do this are:

1. Get a random number (x) with probability distribution $\rho(x)$.
2. Get a random number (y) with a uniform probability distribution in the range $[0, x]$.
3. If $y < g(x)$ for the y and x that we have just calculated, we save that data point. If not, we discard it and try again.

Following this method we could get a probability distribution $g(x)$ from a different probability distribution $\rho(x)$

In conclusion, this method calculates the expectation value of $g(x)$ under the probability function $w(x)$ where we have chosen $g(x) = \frac{f(x)}{w(x)}$, consequently solving the integral of $f(x)$.

2.2.1 Example

To showcase this method, we will evaluate the integral in equation 7. We will use a series of different $g(x)$ functions: two linear probability distributions $g(x) = 2$ and $g(x) = 6/5$, and an invertible function $g(x) = 2 - x$ ($g(x) = -\frac{2}{3}(2 - x)$ once normalized).

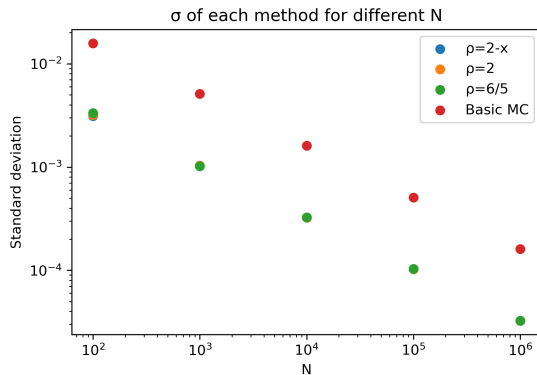


Figure 2: Standard deviation for different probability distributions of ρ (also defined previously as $g(x)$). All three importance sampling integration methods are shown to be of the same accuracy. This method is more efficient than the basic Monte Carlo method.

The last probability distribution has been calculated in appendix A. We will also compare the results with those of the basic Monte Carlo method. The errors of each of them are shown in figure 2 and figure 3. These results show that regardless of the probability distribution used (and as long as it meets the basic requirements), the same result is achieved, and the same uncertainty is found. We encounter the expected outcome, as the only difference is the number of rejected points, increasing the calculation time but not the accuracy. We also see that it is more accurate than the Basic Monte Carlo method.

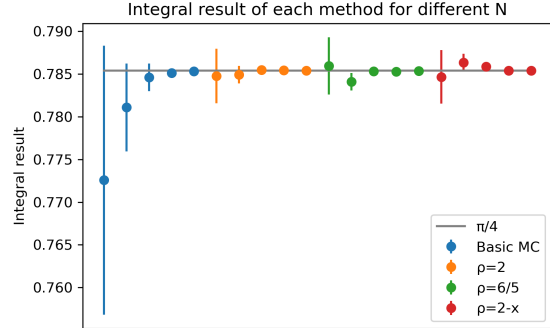


Figure 3: Convergence towards the right result employing different Monte Carlo methods. Each of the colored points shows the results for 100, 1000, 100,000 and 1,000,000 different points from left to right. They have been displaced so it is easier to read but each of the colors should superpose each other.

2.3 Metropolis method

The metropolis method has some similarities to the previous method, but the point selection process is different. Its main advantage with respect to other methods is that it is able to generate points sampled over very complicated distributions in many dimensions. We once again separate the function inside of the integral into a probability distribution $g(x)$ and the rest ($f(x)$).

$$\langle f \rangle = \int f(x)g(x)dx \quad (11)$$

The steps are:

1. We need an initial point to start our sequence. This can be arbitrarily generated in several different ways. In this project, we have decided to use a uniform distribution with numbers of a comparable magnitude. An arbitrary start like 0 could also be used.
2. We then generate a new trial x point following the equation

$$x = x_i + 2\delta(rand - 1/2) \quad (12)$$

where x_i is the previous point, $rand$ is a random number in the range $[0,1]$, and δ is a variable we

will adjust later to get a relation between the accepted and rejected values. This ratio should be around 50%

3. We will then accept the trial value x if $g(x) \geq g(x_i)$, so $x_{i+1} = x$.
4. If the above relation is not fulfilled, we will accept the point if $r \leq \frac{g(x)}{g(x_i)}$ where r is a random number in the range $[0,1]$, so $x_{i+1} = x$.
5. If this is again not the case, we will use the previous point x as the new point, so $x_{i+1} = x_i$.
6. With all the points calculated, we once again make use of equation 1 to get the final result.

This sequence is repeated for the desired number of points. The δ variable is fine-tuned for each specific integral to get an acceptance rate close to 50%.

Unlike the previous methods, metropolis uses a previous point to generate a new one, creating some complications. If the trial point isn't accepted, then the new point is the same as the previous one. Successive points are correlated, meaning points are not genuinely random. The uncertainty of the calculations could be altered, and this is precisely what happens. To fix this problem, a binning process is done. We look for a bin length at least as long as the typical range of correlations. Points are put into bins in groups of 2, 4, 8, etc. The standard error is calculated for each of the bins and, once the uncertainty stabilizes, we can state that we have truly uncorrelated points.

2.3.1 Auto-correlation in metropolis method

Auto-correlation is defined as

$$C(k) = \langle f_i f_{i+k} \rangle - \langle f_i \rangle^2 = \langle f_i f_{i+k} \rangle - \mu^2 \quad (13)$$

where k is the lag (number of points displaced). The variance of the mean of a correlated function \bar{f} is given by

$$\begin{aligned} \text{var}(\bar{f}) &= \langle \bar{f}^2 \rangle - \langle \bar{f} \rangle^2 = \\ &= \frac{1}{N^2} \left[\sum_{i=1}^N \langle f_i \rangle^2 + \sum_{i=1}^N \sum_{k=1}^N \langle f_i f_{i+k} \rangle \right] - \mu^2 \end{aligned} \quad (14)$$

Combining both equations and making use of the fact that $C(0) = \langle f_i^2 \rangle - \mu^2$, we can arrive at

$$\text{var}(\bar{f}) = \frac{1}{N} \left[C(0) + 2 \sum_{k=1}^{N-1} \left(1 - \frac{k}{N}\right) C(k) \right] \quad (15)$$

$C(k)$ typically decays exponentially with k , allowing us to drop the k/N term. So, for large N

$$\text{var}(\bar{f}) \approx \frac{2}{N} C(0) \left[\frac{1}{2} + \sum_{k=1}^{N-1} \frac{C(k)}{C(0)} \right] = \frac{2}{N} \tau_{int} C(0) \quad (16)$$

Rearranging, we get:

$$\tau_{int} = \frac{1}{2} + \sum_{k=1}^{N-1} \frac{C(k)}{C(0)} \quad (17)$$

This quantity is called the integrated auto-correlation time. Shifting the values in the array and comparing them permits checking for auto-correlation. The auto-correlation graph should approach zero at the same time as the bins stabilize on a specific standard deviation. We expect this plot to have a shape following the equation $C_{norm}(k) = C(k)/C(0) = \exp(\frac{-x}{\tau_{slope}})$ once it has been normalized by $C(0)$. To find the value of τ_{slope} , we can take the natural log of C_{norm} and calculate the slope. We expect $\tau_{slope} = \tau_{int}$.

2.3.2 Example

For this method we will be solving the integral

$$I = \int_{-\infty}^{\infty} x^2 \cdot e^{-\frac{x^2}{2}} dx \quad (18)$$

where $f(x) = x^2$ and $g(x) = e^{-\frac{x^2}{2}}$. The exact solution of this example is $\sqrt{2\pi}$. This can be normalized in the following way:

$$I = \frac{\int_{-\infty}^{\infty} x^2 \cdot e^{-\frac{x^2}{2}} dx}{\int_{-\infty}^{\infty} e^{-\frac{x^2}{2}} dx} = 1 \quad (19)$$

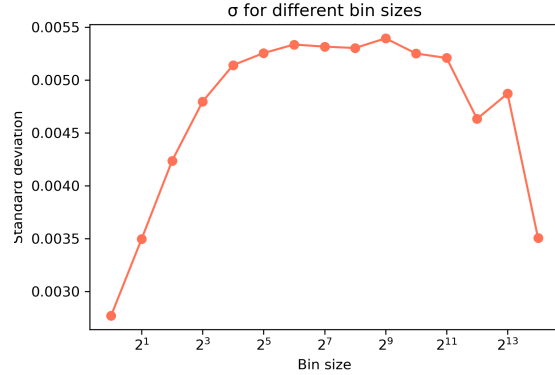


Figure 4: Standard deviation vs the number of bins. We see that it rises up to roughly 0.0053 and stabilizes, indicating that binning using 32 (or maybe 64) points is enough to remove correlation.

After generating the Monte Carlo chain to evaluate the integral, we carry out the binning process to determine the actual standard error of our results. Figure 4 illustrates the uncertainty for the different bins. We can see that it increases to a specific value at which it stabilizes. The last points of the graph can be disregarded since, at that point, very few bins are left. Auto-correlation is shown in figure 5. A logarithmic plot finds the slope at which it falls (τ_{slope}). We then use equation

17 to get τ_{int} . When comparing the two in figure 6 we see that they do indeed match.

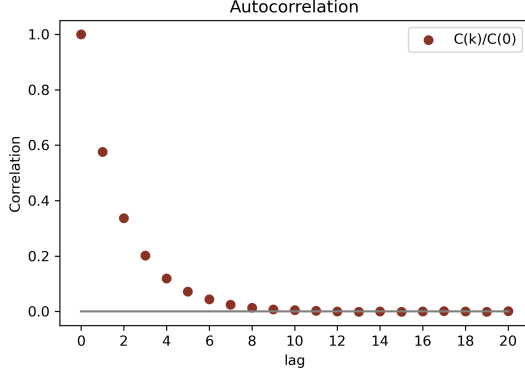


Figure 5: Correlation of a function with itself when shifting its values by a lag.

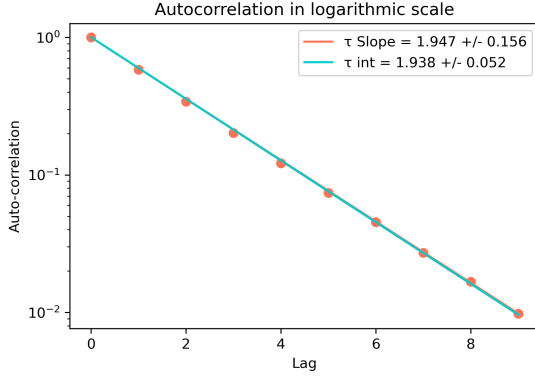


Figure 6: Comparison of the analytical solution τ_{int} to our graphical solution τ_{slope} .

3 Variational method for H_2 molecule

The variational method is a technique widely used in quantum mechanics to approximate the ground state energy and wavefunction of a complex quantum system. The main idea is to select a trial wavefunction from a class of functions known to be physically reasonable, such as products of polynomials and exponential functions, or linear combinations of Gaussian functions. The trial wavefunction is adjusted to minimize the expectation value of the energy calculated using the Schrödinger equation, which describes the time evolution of a quantum system. The variational solution is an upper bound on the true ground state energy of the system. Therefore, by selecting an appropriate trial wavefunction, the method can provide accurate estimates of the ground state energy and wavefunction, which can be utilized to predict the properties of the system. Usually variational methods are used to solve complex systems with many

electrons as it is not possible to solve them analytically [Yuan et al. \(2019\)](#). In our case, we will only have two electrons, which should make it relatively simple to implement. We will use the Born-Oppenheimer approximation to produce accurate results that describe the ground state energy of a two hydrogen atoms system. A diagram of the system we want to solve is shown in figure 7. The potential governing the protons' motion at a certain distance S is given by

$$U(S) = E_0(S) + \frac{e^2}{4\pi\epsilon_0 S} \quad (20)$$

for electronic eigenvalue $E_0(S)$ and electron charge e . The electronic eigenvalue is given by the Schrödinger Equation

$$H(S)\psi_0(r_1, r_2, S) = (K + V(S))\psi_0(r_1, r_2, S) = E_0(S)\psi_0(r_1, r_2, S) \quad (21)$$

Where the Hamiltonian is defined as

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V \quad (22)$$

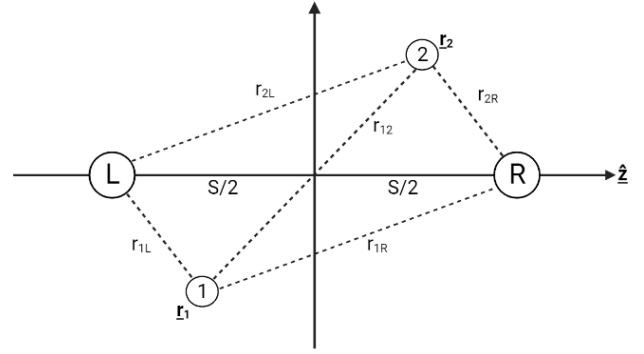


Figure 7: Electron and proton positions. The protons (L,R) are at a fixed position, while the electrons (1,2) are free to move around. [This diagram was done by my project partner Charlie Cane.]

From the Pauli exclusion principle, we determine that the spin wavefunction is antisymmetric (since for a ground state with the electrons having total spin zero, the spin wavefunction is antisymmetric), so the spatial wavefunction must be symmetric under electron interchange. The kinetic term of the electrons is given by

$$K = \frac{-\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) \quad (23)$$

where the protons are separated by a distance S (so they are located at $(-S/2, 0, 0)$ and $(S/2, 0, 0)$). The potential V is given by

$$V = \frac{-e^2}{4\pi\epsilon_0} \left[\frac{1}{r_{1L}} + \frac{1}{r_{2L}} + \frac{1}{r_{1R}} + \frac{1}{r_{2R}} \right] + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (24)$$

We require a trial wavefunction which we improve later on. For now, we to solve the equation

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int d^3r_1 d^3r_2 \psi^*(r_1, r_2) H \psi(r_1, r_2)}{\int d^3r_1 d^3r_2 |\psi(r_1, r_2)|^2} \quad (25)$$

We transform it to use Monte Carlo metropolis integration on it

$$E = \frac{\int d^3r_1 d^3r_2 |\Phi(r_1, r_2)|^2 \left[\frac{1}{\Phi} H \Phi \right]}{\int d^3r_1 d^3r_2 |\Phi(r_1, r_2)|^2} \quad (26)$$

where we take $|\Phi(r_1, r_2)|^2$ to be our probability distribution. We can write the local energy as

$$E(r_1, r_2) = \frac{1}{\Phi} H \Phi = \frac{-\hbar^2}{2m} \frac{1}{\Phi} \sum_{i=1,2} \nabla_i^2 \Phi + V(r_1, r_2) \quad (27)$$

We will assume that we write a trial solution of the form

$$\Phi(r_1, r_2) = \varphi(r_1) \varphi(r_2) f(r_{12}) \quad (28)$$

where

$$\varphi(r_i) = e^{-r_{iL}/a} + e^{-r_{iR}/a} \quad (29)$$

We must fix the parameters to ensure that the wavefunction remains finite. Here, a is still undetermined but it is evaluated in the appendix B to be $a = \frac{a_0}{1+e^{-S/a}}$ where a_0 is the Bohr radius. Using an iterative method, this equation is easily solvable.

We define $f(r)$ to be

$$f(r_{12}) = \exp\left(\frac{r_{12}}{\alpha(1 + \beta r_{12})}\right) \quad (30)$$

where, once again, α and β are undefined. In the appendix C, α is solved to be $\alpha = 2a_0$. β is now the only undetermined parameter, and we can use a variational approach to find where the function is at its lowest. The expression for the kinetic term of the local energy is worked out in the appendix D to be

$$\begin{aligned} & \frac{-\hbar^2}{2m} \frac{1}{\Phi} \sum_{i=1,2} \nabla_i^2 \Phi = \\ & - \frac{\hbar^2}{2m} \left[\frac{\nabla^2 g(r_{1L}) + \nabla^2 g(r_{1R})}{g(r_{1L}) + g(r_{1R})} + \frac{\nabla^2 g(r_{2L}) + \nabla^2 g(r_{2R})}{g(r_{2L}) + g(r_{2R})} \right. \\ & + 2 \left(\frac{\frac{g'(r_{1L})}{r_{1L}} r_{1L} + \frac{g'(r_{1R})}{r_{1R}} r_{1R}}{g(r_{1L}) + g(r_{1R})} - \frac{\frac{g'(r_{2L})}{r_{2L}} r_{2L} + \frac{g'(r_{2R})}{r_{2R}} r_{2R}}{g(r_{2L}) + g(r_{2R})} \right) \\ & \left. \cdot r_{12} \frac{f'(r_{12})}{r_{12} f(r_{12})} + 2 \frac{\nabla^2 f(r_{12})}{f(r_{12})} \right] \quad (31) \end{aligned}$$

where we have defined $g(r)$ as

$$g(r) = \exp\left(-\frac{r}{a}\right) \quad (32)$$

We now go back to equation 26 and 27 so we have a formula for $\frac{1}{\Phi} H \Phi$. We will do Monte Carlo integration using this as the function we are integrating and $|\Phi(r_1, r_2)|^2$ as the probability distribution, following equation 6. The array of electron positions will be calculated by applying metropolis method (equation 12) with $\delta = 0.45\text{\AA}$. As previously discussed, Monte Carlo method adds the problem of having points that are not fully random, which brings us to the next step.

3.1 Auto correlation

So far, we have defined the trial wavefunction. Our objective now is to transform this trial wave function into the closest solution we can, to find the ground state energy. But first, we must test the auto-correlation of our results. For the sake of reproducibility, these are the parameters used: the parameter $\beta = 1\text{\AA}^{-1}$, and the proton separation $S=0.5\text{\AA}$. Both of these are chosen arbitrarily and will be minimized later on. The total number of electron positions, i.e. the array of positions from where the energy is calculated, is chosen to be $n = 2^{16}$. We choose this unnecessarily high number so that, even after binning, we will have a high enough number of points. This will ensure that, later on, the standard error of the integrals will be relatively low.

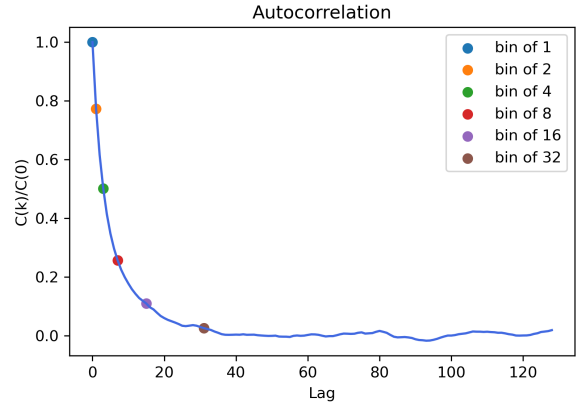


Figure 8: Auto correlation for different lag. Bins of 1 to 32 are shown in different colors. It stabilizes by the 32 bins which is when our data becomes uncorrelated.

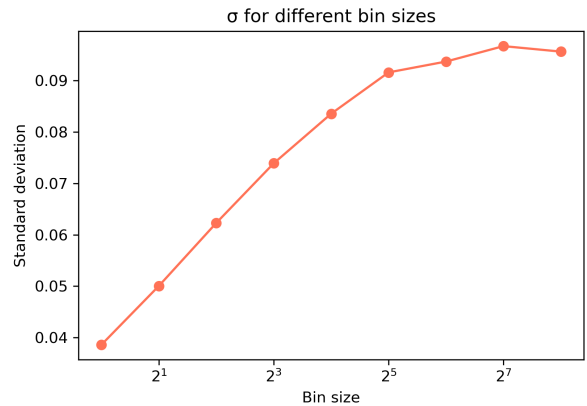


Figure 9: Standard deviation of local energy calculation depending on the bin size. The first point $2^0 = 1$ corresponds to the standard deviation without any binning.

Now that everything is ready, we can calculate the auto-correlation of our electron array. Figure 8 shows the auto-correlation for a particular lag. The colored points show the powers of 2. By lag=32 the auto correlation

has stabilized and fluctuates around 0, therefore we can take 2^5 to be the appropriate bin size for the rest of the calculations. Figure 9 corroborates the results, since the standard error settles at the same bin size.

3.2 Beta parameter

We do several steps to minimize the energy. There are two different free parameters that have to be solved, β and the proton separation S . We first fix the S parameter, and once β has been minimized we determine the optimal value of S . The total energy will be given by a combination of the local energy, i.e., electron interactions, and the proton interactions. The parameter β is only used to find the local energy, so for now we don't need to take into account the energy from proton interactions. Having done a general sweep of the local energy depending on β , we determine that the minimum will lie in the range $[1, 2]\text{\AA}^{-1}$.

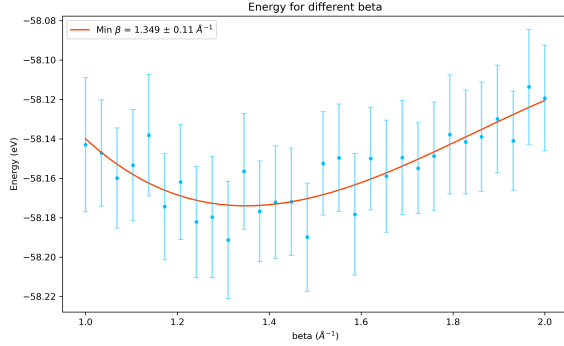


Figure 10: Local energy of the H_2 molecule for different beta in the range of 1 to 2 \AA . Fit is calculated from a third-degree polynomial. We find a minimum at $\beta = 1.349 \pm 0.11\text{\AA}^{-1}$.

We do a variational method to solve β by finding its minimum. Additionally, since we find the results to be very noisy, we calculate each energy 100 times to find the average between them. Since the data was still relatively noisy even after that, we have fit a third-degree polynomial curve as it is the best fit for the data in the given range. The resulting equation is $y(x) = -0.15x^3 + 0.84x^2 - 1.44x - 57.39$. From figure 10 we determine a minimum $\beta = 1.349 \pm 0.11\text{\AA}^{-1}$.

3.3 Proton separation parameter

Now that we have determined a β value of 1.349 we find the separation between the two protons. The total energy of the system that we must minimize is given by all the interactions between the electrons and protons. For each of the plots in this section 50 different proton separations are calculated evenly spaced in the given range. The same parameters are used as in the previous section.

From equation 20, we can see that both the local energy and the proton Coulomb potential, depend on the

S parameter. The local energy generates an attractive (negative) force that increases with proton separation. The proton Coulomb potential generates a repellent (positive) force that decreases with proton separation. These are shown in figure 11. Each of the plots have been given a fit. The proton interaction energy is just given by the second term in equation 20. The electron interaction energy has been given a logarithmic fit. The resulting equation is $y(x) = 14.62 \log(x) - 49.96$. We can also see that at high proton separations, the local energy plot diverges. For this reason, when calculating the fit, only the first 20 points have been used as the later divergence would give a bad fit. We can see that the fit follows the top of the two divergences.

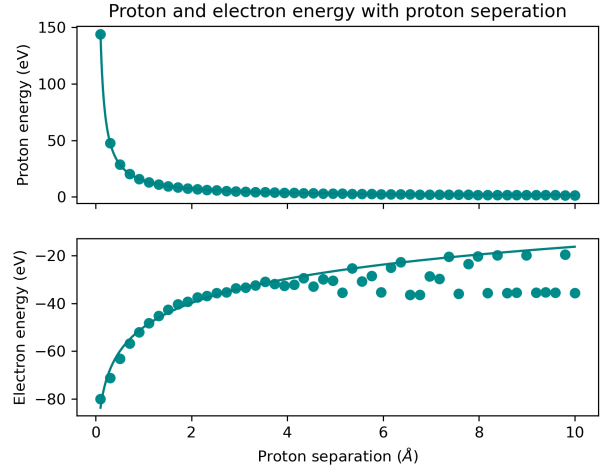


Figure 11: Energy of the proton (top) and electron (bottom) interactions at 50 proton separations between 0.1 \AA and 10 \AA . Fit from the top plot follows the second term in equation 20 while the bottom plot has a logarithmic fit (using only the first 20 points).

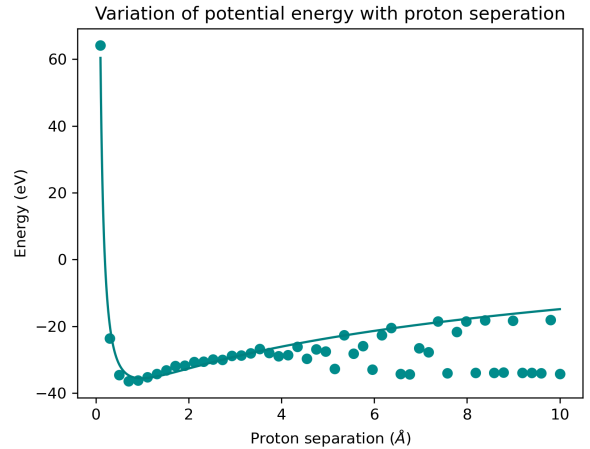


Figure 12: Total potential of the system at 50 proton separations between 0.1 \AA and 10 \AA . The fit is generated from the addition of the fits from figure 11.

From the fit, we find a minimum at $S = 0.77 \pm 0.03\text{\AA}$. There are a different reasons why this could be the

case, which will be discussed later on. From the two plots, we expect that putting them together gives a minimum and a lowest total energy. The total energy is shown in figure 12 with a range $S = [0.1, 10] \text{ \AA}$. We see that by just adding the two previous fits we get a reasonably good final fit. However, it is not very precise, so to find the best solution we zoom in to the range $S=[0.5, 1.5]\text{\AA}$, shown in figure 13. From the fit, we determine a minimum energy at proton separation $S = 0.77 \pm 0.03 \text{ \AA}$. At this proton separation we find a potential of $U(0.77) = -36.44 \pm 0.16 \text{ eV}$.

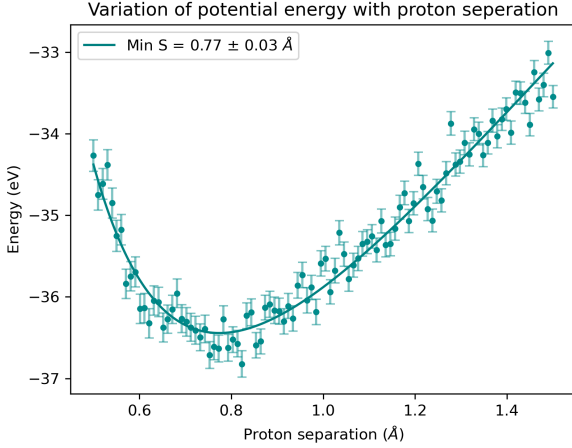


Figure 13: Total potential of the system at 50 proton separations between 0.1 \AA and 10 \AA . From the fit we can determine a minimum at $S = 0.77 \pm 0.03 \text{ \AA}$ with potential $U(0.77) = -36.44 \pm 0.16$.

4 Time evolution of H_2 molecule

We have now optimised the variational solution (to minimize the energy), but now need the imaginary time evolution to evolve onto the true ground state. Going back to the Schrödinger Equation, and implementing time dependency, we write

$$\begin{aligned} i\hbar \frac{\partial \Psi(r, t)}{\partial t} &= (E_n - H)\Psi(r, t) \\ \hbar \frac{\partial \Psi(r, \tau)}{\partial \tau} &= (E_n - H)\Psi(r, \tau) \end{aligned} \quad (33)$$

where we have used $\tau = it$ where τ is the imaginary time.

If we define a new function $G = \Phi(r)\Psi(r, \tau)$ where at time $\tau = 0$, $G(r, 0) = |\Psi|^2$ we can rewrite the Schrödinger Equation as

$$\frac{\partial G(r, \tau)}{\partial \tau} = \frac{1}{\hbar} (E_n - \Phi(r)H \frac{1}{\Phi(r)})G(r, \tau) \quad (34)$$

We define Ψ to be

$$\Psi(\underline{r}, \tau) = \exp \left[\int_0^\tau E_n(\tau') d\tau' / \hbar \right] e^{-H\tau/\hbar} \Phi(\underline{r}) \quad (35)$$

Using the hermicity of H state

$$E(\tau) = \frac{\langle \Phi | H | \Psi(\tau) \rangle}{\langle \Phi | \Psi(\tau) \rangle} = \frac{\int d\underline{r} \Phi(\underline{r}) \Psi(\underline{r}, \tau) E(\underline{r})}{\int d\underline{r} \Phi(\underline{r}) \Psi(\underline{r}, \tau)} \quad (36)$$

where $E(\tau \rightarrow \infty) = E_n$ or the ground state energy. As stated in equation 22 the Hamiltonian is

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + V \quad (37)$$

We want to evaluate the second term of 34. For that, we must explicitly write out the local energy which we will use as a replacement for the potential (V) whenever it appears.

$$E(\underline{r}) = \frac{1}{\Phi} H \Phi = \frac{1}{\Phi} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Phi}{\partial r_i^2} \right) + V \quad (38)$$

where $\frac{\partial^2}{\partial r_i^2}$ denotes the second order derivative with respect to each of the six electron coordinates.

$$\begin{aligned} H \left(\frac{1}{\Phi} G \right) &= -\frac{\hbar^2}{2m} \frac{\partial^2 \Phi}{\partial r_i^2} \left(\frac{1}{\Phi} G \right) + V \frac{1}{\Phi} G \\ &= -\frac{\hbar^2}{2m} \frac{1}{\Phi} \frac{\partial^2 G}{\partial r_i^2} - \frac{\hbar^2}{2m} \frac{1}{\Phi} \left[2 \left(\frac{1}{\Phi^2} \frac{\partial \Phi}{\partial r_i} \frac{\partial \Phi}{\partial r_i} - \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial r_i^2} \right) - 2 \frac{1}{\Phi} \frac{\partial \Phi}{\partial r_i} \frac{\partial G}{\partial r_i} \right] \\ &\quad + \epsilon(\underline{r}) \frac{1}{\Phi} G \end{aligned} \quad (39)$$

The second term in equation 39 simplifies to

$$\frac{\hbar^2}{2m\Phi} \frac{\partial}{\partial r_i} \left[\frac{1}{\Phi} \frac{\partial \Phi}{\partial r_i} G \right] = \frac{\hbar}{\Phi} \frac{\partial}{\partial r_i} (D_i G) \quad (40)$$

Therefore:

$$-\frac{1}{\hbar} \Phi H \left(\frac{1}{\Phi} G \right) = \frac{\hbar}{2m} \frac{\partial^2 G}{\partial r_i^2} - \frac{\partial}{\partial r_i} (D_i G) - \frac{1}{\hbar} \epsilon(\underline{r}) G \quad (41)$$

Substituting this into equation 34, we have

$$\begin{aligned} \frac{\partial G(r, \tau)}{\partial \tau} &= \frac{\hbar}{2m} \frac{\partial^2 G(r, \tau)}{\partial r_i^2} - \frac{\partial}{\partial r_i} [D(r)_i G(r, \tau)] \\ &\quad - \frac{1}{\hbar} (E(r) - E_n) G(r, \tau) \end{aligned} \quad (42)$$

where

$$D(r)_i = \frac{\hbar}{m} \frac{1}{\Phi(r)} \frac{\partial \Phi(r)}{\partial r_i} = \frac{\hbar}{m} \frac{\partial \ln(\Phi(r))}{\partial r_i} \quad (43)$$

We have labeled $E(r) = E_r$ as the local energy, and E_n as the average of $E(r)$ over a distribution $G(r, \tau)$. We now draw a comparison between equation 42 and a Diffusion equation

$$\begin{aligned} \frac{\partial G}{\partial \tau} &= \nabla \cdot (D \nabla G) + S \\ &= D \nabla^2 G + \nabla D \nabla G + S \end{aligned} \quad (44)$$

where S is just some function. The first term in equation 42 acts to diffuse G , the drift function D tends to confine G where Φ is large. The last term increases G

most where E is smallest. We now look back on why we have done the last few steps. By starting from the Schrödinger Equation, and evolving the wavefunction in imaginary time, we see that we can treat it just like a diffusion equation.

The evolution of G over a small time step $\tau \rightarrow \tau + \Delta\tau$ can be expressed at order $\Delta\tau$ as

$$G(\underline{r}, \tau + \Delta\tau) = G(\underline{r}, \tau) + \Delta\tau \frac{\partial G(\underline{r}, \tau)}{\partial \tau} \quad (45)$$

Integral kernel $P(\underline{r}, \underline{r}'; \Delta\tau)$ is defined as

$$P(\underline{r}, \underline{r}'; \Delta\tau) = \exp\{-E(\underline{r}) - E_n(\tau)\Delta\tau/\hbar\} \times \left(\frac{m}{2\pi\hbar\Delta\tau}\right)^{3N/2} \exp\left\{-\frac{[\underline{r} - \underline{r}' - D(\underline{r}')\Delta\tau]^2}{2\hbar\Delta\tau/m}\right\} \quad (46)$$

where N denotes the number of electrons. In this case $N=2$. The parameters \underline{r}' and \underline{r} correspond to the electron positions and the new time evolved positions respectively. The first exponential increases the probability of the electrons jumping to a region where the local energy is lowest, while the second is a normalized Gaussian distribution with variance $\hbar\Delta\tau/m$ and mean $D\Delta\tau$. Using P we can write

$$G(\underline{r}, \tau + \Delta\tau) = \int d\underline{r}' P(\underline{r}, \underline{r}', \tau + \Delta\tau) G(\underline{r}', \tau) \quad (47)$$

The time evolving function $P(\underline{r}, \underline{r}'; \tau)$ will transform $G(\underline{r}', \tau)$ (with the old electron positions) into $G(\underline{r}, \tau + \Delta\tau)$ (with the new electron positions). We must lastly make a choice of E_n as to keep $\int d\underline{r} G(\underline{r}, \tau) = \text{constant}$

$$\begin{aligned} \frac{d}{d\tau} G(\underline{r}, \tau) d\underline{r} &= \int d\underline{r} \frac{\partial G(\underline{r}, \tau)}{\partial \tau} \\ &= \int d\underline{r} \left(\frac{-\hbar}{2m} \frac{\partial^2 G}{\partial \underline{r}^2} - \frac{\partial}{\partial \underline{r}} (D(\underline{r}) G(\underline{r}, \tau)) \right) \\ &\quad - \frac{1}{\hbar} (E(\underline{r}) - E_n(\tau)) G(\underline{r}, \tau) \\ &= \frac{-1}{\hbar} \int d\underline{r} (E(\underline{r}) G(\underline{r}, \tau) - E_n(\tau) G(\underline{r}, \tau)) \\ &= \frac{-1}{\hbar} \int d\underline{r} (E(\tau) - E_n(\tau)) G(\underline{r}, \tau) \end{aligned} \quad (48)$$

where we have used $E(\tau) = \frac{\int E(\underline{r}) G(\underline{r}, \tau) d\underline{r}}{\int G(\underline{r}, \tau) d\underline{r}}$ to incorporate $E(\tau)$. Therefore we choose $E_n(\tau) = E(\tau)$.

4.1 Wavefunction time evolution algorithm

We show the algorithm with which we evolve the wavefunction to the ground state.

1. Start from the original ensemble of electron positions (\underline{r}').

2. Evolve positions in time using the formula

$$\underline{r} = \underline{r}' + D \cdot \Delta\tau + \chi \quad (49)$$

where χ variable is defined as a normal distribution with mean=0 and standard deviation $\sqrt{\hbar \cdot \Delta\tau/m}$ where $\Delta\tau$ is the time step and m is the electron mass. D is the drift function. The time step $\Delta\tau$ is a variable that we can choose. However, it must be of the order of the other variables. To find it, we calculate $\sqrt{\hbar \cdot \Delta\tau/m}$ and look for a standard deviation of a few percentages of an Angstrom (table 1). This leads to a time step $\Delta\tau = 10^{-19}$.

3. We must now update the weights of each of the new electron positions. Firstly, the energy $E(\tau)$ is

$$E(\tau) = \left(\frac{\hbar}{\Delta\tau}\right) \log \left[\frac{N}{\sum w'_i \exp(-E(\underline{r}_i)\Delta\tau)} \right] \quad (50)$$

From it we can find the new weights, which must remain normalized as $\frac{1}{N} \sum w_i = 1$

$$w_i = w'_i \cdot \exp \left[\frac{-(E(\underline{r}_i) - E(\tau))\Delta\tau}{\hbar} \right] \quad (51)$$

4. With the new weights, we find the local energy. Having done that, we reiterate until the energy stabilizes. Once it is stable, we decrease the size of the time step $\Delta\tau$ and keep evolving in time with smaller time steps. We do this by decreasing the time steps for a total of 20 times, halving it each time from 10^{-19} , down to $1.9 \cdot 10^{-25}$.

$\Delta\tau$ (s)	σ (Å)
10^{-17}	0.34
10^{-18}	0.1
10^{-19}	0.034
10^{-20}	0.01

Table 1: Standard deviation as a function of the time step size

4.2 Time evolution results

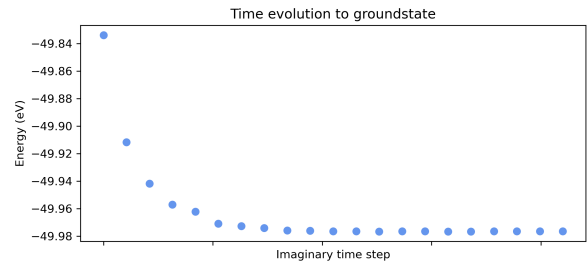


Figure 14: A plot of the energy when evolved in imaginary time. Each point is associated to a different time step from bigger (left) to smaller (right). This plot shows 1 of the 100 runs that were made to find the average energy.

Following this method, we obtain figure 14. By doing the method 100 times (as the results oscillate from run

to run depending on the initial array of electrons) we find that the average energy is $E_n = -50.068 \pm 0.088 \text{ eV}$. The energy of a hydrogen atom ground state is $E_H = -13.598 \text{ eV}$ (Berkeland et al. 1994). The proton-proton energy will be given by their potential energy $E_p = \frac{e^2}{4\pi\epsilon_0 S} = 18.701 \text{ eV}$. The binding energy of the molecule will be given by

$$\begin{aligned} E_b &= 2E_H - E_p - E_n \\ &= 2 \cdot (-13.598) - 18.701 - (-50.068) \\ &= 4.171 \pm 0.088 \text{ eV} \end{aligned} \quad (52)$$

5 Helium atom

A helium atom is very similar structurally to the H_2 molecule we have been using. It has two electrons and two protons just like the H_2 molecule. However, the protons are bound together very closely and it also has two neutrons that will interact with the protons through the strong force. This force is what will keep them together instead of repelling each other, like we see with the protons. The neutrons do not have electrical charge so they will not interact with the electrons. Having stated the key similarities and differences between the two, we know that the local energy will be calculated with the exact same algorithm that we have used for the H_2 molecule. We will not be able to find the total energy of the system or its binding energy, as this will involve finding the strong interactions between the neutrons and protons. The only parameter that must be altered is the proton separation from $S = 0.77 \text{ \AA}$ that we have found for H_2 , to $S=0$. We are fundamentally treating the protons as just one point-like particle with twice as much charge.

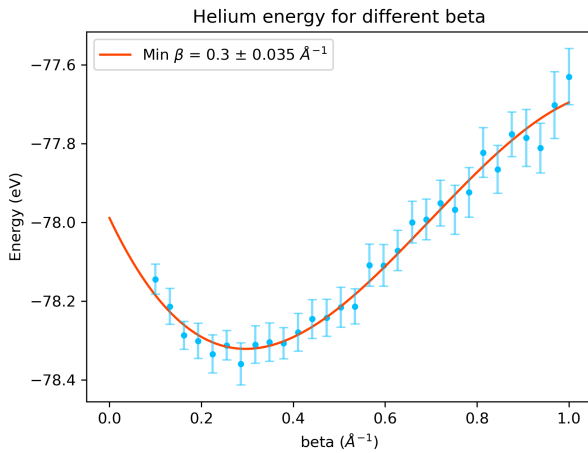


Figure 15: Energy of the Helium atom for different beta in the range of 0 to 1 \AA^{-1} . Fit is calculated from a third-degree polynomial. We find a minimum at $\beta = 0.3 \pm 0.033 \text{ \AA}^{-1}$ with energy $E = -78.32 \pm 0.11 \text{ eV}$.

With the problem set up, we now just need to find the β parameter that minimizes the energy. We use $n = 2^{16}$ number of points and binning down 32 points into 1, just

like before as the auto-correlation between points should not be affected by the previous calculations. Figure 15 shows that β minimizes the function at $\beta = 0.3 \pm 0.033 \text{ \AA}^{-1}$. The local energy is found to be $E = -78.32 \pm 0.11 \text{ eV}$.

6 Discussion

Comparing our results with other experiments such as Essén (1977), we are in the appropriate range. In the cited article, it is discussed that, although the experimental data suggests a solution of $E_b \approx 4.75 \text{ eV}$, which can be corroborated in Chapter 4 of Boal (1996) and in Hirschfelder & Linnett (2004), using the Born-Oppenheimer approximation they arrive at a binding energy of $E_b \approx 4.25 \text{ eV}$. This result is just inside the boundaries of our solution of $4.171 \pm 0.088 \text{ eV}$. We have found the proton separation to be $S = 0.77 \pm 0.02 \text{ \AA}$. The accepted value for proton separation is 0.74 \AA , verified in Hirschfelder & Linnett (2004). This result falls just outside the range of our result. However, they do seem to indicate that our methods worked correctly.

Regarding the helium atom, we found a local energy of $E = -78.32 \pm 0.11 \text{ eV}$. In Landau & Lifshitz (1977), it is stated that the experimental result of the ground state energy is $E = -78.9 \text{ eV}$. However, we have not done that imaginary time evolution to the ground state in the case of the helium atom, so these results are not directly comparable. Furthermore, from the time evolution we have seen in the hydrogen molecule an energy decrease of a few decimals would be expected. With more time, this could be calculated. Nevertheless, the objective of looking at the helium atom was a proof of concept rather than actually attempting to find its ground state energy.

An interesting result that we did not expect, is the divergence of the energy in figure 11 and figure 12. The logarithmic fit that we have implemented suggests that the values that keep increasing are correct and the ones that stabilize are due to a fault in the code or method. I am going to explain some of our hypotheses, but further research would be needed to find exactly why it happens. One of the possibilities is that when one separates the protons enough, the energy varies between one electron following each proton or both electrons following a single proton. Alternatively, there are some points in space between the two protons where the electrons get stuck in a potential that minimizes the energy, but this would be unphysical as the electrons would not be free to move around. We have not explored these options further, as they are not the main focus of the project.

7 Conclusion

Summarizing, we have looked at Monte Carlo or probabilistic methods, from calculating integrals, to calculating probability distributions. In the case of the Metropo-

lis method, we have also calculated the errors, looking at the correlations between the points and binning when they were not uncorrelated. Implementing the Born-Oppenheimer approximation, we have used variational methods, by generating a physically reasonable trial wavefunction and minimizing the free parameters. In our case, the proton separation S and the parameter β had to be minimized. We found $S = 0.77 \pm 0.02 \text{\AA}$ and $\beta = 1.349 \pm 0.11 \text{\AA}^{-1}$. The proton separation is close to the experimental result of $S = 0.74 \text{\AA}$. By treating the imaginary time dependent Schrödinger Equation as a diffusion equation we can evolve the energy into its ground state. We find a ground state energy of $E_b = 4.171 \pm 0.088 eV$. The experimental ground state energy of the hydrogen molecule is $E_b \approx 4.75$. However, other papers that used the Born-Oppenheimer approximation have found a result of $E_b \approx 4.25$, which falls inside of our error boundaries. Lastly, we have used the same method at proton separation $S = 0 \text{\AA}$ to simulate a helium atom and found a local energy of $E = -78.32 \pm 0.11 \text{ eV}$. In the future, to improve the project accuracy, we could include larger number of runs, a larger number of electron positions, a more aggressive binning (of 64 instead of 32), more β values, smaller difference between proton separations or some other improvement to the parameters chosen could result in a slightly more precise result. By changing some of the equations, we could apply the same methods to atoms and molecules with more electrons.

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A Solving the inverse of $\rho(x) = 2 - x$

Steps were taken from [Feiguin \(2009a\)](#). We start by normalizing the equation in our integral range

$$I = \int_0^1 (2 - x)dx = \left[\frac{x^2}{2} - 2x \right]_0^1 = -\frac{3}{2} \quad (53)$$

We define $\rho = -\frac{2}{3}(2 - x)$, so it is properly normalized. Next, we solve the differential equation

$$\frac{dy}{dx} = \rho(x) \quad (54)$$

$$\begin{aligned} x &= \int_0^y \rho(y') dy' \\ x &= -\int_0^y \frac{2}{3}(y' - 2) dy' \\ x &= -\frac{y^2}{3} + \frac{4y}{3} \end{aligned}$$

$$-\frac{y^2}{3} + \frac{4y}{3} - x = y^2 - 4y + 3x = 0$$

$$y(x) = 2 \pm \sqrt{4 - \frac{3x}{2}} \quad (55)$$

We have found the inverse of the function. We take $y(x) = 2 - \sqrt{4 - \frac{3x}{2}}$ since we are interested in the range $[0,1]$

B Finding constraints of a

When an electron approaches one of the protons, we must ensure we have a finite solutions, so no term blows up. We will do the case of electron 1 approaching proton L but this will have a similar results with every combination.

$$\lim_{r_{1L} \rightarrow 0} \left[\frac{-\hbar^2}{2m} \frac{1}{\varphi(r_{1L})} \nabla_1^2 \varphi(r_{1L}) - \frac{e^2}{4\pi\epsilon_0 r_{1L}} \right] = \text{finite} \quad (56)$$

when $r_{1L} = 0$, $\varphi(r_{1L} = 0) = e^{-0/a} + e^{-S/a} = 1 + e^{-S/a}$
Using

$$\nabla^2 f = \frac{1}{r^{N-1}} \frac{\partial}{\partial r} \left(r^{N-1} \frac{\partial f}{\partial r} \right) \quad (57)$$

we can solve for $\nabla_1^2 \varphi(r_{12})$

$$\begin{aligned} \nabla_1^2 \varphi(r_{1L}) &= \frac{1}{r_{1L}^2} \frac{\partial}{\partial r_{1L}} \left(r_{1L}^2 \frac{\partial \exp(\frac{-r_{1L}}{a})}{\partial r} \right) + \text{finite} \\ &= \frac{-1}{ar_{1L}^2} \left(2r_{1L} - \frac{r_{1L}^2}{a} \right) e^{-\frac{r_{1L}}{a}} \end{aligned}$$

Plugging this result into equation 56 we get

$$\lim_{r_{1L} \rightarrow 0} \left[\frac{-\hbar^2}{2m(1 + e^{-S/a})} \frac{-2}{ar_{12}} - \frac{e^2}{4\pi\epsilon_0 r_{1L}} \right] + \text{finite} = \text{finite}$$

Now we need the inner part of the limit to be 0 so we require

$$\frac{\hbar^2}{am(1 + e^{-S/a})} = \frac{e^2}{4\pi\epsilon_0}$$

and comparing with the Bohr radius $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$ we can determine

$$a(1 + e^{-S/a}) = a_0 \quad (58)$$

C Finding constraints on α

When an electron approaches another electron, we must also make sure to get a finite answer. Using a similar method to the previous appendix we calculate

$$\lim_{r \rightarrow 0} \left[\frac{-\hbar^2}{2m} \frac{1}{f(r_{12})} \nabla^2 f(r_{12}) + \frac{e^2}{4\pi\epsilon_0 r} \right] = \text{finite} \quad (59)$$

Using equation 57

$$\nabla f(r_{12}) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\exp(\frac{r}{\alpha(1+\beta r)})}{\alpha(1+\beta r)^2} \right) + \text{finite} \quad (60)$$

$$= \left[\frac{1}{r} \frac{2}{\alpha(1+\beta r)^3} + \frac{1}{\alpha^2(1+\beta r)^4} \right] \exp\left(\frac{r}{\alpha(1+\beta r)}\right) + \text{finite} \quad (61)$$

Plugging this into equation 59 we get

$$\lim_{r \rightarrow 0} \left\{ \frac{-2\hbar^2}{2m \exp(\frac{r}{\alpha(1+\beta r)})} \left[\frac{2}{r\alpha(1+\beta r)^3} + \frac{1}{\alpha^2(1+\beta r)^4} \right] \exp\left(\frac{r}{\alpha(1+\beta r)}\right) + \frac{e^2}{4\pi\epsilon_0 r} \right\} + \text{finite}$$

$$= \lim_{r \rightarrow 0} \left[\frac{-2\hbar^2}{mr\alpha} + \frac{e^2}{4\pi\epsilon_0 r} \right] + finite = finite \quad (62)$$

where all the $(1 + \beta r)$ terms have turned to 1 as since $r=0$. Since we require that the inner part of the sum to equal 0, we can write

$$\frac{2\hbar^2}{mr\alpha} = \frac{e^2}{4\pi\epsilon_0 r} \quad (63)$$

Comparing this equation with the Bohr radius we can determine $\alpha = 2a_0$

D Local energy derivation

[This appendix was written by my project partner Charlie Cane but we both went through the calculations together]
To calculate the local energy, we will first impose that

$$\phi(\mathbf{r}_i) = e^{-r_{iL}} + e^{-r_{iR}} \equiv g(r_{iL}) + g(r_{iR}) \quad (64)$$

So that $g(\mathbf{r}) = e^{-r/a}$. Note that for a function $f(\mathbf{r})$ of radius only:

$$\nabla^2 f(\mathbf{r}) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) = 2 \frac{f'}{r} + f'' \quad (65)$$

Also note

$$\nabla_{(1)} r_{12} = \frac{\mathbf{r}_{12}}{r_{12}}, \quad \nabla_{(2)} r_{12} = -\frac{\mathbf{r}_{12}}{r_{12}}, \quad \nabla_{(i)} r_{iL,R} = \frac{\mathbf{r}_{iL,R}}{r_{iL,R}} \quad (66)$$

and,

$$\nabla_{(1)} \cdot (\mathbf{r} f(r)) = 3f(r) + r f'(r). \quad (67)$$

Now we can begin to calculate the local energy starting with the divergence:

$$\nabla_{(1)} [\phi(\mathbf{r}_1) f(r_{12})] = \left(\frac{g'(r_{1L}) \mathbf{r}_{1L}}{r_{1L}} + \frac{g'(r_{1R}) \mathbf{r}_{1R}}{r_{1R}} \right) f(r_{12}) + \phi(\mathbf{r}_1) f'(r_{12}) \frac{\mathbf{r}_{12}}{r_{12}} \quad (68)$$

and so the Laplacian is:

$$\begin{aligned} \nabla_{(1)}^2 [\phi(\mathbf{r}_1) f(r_{12})] &= \left(\frac{3g'(r_{1L})}{r_{1L}} + \left(\frac{g''(r_{1L})}{r_{1L}} - \frac{g'(r_{1L})}{r_{1L}^2} \right) r_{1L} + \frac{3g'(r_{1R})}{r_{1R}} + \left(\frac{g''(r_{1R})}{r_{1R}} - \frac{g'(r_{1R})}{r_{1R}^2} \right) r_{1R} \right) \\ &\times f(r_{12}) + 2 \left(\frac{g'(r_{1L}) \mathbf{r}_{1L}}{r_{1L}} + \frac{g'(r_{1R}) \mathbf{r}_{1R}}{r_{1R}} \right) \cdot \frac{\mathbf{r}_{12}}{r_{12}} f'(r_{12}) \\ &+ \phi(\mathbf{r}_1) \left(3 \frac{f'(r_{12})}{r_{12}} + \left(\frac{f''(r_{12})}{r_{12}} - \frac{f'(r_{12})}{r_{12}^2} \right) r_{12} \right) \end{aligned} \quad (69)$$

We arrive at the same result for $\nabla_{(2)}^2 [\phi(\mathbf{r}_2) f(r_{12})]$ other than a change of sign from $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. We can condense this to:

$$\begin{aligned} \nabla_{(1)}^2 [\phi(\mathbf{r}_1) \phi(\mathbf{r}_2) f(r_{12})] &= \phi(\mathbf{r}_2) \left[(\nabla^2 g(r_{1L}) + \nabla^2 g(r_{1R})) f(r_{12}) \right. \\ &\quad + 2 \left(\frac{g'(r_{1L}) \mathbf{r}_{1L}}{r_{1L}} \cdot \mathbf{r}_{12} + \frac{g'(r_{1R}) \mathbf{r}_{1R}}{r_{1R}} \cdot \mathbf{r}_{12} \right) \frac{f'(r_{12})}{r_{12}} \\ &\quad \left. + \phi(\mathbf{r}_1) \nabla^2 f(r_{12}) \right] \end{aligned} \quad (70)$$

So, that we can form an equation for the local energy

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{1}{\Phi} \sum_{i=1,2} \nabla_i^2 \Phi &= -\frac{\hbar^2}{2m} \left[\frac{\nabla^2 g(r_{1L}) + \nabla^2 g(r_{1R})}{g(r_{1L}) + g(r_{1R})} + \frac{\nabla^2 g(r_{2L}) + \nabla^2 g(r_{2R})}{g(r_{2L}) + g(r_{2R})} \right. \\ &\quad + 2 \left(\frac{\frac{g'(r_{1L}) \mathbf{r}_{1L}}{r_{1L}} + \frac{g'(r_{1R}) \mathbf{r}_{1R}}{r_{1R}}}{g(r_{1L}) + g(r_{1R})} - \frac{\frac{g'(r_{2L}) \mathbf{r}_{2L}}{r_{2L}} + \frac{g'(r_{2R}) \mathbf{r}_{2R}}{r_{2R}}}{g(r_{2L}) + g(r_{2R})} \right) \\ &\quad \left. \bullet \mathbf{r}_{12} \frac{f'(r_{12})}{r_{12} f(r_{12})} + 2 \frac{\nabla^2 f(r_{12})}{f(r_{12})} \right] \end{aligned} \quad (71)$$

We have the following derivatives for $g(r)$

$$\begin{aligned} g(r) &= e^{-r/a}, \quad g'(r) = -\frac{1}{a}g(r), \quad g''(r) = \frac{1}{a^2}g(r), \\ \nabla^2 g(r) &= \frac{2g'}{r} + g'' = \left(\frac{-2}{ra} + \frac{1}{a^2}g \right) \end{aligned} \quad (72)$$

and similarly, for $f(r)$

$$\begin{aligned} f(r) &= \exp \left[\frac{r}{\alpha(1+\beta r)} \right], \quad f'(r) = \frac{1}{\alpha} \frac{1}{(1+\beta r)^2} f(r), \quad f''(r) = \left[\frac{-2\beta}{\alpha(1+\beta r)^3} + \frac{1}{\alpha^2(1+\beta r)^4} \right] f(r), \\ \nabla^2 f(r) &= \left[\frac{2}{\alpha(1+\beta r)^3 r} + \frac{1}{\alpha^2(1+\beta r)^4} \right] f(r) \end{aligned} \quad (73)$$

Now substituting these back into the equation for the local energy we have

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{1}{\Phi} \sum_{i=1,2} \nabla_i^2 \Phi &= -\frac{\hbar^2}{2m} \left[\frac{2}{a^2} - \frac{2}{a} \left(\frac{\frac{1}{r_{1L}} + \frac{1}{r_{1R}} e^{(r_{1L}-r_{1R})/a}}{1 + e^{(r_{1L}-r_{1R})/a}} \right) - \frac{2}{a} \left(\frac{\frac{1}{r_{2L}} + \frac{1}{r_{2R}} e^{(r_{2L}-r_{2R})/a}}{1 + e^{(r_{2L}-r_{2R})/a}} \right) \right. \\ &\quad + 2 \left(\frac{1}{a} \frac{\frac{\mathbf{r}_{2L} \cdot \mathbf{r}_{12}}{r_{2L}} + \frac{\mathbf{r}_{2R} \cdot \mathbf{r}_{12}}{r_{2R}} e^{(r_{2L}-r_{2R})/a}}{1 + e^{(r_{2L}-r_{2R})/a}} - \frac{1}{a} \frac{\frac{\mathbf{r}_{1L} \cdot \mathbf{r}_{12}}{r_{1L}} + \frac{\mathbf{r}_{1R} \cdot \mathbf{r}_{12}}{r_{1R}} e^{(r_{1L}-r_{1R})/a}}{1 + e^{(r_{1L}-r_{1R})/a}} \right) \frac{1}{\alpha r_{12}(1+\beta r_{12})^2} \\ &\quad \left. + \frac{4}{\alpha r_{12}(1+\beta r_{12})^3} + \frac{2}{\alpha r_{12}(1+\beta r_{12})^4} \right] \end{aligned} \quad (74)$$

After rearranging, we finally arrive at the variable wavefunction as seen in equation 31.

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{1}{\Phi} \sum_{i=1,2} \nabla_i^2 \Phi &= -\frac{\hbar^2}{m} \frac{1}{a} \left[\frac{1}{a} - \left(\frac{\frac{1}{r_{1L}} + \frac{1}{r_{1R}} e^{(r_{1L}-r_{1R})/a}}{1 + e^{(r_{1L}-r_{1R})/a}} \right) - \left(\frac{\frac{1}{r_{2L}} + \frac{1}{r_{2R}} e^{(r_{2L}-r_{2R})/a}}{1 + e^{(r_{2L}-r_{2R})/a}} \right) \right. \\ &\quad + \left(\frac{\frac{\mathbf{r}_{2L}}{r_{2L}} + \frac{\mathbf{r}_{2R}}{r_{2R}} e^{(r_{2L}-r_{2R})/a}}{1 + e^{(r_{2L}-r_{2R})/a}} - \frac{\frac{\mathbf{r}_{1L}}{r_{1L}} + \frac{\mathbf{r}_{1R}}{r_{1R}} e^{(r_{1L}-r_{1R})/a}}{1 + e^{(r_{1L}-r_{1R})/a}} \right) \bullet \frac{\mathbf{r}_{12}}{\alpha r_{12}(1+\beta r_{12})^2} \\ &\quad \left. + \frac{2a}{\alpha r_{12}(1+\beta r_{12})^3} + \frac{a}{\alpha r_{12}(1+\beta r_{12})^4} \right] \end{aligned} \quad (75)$$