1 Introduction

2 Methods

The Helium atom consists of two electrons orbiting a nucleus, where we label the distance between electron 1 and the nucleus, and electron 2 and the nucleus as $r_1 = \sqrt{x_1^2 + y_1^2 + z_1^2}$ and $r_2 = \sqrt{x_2^2 + y_2^2 + z_2^2}$, respectively.

We model the total potential energy of the system as

$$V(r_1, r_2) = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Where the interaction between each electron and the nucleus is given by the two first terms, and the mutual electron-electron repulsion is given by the last. The distance between the electrons is $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

The Hamiltonian of the system is then

$$\widehat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

The radii $\{r_1,\ r_2,\ r_{12}\}$ of this project have been scaled, and are thus dimensionless.

The Laplace operator of a function f in three dimensions, $\nabla^2 f$, can be represented as

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)f + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial^2\varphi}f$$

in sperical coordinates, and as

$$\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right)f$$

in cartesian coordinates. i

2.1 The Variational Principle

The Variation Principle states that if we have a Hamiltonian $\widehat{\mathbf{H}}$ and a trial wavefunction ψ_T, an upper bound for the ground state energy is given by

$E_0 \leq \langle H \rangle$

$= \dfrac{\int d\mathbf{r_1} d\mathbf{r_2}\psi_{Ti}^*(\mathbf{r_1},\mathbf{r_2},\mathbf{r_{12}})\widehat{\mathbf{H}}(\mathbf{r_1},\mathbf{r_2},\mathbf{r_{12}})\psi_{Ti}(\mathbf{r_1},\mathbf{r_2},\mathbf{r_{12}})}{\int d\mathbf{r_1} d\mathbf{r_2}\psi_{Ti}^*(\mathbf{r_1},\mathbf{r_2},\mathbf{r_{12}})\psi_{Ti}(\mathbf{r_1},\mathbf{r_2},\mathbf{r_{12}})}$

2.2 Variational Monte Carlo (VMC)

The integrals to be solved in the variational method, are often too large to be solved by traditional integral methods.

Therefore, we introduce the brute-force Monte Carlo method to solve the integrals.

2.2.1 VMC Algorithm

- Initialization.

  - Set a fixed number of MC steps.

  - Choose initial position $\mathbf{R}$ and variational parameters $\boldsymbol{\alpha}$.

  - Calculate $|\psi_T(\mathbf{R})|^2$

- Set energy and variance and start the MC calculation.

  - Find the trial position $\mathbf{R}' = \mathbf{R} + \delta \times r$, where $r \in [0,1]$ is randomly selected.

  - Use the Metropolis algorithm to determine if the move $w = \frac{P(\mathbf{R}')}{P(\mathbf{R})}$ is accepted or rejected.

  - Given that the move is accepted, set $\mathbf{R} = \mathbf{R}'$.

  - Update averages.

- Compute final averages.

2.3 The Metropolis Algorithm

2.4 Importance Sampling

2.5 Statistical Analysis

The MC calculation are a set of computational *experiments*, and to evaluate the results we need to implement statistical analysis of these experiments to find *statistical* errors.

For this purpose, we implement the *blocking technique*.

2.5.1 Blocking Implementation

- Compute MC calculation, store samples in array.

- Loop over a set of block sizes n_b.

- For each n_b, calculate the mean of the block and store these values in a new array.

- Take the mean and variance of this array.

- Store results.

2.6 The Trial Wavefunctions for Helium

To conclude if the computational methods are implemented correctly, we should check that the results are reasonable. We do this by finding a mathematical approximation of the closed form expression.

Given the trial wavefunction $\psi_T(\mathbf{R}, \boldsymbol{\alpha})$, we define a new quantity

$$E_L = \frac{1}{\psi_T}\widehat{\mathbf{H}}\psi_T$$

where $\boldsymbol{\alpha}$ is a set of variational parameters. E_{L1} is called the local energy

2.6.1 The first trial wavefunction

We first model the variational solution with a trial function of one variation parameter α. It has the form

$$\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}) = \exp\left(-\alpha(r_1 + r_2)\right)$$

The only part of the operator $\widehat{\mathbf{H}}$ that affects the wavefunction are the Laplace operators.

Since ψ_{T1} is only spatially dependent on r_1 and r_2, the Laplaces of ψ_{T1} reduces to

$$\nabla_i^2 \psi_{T1} = \left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i}\right)\psi_{T1} = \left(\alpha^2 - \alpha\frac{2}{r_i}\right)\psi_{T1}$$

for $i = 1,\ 2$, since

$$\frac{\partial}{\partial r_i}e^{-\alpha(r_1+r_2)} = -\alpha e^{-\alpha(r_1+r_2)}$$

$$\frac{\partial^2}{\partial r_i^2}e^{-\alpha(r_1+r_2)} = \alpha^2 e^{-\alpha(r_1+r_2)}$$

This gives us the following trial energy

$$E_{L1} = \frac{1}{\psi_{T1}}\left(-\alpha^2 + \alpha\left(\frac{1}{r_1} + \frac{1}{r_1}\right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right)\psi_{T1}$$

$$= (\alpha - 2)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} - \alpha^2$$

The 2 in the $\alpha - 2$ term is the number of protons, Z.

2.6.2 The second trial wavefunction

To approximate the closed-form solution even better, we assume another trial wavefunction based on ψ_{T1}, namely

$$\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\left(-\alpha(r_1 + r_2)\right)\exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right)$$

The second part is dependent on the distance between the electrons, and is called the correlation part, which accounts for the effect between the electrons.

One can then in the same way as for ψ_{T1} calculate the local energy. The correlations part will give us some trouble when we try to calculate the Laplacian. This is due to the distance between $\mathbf{r}_1$ and $\mathbf{r}_2$, since this quantity is dependent on the angles φ and θ. It has the form

$$E_{L2} = E_{L1} + \frac{1}{2(1 + \beta r_{12})^2}\left(\frac{\alpha(r_1 + r_2)}{r_{12}}(1 - \frac{\mathbf{r}_1^T \mathbf{r}_2}{r_1 r_2})\right.$$
$$\left. - \frac{1}{2(1 + \beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1 + \beta r_{12}}\right)$$

2.7 The Trial Wavefunction for Beryllium

We can use a trial wavefunction on the same form as for Hydrogen and Helium

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) =$$

$$Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \phi_3(\mathbf{r_3}), \phi_4(\mathbf{r_4})\right)\prod_{i<j}^{4}\exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right)$$

where we approximate the Slater determinant Det as

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) \propto$$
$$\left(\phi_{1s}(\mathbf{r_1})\phi_{2s}(\mathbf{r_2}) - \phi_{1s}(\mathbf{r_2})\phi_{2s}(\mathbf{r_1})\right)\left(\phi_{1s}(\mathbf{r_3})\phi_{2s}(\mathbf{r_4}) - \phi_{1s}(\mathbf{r_4})\phi_{2s}(\mathbf{r_3})\right)$$

where the Hydrogen wavefunctions for the two spin orbitals are given by

$$\phi_{1s}(\mathbf{r_i}) = e^{-\alpha r_i}$$

and

$$\phi_{2s}(\mathbf{r_i}) = (1 - \alpha r_i/2)\, e^{-\alpha r_i/2}.$$

3   Results

4   Discussion