Solution of Schrodinger Equation for Helium Atom Revisited

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Overview

- Introduction
- Theoretical Background
- Variational Approach
- Numerical Technique
- Implementation Details
- Calculations and Results
- Challenges
- Conclusion

Introduction

- **Objective** : To calculate the ground state energy of Helium Atom
- **Why this problem ?**
  An accurate solution of time independent Schrodinger equation for electrons in atoms can provide foundation of atomic and molecular properties.
  However, only Schrodinger equation of Hydrogen atom and ions with single electrons can be solved exactly.
- **importance of the Variational method:**
  Provides approximate solutions of accurate energy spectra of Helium atom.

Theoretical Background

- **Helium Atom Hamiltonian :**

$$\hat{H} = \frac{-\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|}$$

- **Complexity :**
  No exact solution due to the presence of Coulomb interaction between electrons
- **How to resolve ? :**
  Using Variational Method !

Variational Approach

- **Principle :** The ground state energy is the minimum expectation value of the Hamiltonian.

$$E_0 \leq \frac{< \Psi_{trial} | \hat{H} | \Psi_{trial} >}{< \Psi_{trial} | \Psi_{trial} >}$$

  The closer the trial wavefunction Ψ_{trial} is to true wavefunction, the better the approximation.

- **Trial Wavefunction :**
  1S state : In 1S state of Helium (or Helium like atom), both the electrons occupy single-electron orbitals ϕ_{100} with anti-symmetric spin singlet state.Therefore, the spatial part of two-electron wavefunction must be symmetric under exchange.

The ansatz wavefunction will be of the form :

$$\Psi_{1S}(r_1, r_2) = \phi_{100}(r_1)\phi_{100}(r2)F_{1S}(s, t, u)$$

where,

$$\phi_{nlm} = e^{-Zr/n}R_{nl}(r)Y_{lm}(\theta, \phi)$$

s,t,u are the three independent symmetric variables:

$$s = r_1 + r_2$$

$$t = r_1 r_2$$

$$u = |r_1 - r_2|$$

$F_{1S}(s, t, u)$ depends on the positions of the electrons from the nucleus as well as their relative distance. It has a polynomial form:

$$F_{1S}(s, t, u) = \sum_{\lambda_1,\lambda_2,\lambda_3 \geq 0} C^{1S}_{\lambda_1\lambda_2\lambda_3} s^{\lambda_1} t^{\lambda_2} u^{\lambda_3}$$

$$F_{1S}(s, t, u) = \sum_{\lambda_1,\lambda_2,\lambda_3 \geq 0} C^{1S}_{\lambda_1\lambda_2\lambda_3} f_{\lambda_1\lambda_2\lambda_3}(s, t, u)$$

The order of the polynomial is the maximum value of $M = \lambda_1 + 2\lambda_2 + \lambda_3$ that can be fixed depending on the required accuracy of energy eigenvalue.
For a given M, we find different sets of respective λ_i. For example:
$M = 0 \iff (0,0,0)$
$M = 1 \iff (1,0,0), (0,0,1)$
$M = 2 \iff (2,0,0), (0,1,0), (0,0,2), (1,0,1)$
If we consider $M_{max} = 2$, we have 7 linearly independent basis states labeled by k = 1, ... , 7 as

$$\Phi_{1S}^{k} = e^{-Z(r_1+r_2)} f_{\lambda_1\lambda_2\lambda_3}(s,t,u)$$

- **Hamiltonian Matrix element :** We can determine the Hamiltonian matrix element in this restricted Hilbert Space determined by M_{max}

$$H_{ij} = \frac{< \Phi_{1S}^{i} | H_{2e} | \Phi_{1S}^{j} >}{< \Phi_{1S}^{i} | \Phi_{1S}^{j} >}$$

- **Basis Functions (Non Orthogonal)**

$$\Phi_{1S}^{1} = e^{-2(r_1+r_2)}$$
$$\Phi_{1S}^{2} = e^{-2(r_1+r_2)}\ (r_1 + r_2)$$
$$\Phi_{1S}^{3} = e^{-2(r_1+r_2)}\ |r_1 - r_2|$$
$$\Phi_{1S}^{4} = e^{-2(r_1+r_2)}\ (r_1 r_2)$$
$$\Phi_{1S}^{5} = e^{-2(r_1+r_2)}\ (r_1 + r_2)^2$$
$$\Phi_{1S}^{6} = e^{-2(r_1+r_2)}\ |r_1 - r_2|^2$$
$$\Phi_{1S}^{7} = e^{-2(r_1+r_2)}\ (r_1 + r_2)\,|r_1 - r_2|$$

Numerical Techniques

- **Monte Carlo Integration :** Numerical technique which rely on random sampling to approximate their results.
  Suppose we want to integrate a one-dimensional function f(x) from a to b:

$$F = \int_a^b f(x)dx$$

  Given a set of N uniform random variables $X_i \in$ [a,b) with a corresponding pdf of $\frac{1}{b-a}$, the Monte Carlo estimator of computing F is,

$$F \approx (b-a)\frac{1}{N}\sum_0^N f(X_i)$$

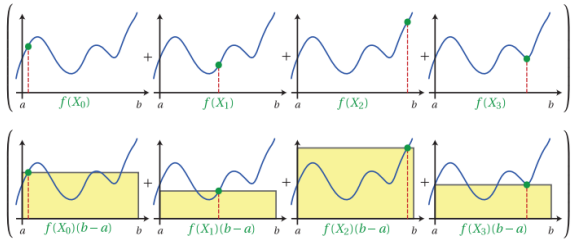

Figure: An illustration of the two interpretations of the basic Monte Carlo estimator using 4 samples: computing the mean value, or height, of the function and multiplying by the interval length (top), or computing the average of several rectangular areas (bottom).

- **Why Monte Carlo ? :** The basic Monte Carlo estimator above can easily be extended to multiple dimensions, and, in contrast to deterministic techniques, the convergence rate for Monte Carlo is independent of the number of dimensions in the integral.

- **Multi-dimensional integration**:

$$F = \int_{\mu(x)} f(x) d\mu(x)$$

$$F = \int_{\mu(x)} \frac{f(x)}{Pdf(x)} Pdf(x) d\mu(x)$$

$$F = E\left[\frac{f(x)}{Pdf(x)}\right]$$

$$F = \lim_{N \to \infty} \frac{1}{N} \sum_{0}^{N} \frac{f(x_i)}{Pdf(x_i)}$$

- **Metropolis Algorithm :**
  - The Metropolis–Hastings algorithm generates a sequence of sample values in such a way that, as more and more sample values are produced, the distribution of values more closely approximates the desired distribution.
  - These sample values are produced iteratively in such a way, that the distribution of the next sample depends only on the current sample value, which makes the sequence of samples a Markov chain.
  - Then, with some probability, the candidate is either accepted, in which case the candidate value is used in the next iteration, or it is rejected in which case the candidate value is discarded, and the current value is reused in the next iteration.
  - The method used to propose new candidates is characterized by the probability distribution $g(x|y)$ of a new proposed sample x given the previous sample y. This is called the Sampling function or Proposal function.

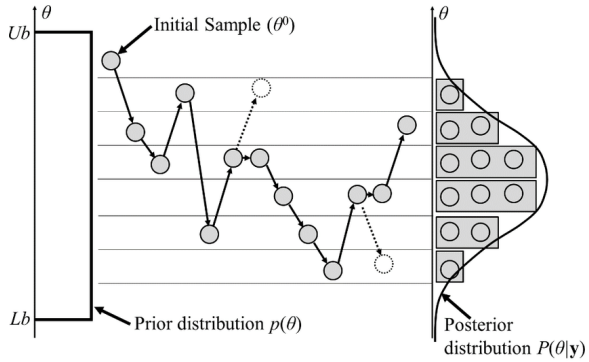

Figure: Metropolis Sampling

- **Algorithm :**
  - **Initialize** : Pick an initial state x_0 and set t = 0.
  - **Iterate**:

    Generate a random candidate x' according to $g(x'|x)$.

    Calculate acceptance probability $A(x', x_t) = min\left(1, \frac{P(x')}{P(x_t)} \frac{g(x_t|x')}{g(x'|x_t)}\right)$

    Accept or Reject:

    - generate a uniform random number u $\in$ [0,1].
    - if u $\leq$ A(x', x_t), then accept new state and set $x_{t+1} = x'$.
    - if $u > A(x', x_t)$, then reject new state and set $x_{t+1} = x_t$.

    Increment: set t = t + 1

Implementation Details

- **Sampling Process**:
  - To sample 6 random variables r_1, θ_1, ϕ_1, r_2, θ_2, ϕ_2.
  - The sampling has to be done following a certain **Probability distribution function**.

What should be the Pdf ?

- **Matrix Construction**:

$$H_{ij} = \frac{< \Phi^i_{1S} | H_{2e} | \Phi^j_{1S} >}{< \Phi^i_{1S} | \Phi^j_{1S} >}$$

$$H_{ij} = \frac{\int \Phi^*_i H_{2e} \Phi_j r_1^2 r_2^2 \sin(\theta_1) \sin(\theta_2) dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2}{\int \Phi^*_i \Phi_j r_1^2 r_2^2 \sin(\theta_1) \sin(\theta_2) dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2}$$

$$H_{ij} = \frac{\int f(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2}{\int q(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2}$$

$$H_{ij} = \frac{\int \frac{f}{p} p dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2}{\int \frac{q}{p} p dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2}$$

$$H_{ij} = \frac{\frac{1}{N}\sum \frac{f}{p}}{\frac{1}{N}\sum \frac{q}{p}}$$

- The elements of Hamiltonian matrix involves solving some complex integration that has been done using Monte Carlo method.
- The integration here is 6-dimensional.
- The random points (r_1, θ_1, ϕ_1, r_2, θ_2, ϕ_2) has been sampled following a Pdf. To perform sampling such that it follows the Pdf, we have to apply Metropolis algorithm.

- **Matrix Diagonalization and minimum energy eigenvalue :**
  - Before performing diagonalization, we must recall that the basis functions we considered at beginning is non-orthogonal.
  - To get Orthogonal basis functions, we perform **Gram Schmidt procedure**.
  - To get Hamiltonian matrix using orthogonal basis functions,
    $H_{orth} = < \Phi_k | H | \Phi_l >$
    $H_{orth} = \sum_{m,n} < \Phi_k | \epsilon_m >< \epsilon_m | H | \epsilon_n >< \epsilon_n | \Phi_l >$
    $H_{orth} = S_{km} H_{non-orth} S^{\dagger}_{nl}$
  - Here Φ and ϵ are orthogonal and non-orthogonal basis functions respectively and S is a transformation matrix.
  - To get transformation matrix elements again involves solving complex integration which we evaluate using Monte Carlo method in which Sampling is done following the same Pdf.

$$S_{km} = < \Phi_k | \epsilon_m >$$

$$S_{km} = \int \Phi_k^* \epsilon_m dV$$

$$S_{km} = \int \Phi_k^* \epsilon_m r_1^2 r_2^2 \sin(\theta_1) \sin(\theta_2) dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d_{\phi 2}$$

$$S_{km} = \int \frac{f(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)}{p(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)} p(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d_{\phi 2}$$

$$S_{km} = \frac{1}{N} \sum \frac{f}{p}$$

- After getting the Orthogonal Hamiltonian matrix, we calculate the energy eigenvalues.
- The minimum of all the energy eigenvalues will be the required **ground state energy**.

Calculations and Results

- The Probability distribution function considered is:

$$Pdf = \left(\sum_{i=1}^{i=7} \Phi_i \right)^2 r_1^2 r_2^2 \sin(\theta_1) \sin(\theta_2)$$

- In the metropolis algorithm, we are proposing a new sample r using normal distribution and angular variables θ and ϕ using uniform distribution.

- **Some plots specific to H_{11} :**

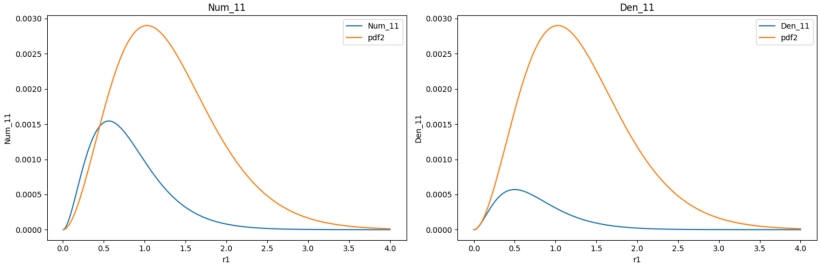

Figure: Numerator and Denominator of H_{11} and Pdf

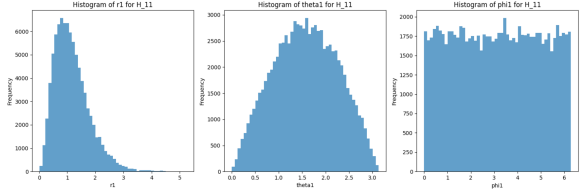

Figure: Histogram of r_1, θ_1 and ϕ_1

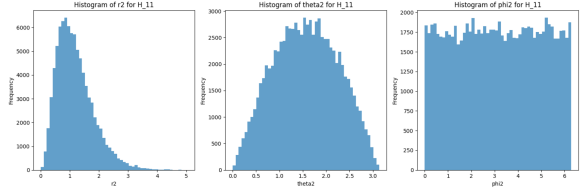

Figure: Histogram of r_2, θ_2 and ϕ_2

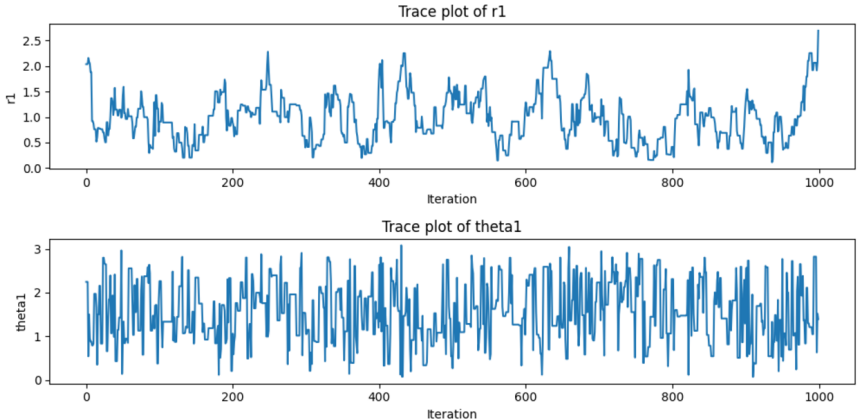

Figure: Trace of the samples for r_1 and θ_1 variable

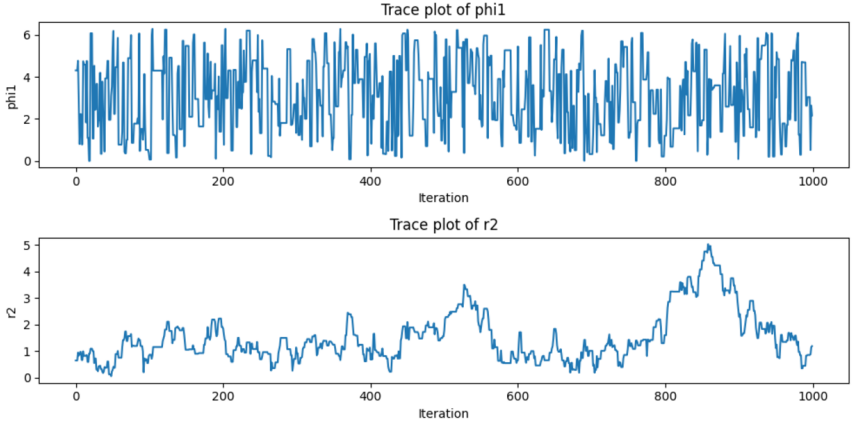

Figure: Trace of the samples for ϕ_1 and r_2 variable

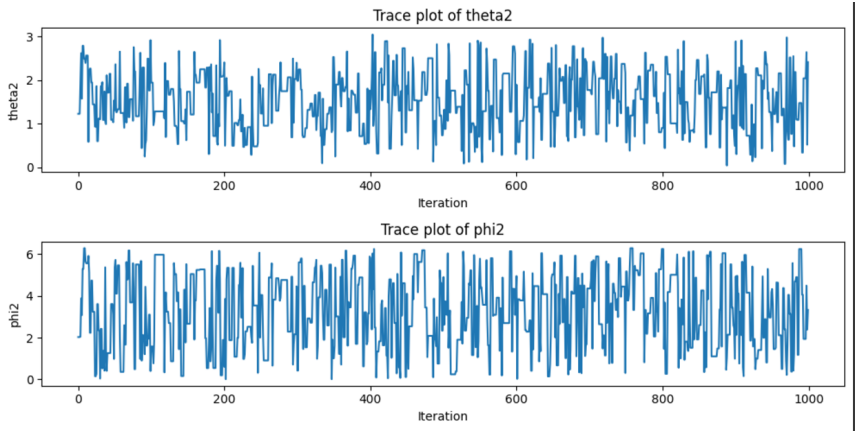

Figure: Trace of the samples for θ_2 and ϕ_2 variable

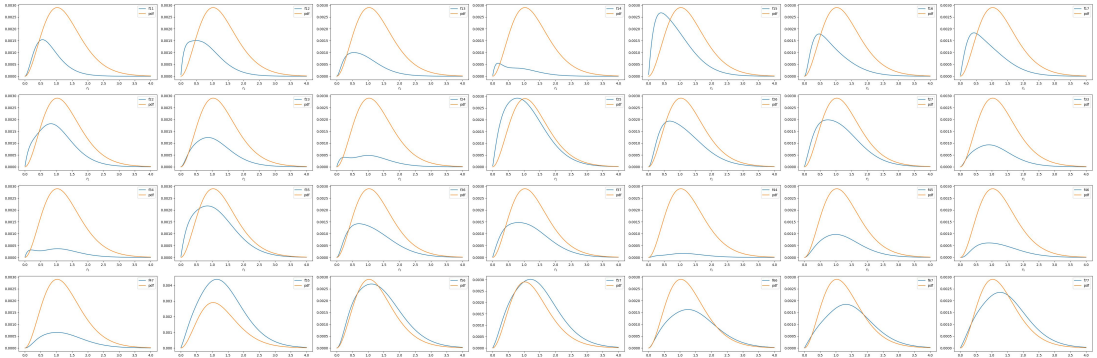

Figure: Numerators of H_{ij} and Pdf

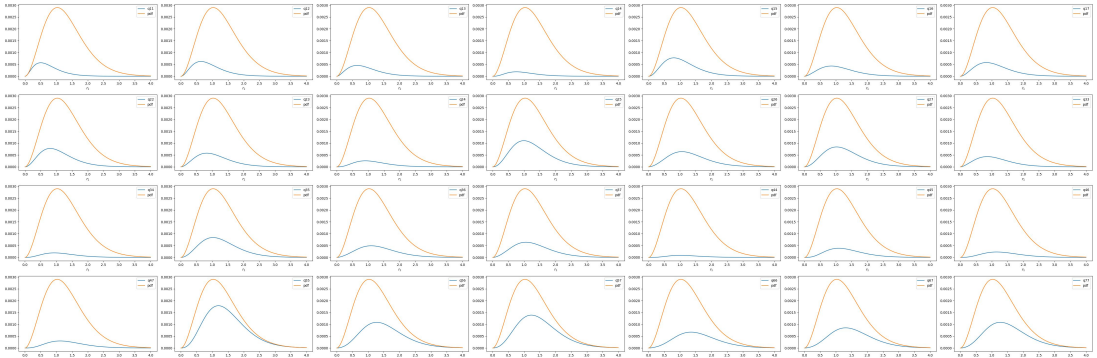

Figure: Denominators of H_{ij} and Pdf

- **Ground State Energy of Helium Atom obtained (while running the code many times):**
  1st run: -2.7472069036041455
  2nd run: -2.826970735747283
  3rd run: -2.919218216550645
  4th run: -2.9013580650979147
  5th run: -2.6270791978362107

Actual ground state energy of Helium Atom(in atomic units) ≈ -2.9033

Challenges

- **To determine the single Pdf function** to calculate all elements of Hamiltonian matrix and also the transformation matrix.
- To estimate burn-in period and standard deviation parameter in the Metropolis algorithm.
- While performing Metropolis sampling, what Sampling function to choose for radial and angular variables.
- **The most important: Convergence Issue**
  - Monte Carlo results fluctuated significantly with each run, showing no consistent convergence in Hamiltonian matrix elements or minimum energy eigenvalues.
  - By obtaining the best possible standard deviation parameter and burn-in period in metropolis algorithm, we can try to decrease the deviation in the result on every run.
  - To achieve accuracy upto 4-5 decimal places was difficult despite increasing sample size.

Conclusion

- **Insights on Monte Carlo Integration :**
  - Monte Carlo integration provides a practical yet challenging approach to solve the Helium atom problem, highlighting the balance between computational efficiency and accuracy in numerical quantum mechanics.
  - Efficiently tackled the 6D integrals for Hamiltonian and transformation matrix elements in the Helium atom problem.
- **Insights on Sampling :**
  - The Metropolis algorithm improved sampling efficiency by focusing on high-probability regions.
  - However, randomness introduced fluctuations, requiring large sample sizes for stability.