

Implementation of Hylleraas Method and Calculation of Ground State Energy of Helium Atom

Final Project
Electronic Structure Theory (CHEM6664)

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1 Introduction

The Helium atom is the smallest problem, which cannot be exactly solved in quantum chemistry. There have been many attempts to obtain accurate solutions to the ground state of the Helium atom using various electronic structure methods. In 1929, Egil Hylleraas introduced a new idea, by including a factor r_{12} into the wavefunction.[1] r_{12} is the distance between two electrons and represents the explicit correlation between them, this method can be considered as the precursor of all modern explicitly-correlated methods. Using a six-term expansion, Hylleraas was able to obtain agreement with experimental results within 0.01 eV. Since then, the Helium atom ground state has been investigated using higher numbers of terms in expansions and new Hylleraas-like methods.[2-5]

This project tries to implement the Hylleraas method and solve for the ground state energy of the Helium atom.

2 Theory and Computational Details

Consider a non-relativistic electronic Hamiltonian of the form:

$$\hat{H} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}, \quad (1)$$

where, \hat{T}_e is the kinetic energy operator, and \hat{V}_{ne} and \hat{V}_{ee} are electron-nuclear and electron-electron potential energy operators respectively. They are defined as:

$$\hat{T}_e = -\frac{1}{2}\hat{\nabla}_1^2 - \frac{1}{2}\hat{\nabla}_2^2, \quad (2)$$

$$\hat{V}_{ne} = -\frac{Z}{r_1} - \frac{Z}{r_2}, \quad (3)$$

$$\hat{V}_{ee} = \frac{1}{r_{12}}. \quad (4)$$

To compute the matrix elements, one must switch to Hylleraas coordinates and transform the integral expressions. For a spherically symmetric function given by,

$$\Phi_{n,l,m} = r_1^n r_2^l r_{12}^m \exp(-\alpha r_1 - \beta r_2 - \gamma r_{12}), \quad (5)$$

the corresponding integral is given by

$$K_{n,l,m} = \int \Phi_{n,l,m} d\mathbf{r}_1 d\mathbf{r}_2 \quad (6)$$

Eq. 6 has a programmable closed-form expression that has been implemented for calculating integrals. The overlap and Hamiltonian matrix elements can be computed using $K_{n,l,m}$.

For this project, only S states of the Helium atom is considered, so the wavefunction can be a spherically symmetric function. The Hylleraas wavefunction, which has an additional r_{12} factor can be defined as:

$$\Phi_{n,l,m} = r_1^n r_2^l r_{12}^m \exp(-\alpha r_1/2 - \beta r_2/2 - \gamma r_{12}/2), \quad (7)$$

where, n , l , and m are non-negative integers and α , β and γ has pre-determined values. The matrix elements can be expressed in terms of the integral $K_{n,l,m}$.

$$S_{ij} = K_{n_i+n_j, l_i+l_j, m_i+m_j}, \quad (8)$$

$$V_{ij}^{ne} = -Z(K_{n_i+n_j-1, l_i+l_j, m_i+m_j} + K_{n_i+n_j, l_i+l_j-1, m_i+m_j}), \quad (9)$$

$$V_{ij}^{ee} = K_{n_i+n_j, l_i+l_j, m_i+m_j-1}, \quad (10)$$

where S_{ij} , V_{ij}^{ne} and V_{ij}^{ee} are matrix elements corresponding to overlap, electron-nuclear potential, and electron-electron potential, respectively, and Z is the nuclear charge. The expression for T_{ij}^e , the kinetic energy matrix element is more involved and is not included here. After constructing the overlap and Hamiltonian matrices, the following secular equation can be solved to obtain eigenvalues and eigenvectors.

$$\mathbf{Hc} = E\mathbf{Sc}, \quad (11)$$

where H is the Hamiltonian matrix, S is the overlap matrix, and E is the electronic energy. The obtained eigenvalues correspond to the orbital energies.

The code was implemented using C++, using methods from Boost library for calculating factorials and binomial coefficients and Eigen library for matrix algebra. To validate the code, matrix elements and ground state energies were compared to given values using a single-element basis set and a three-element basis set. The ground state energy value of the Helium atom was computed using different basis sets with N varying from 0 to 15, where $0 \leq n + l + m \leq N$.

The source code is available at: <https://github.com/ajay-mk/Hylleraas-Method>

3 Results and Discussion

A single-element basis with $n = l = m = 0$ and $\alpha = \beta = 1.6875, \gamma = 0$ was used to validate the code. The overlap and Hamiltonian values were compared to the given values, and matched up to six decimal places. The resulting ground state energy is -2.84765625

N	Number of basis functions	Energy (E_h)
0	1	-2.835
1	4	-2.8912 2019 5476 264
2	10	-2.9034 2317 2705 585
3	20	-2.9036 2819 4293 702
4	35	-2.9037 0110 4391 914
5	56	-2.9037 1621 7626 577
6	84	-2.9037 2121 4806 015
7	120	-2.9037 2300 4732 314
8	165	-2.9037 2373 1320340
9	220	-2.9037 2405 1795 455
10	286	-2.9037 2420 3737 402
11	364	-2.9037 2428 0190 972
12	455	-2.9037 2432 0661 539

Table 1: Ground state energies and number of basis functions for N varying from 0 to 12. The exponents used are $\alpha = \beta = 1.8$ and $\gamma = 0$.

E_h . A three-element basis was also used, and the resulting matrix elements and ground state energy matched with the given values up to nine decimals. The resulting ground state energy is $-2.8940938952 E_h$.

To calculate the ground state energy of the Helium atom, we start with $N = 0$, which corresponds to a single element basis. The exponents used are $\alpha = \beta = 1.8$ and $\gamma = 0$. N was varied from 0 to 12, and results are given in Table 1. The energy values converge as N increases, and convergence to the sixth decimal is obtained.

In literature, there is good agreement of Helium ground state energy between various explicitly-correlated methods up to sixteen decimal points. The ground state energy is $-2.9037 2437 7034 1195 E_h$. [2, 4] On comparing with the computed numbers, this matches up to seven decimal places for $N = 12$. Going up to $N = 13$ or 14 could have helped ensure the convergence of the seventh decimal, but this was computationally expensive, and numerical inaccuracies started appearing for higher N values. This can be solved using multi-precision libraries.

The ionisation potential of Helium can be computed using $E_{He^+} - E_{He}$, where, $E_{He^+} = 2 E_h$. From the results, the ionization potential value can be calculated to be $0.90372243 E_h$, which also matches with calculations from the literature. Converting this to cm^{-1} , the computed value is $198,344.15 \text{ cm}^{-1}$, which is not in exact agreement with the experimental value of $198,310.74 \text{ cm}^{-1}$. [6] The error could be due to the approximations invoked. While defining the electronic Hamiltonian, relativistic effects are not included, which could lead to error in the values. In conclusion, the Hylleraas method is a great tool for estimating the ground state energy, but a more sophisticated implementation would be needed for higher accuracy.

References

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