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Variational Energies for the Rydberg P States of Helium

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By

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Abstract

The aim of this work is to solve the quantum mechanical three-body problem for helium, and to obtain high precision eigenvalues for the higher-lying Rydberg states where previous methods have been of limited accuracy. A variational method in correlated Hylleraas coordinates is used involving three distinct distance scales, called a triple basis set. The eigenvalues and matrix elements of other operators are computed for P states of helium up to $n = 15$ using the varational method with a triple basis set in Hylleraas coordinates. The construction of the wave functions, as well as the behaviour of the asymptotic, intermediate and short range nonlinear scale parameters is discussed. The convergence and accuracy of both the eigenvalues and the matrix elements of other operators is compared to those obtained using a double basis set. It is shown that the accuracy is improved by at least two orders of magnitude for basis sets of comparable size. The accuracy of the eigenvalues is compared to the quasi-exponential method developed by Azbanaev et al [1] requiring up to 100 digit arithmetic. The comparison verifies the accuracy of the present results for the low-lying states of helium, and demonstrates that the results for the higher-lying states up to n = 15 are by far the most accurate in the literature.

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Chapter 1

Introduction

The three-body problem is one of the oldest problems in physics. Originating from the earliest days of classical physics with Newton, mathematicians and natural philosophers observed that there does not exist a closed form solution for any system of three or more celestial objects, such as two planets and a sun. While two-body systems lead to Kepler elliptical orbits, the motion of three-body systems is chaotic and nonrecurring. Thus, various approximation approaches have been used to differing degrees of accuracy in an attempt to model three-body planetary systems [2]. With the advent of quantum mechanics and atomic physics in the early 20^{th} century, the same methods are now used quite extensively to model three-body quantum systems, such as helium.

In 1767, Euler proposed one such approach which is now referred to as "Euler's Three-Body Problem" [3]. Euler proposed that the problem does indeed have a closed form solution in the approximation that two bodies are fixed, and act on the third body with an inverse square force. However, this ignores the interaction between the two centers, and thus the solution becomes chaotic once the interaction is introduced. Euler's work was expanded upon by Lagrange in 1772 [4] who discovered a closed form solution when three bodies form an equilateral triangle. Valid for any set of mass ratios, the motion can be expressed in terms of Keplerian ellipses.

Quantum three-body systems are equally as difficult to solve analytically as classical ones. The quantum three-body system is dependent on the Hamiltonian of each body.

Just as with the classical three-body problem, the Hamiltonian depends on the of all three bodies and their interactions, creating a chaotic system. The quantum wave function is obtained by solving the Schrödinger equation, which was introduced by Schrödinger in 1926 [5]. Just as with the classical counterpart, the Schrödinger equation can be solved exactly for quantum two-body systems, such as the hydrogen atom, and hence it was necessary to develop approximation methods for the three-body Schrödinger equation. Great strides were made towards this problem in 1928, when Hylleraas [6, 7] first calculated the ground state energy of helium using the Schrödinger equation in correlated "Hylleraas coordinates." In agreement from experimental calculations of the ground state energy performed in 1924 by Lyman [8], this was the first demonstration that the Schrödinger equation did indeed work for atoms with more than one electron. This was made possible due to the variatonal principle, which will be discussed in detail in Chapter 2, which states that any "variational" wave functions that approximates the real wave functions and is dependent on variational parameters has an energy eigenvalue that is an upper bound to the real energy eigenvalue. As the accuracy (and size) of the variational wave function increases, the upper bound moves progressively downward towards the exact energy. It can never fall below the exact energy, provided that the spectrum is bounded from below.

A substantial increase in the accuracy of the theoretical ground state of energy came with the invention of computers, which opened the door to many of the approximation methods used to solve three-body systems. In 1958, Pekeris used the first computer in Israel, WEIZAC, to compute the ground state energy, along with the 2^3S state, to about 9 significant figures [9, 10]. This was performed by using the same method as Hylleraas, simply with larger basis sets and significantly more computational power. However, achieving any degree of accuracy was only possible for low lying states, and constructing good wave functions capable of obtaining eigenvalues was impossible for any state past $n = 3$.

Another significant increase in accuracy came from expanding the Hylleraas method by introducing a wave function with two sets of variational parameters. First performed by Drake [11–16], this allowed for significant improvements in accuracy, with nonrelativistic ground state energy accurate to up to 22 significant figures [17]. This form of variational wave function can give very accurate results, whilst only requiring quadruple (32 significant figures) arithmetic and not being significantly computationally intensive, with the largest

eigenvalue calculation and matrix diagonalization iteration taking a maximum of 2 hours. However, there still exists a computational limitation due to numerical cancellation and thus a loss of numerical stability at large basis set values (typically $N \approx 2000$). Although 22 figure accuracy in the energy may be sufficient for the current state of accuracy for atomic physics experiments, matrix elements for other operators are usually accurate to a maximum of approximately half as many significant figures, and thus are only accurate to 10 significant figures. Another limitation is that the lack of numerical stability near the benchmark of 22 significant figures makes for occasional difficulty with obtaining a converged value. However, due to the speed of convergence, and the computational simplicity, this is often the preferred method of obtaining energy eigenvalues for three-body systems. A major improvement of the double basis set method is that high precision can be maintained for the higher-lying Rydberg states.

Further improvements to the method of using a variational wave functions with two sets of variational parameters can be made by introducing a third set of variational parameters. First proposed by Drake [18], this yet again allowed for a significant bump in the accuracy, both absolute (achieving accuracy in energy eigenvalues for the ground state of helium to 21 decimal points) and at each basis set level. It also allowed for a significant increase in the computational stability and efficiency.

Other authors have found variational solutions to the three-body problem by altering the form and number of variational parameters in an attempt to maximize the computational efficiency and accuracy of the calculations. One such method is to construct construct quasi-random exponential trial wavefunctions [1]. This method involves performing Monte-Carlo like sampling, and thus require significant computational complexity in both time and space due to the large number of basis functions that must be sampled. This method also typically requires multiple (arbitrary) precision arithmetic beyond standard quadruple precision arithmetic, which also leads to significantly longer computation times. Although able to obtain very accurate results (up to 35 digits for energy eigenvalues), it requires 100 digit arithmetic to avoid numerical cancellation and thus the necessary computational power and time is very high. Due to the current levels of experimental accuracy within atomic and molecular physics, this level of computational accuracy is not necessary.

1.1 Purpose

The purpose of this work is to develop and investigate the improvements of constructing variational wavefunctions with three sets of nonlinear scale parameters to calculate energy and other operator values of three-body quantum systems. Furthermore, the objective is to maximize the accuracy that can be obtained within the constraints of standard quadruple-precision arithmetic, and to extend the calculations to the higher-lying Rydberg states with $n > 2$ where other variational methods fail. As will be shown, the gain in accuracy from triple basis sets is about three orders of magnitude for basis sets of comparable size.

Chapter 2

Theory

2.1 Three Body Problem

The three-body problem is one of the oldest problems in physics. There exists no closed form solution for a system of three interacting bodies, and thus approximation methods are required. Numerous numerical approximation methods are used, such as many-body perturbation theory, central field approximations and variational methods, with varying degrees of accuracy [2]. This analysis will focus on the variational method, which has been well established as the most accurate way of computing eigenvalues of quantum three body systems.

2.1.1 Center of Mass Coordinates

The Hamiltonian for a three body quantum system in atomic units is given by the sum of the kinetic and potential energies

$$H = \frac{1}{2M}p_N^2 + \frac{1}{2m}(p_1^2 + p_2^2) + e^2(\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}) \tag{2.1}$$

where subscripts 1 and 2 denote the first and second electron, subscript N denotes the nucleus, and r_{12} is the distance between the two electrons. As noted by Hylleraas [6, 7], the Schrödinger equation $H\Psi = E\Psi$ in this instance is thus a three dimensional eigenvalue

problem. The natural coordinates of the system are r_1, r_2, and r_{12}. Equivalently, the system is uniquely described by the coordinates r_1, r_2, and θ_{12}, the angle between the vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$.

In general, nine coordinates are required to locate the nucleus and the two electrons. However, three of these can be used to locate the center of the mass of the system, which can be ignored for an atom in free space. Of the remaining six coordinates, three specify the orientation in space of the triangle formed by the nucleus and two electrons, as shown by 2.1. These are also cyclic or ignorable coordinates since space is isotropic. What remains are the three interparticle coordinates r_1, r_2, and r_{12}, forming the triangle in 2.1.

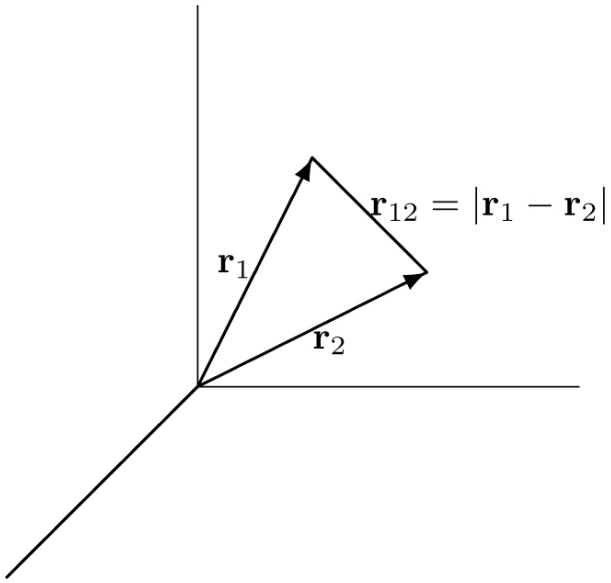

FIGURE 2.1: Hylleraas center of mass coordinates. The two electrons are located at $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, and the nucleus at the origin, respectively.

To eliminate the centre of mass motion, the usual centre of mass transformations can be made.

$$\boldsymbol{R} = \frac{1}{(M+2m)a_\mu}(M\boldsymbol{r}_N + m(\boldsymbol{r}_1 + \boldsymbol{r}_2)) \tag{2.2}$$

$$\boldsymbol{s}_1 = \frac{\boldsymbol{r}_1 - \boldsymbol{r}_N}{a_\mu} \tag{2.3}$$

$$\boldsymbol{s}_2 = \frac{\boldsymbol{r}_2 - \boldsymbol{r}_N}{a_\mu}, \tag{2.4}$$

where $a_\mu = \frac{ma_0}{\mu}$ is the reduced Bohr radius, with $\mu = \frac{mM}{m+M}$ the reduced electron mass and $a_0 = \frac{\hbar^2}{me^2}$ is the Bohr radius. In this coordinate system, $\boldsymbol{R}$ is the centre of mass coordinate, and $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$ are the relative coordinates with $s_{12} = |\boldsymbol{s}_1 - \boldsymbol{s}_2|$. The Hamiltonian, in this coordinate system, reduces to

$$H = -\frac{1}{2}\nabla^2_{s_1} - \frac{1}{2}\nabla^2_{s_2} - \frac{\mu}{M}\nabla_{s_1}\cdot\nabla_{s_2} - \frac{Z}{s_1} - \frac{Z}{s_2} + \frac{1}{s_{12}}. \tag{2.5}$$

The term invoing $\nabla_{s1}\cdot\nabla_{s_2}$ is called the *mass polarization* term. Since $M >> m$, the multiplying factor $\frac{\mu}{M}$ is much less than unity. Thus, this term can be regarded as a small correction (called the *finite mass correction*) to the *infinite nuclear mass* Hamiltonian

$$H = -\frac{1}{2}\nabla^2_{s1} - \frac{1}{2}\nabla^2_{s2} - \frac{Z}{s_1} - \frac{Z}{s_2} + \frac{1}{s_{12}}. \tag{2.6}$$

This can be further simplified by introducing the *Z-scaled atomic units* $\rho = Zs$, and $\epsilon = E/Z^2$. Thus, the infinite nuclear mass Hamiltonian becomes

$$H = -\frac{1}{2}\nabla^2_{\rho_1} - \frac{1}{2}\nabla^2_{\rho_2} - \frac{1}{\rho_1} - \frac{1}{\rho_2} + \frac{1}{Z\rho_{12}}. \tag{2.7}$$

The Schrödinger equation to be solved is thus

$$H\Psi = \epsilon\Psi. \tag{2.8}$$

Our approach is first to solve the infinite nuclear mass problem, and then include finite nuclear mass effects as a second step in which the mass polarization operator is included explicitly in the Hamiltonian.

2.1.2 Variational Method

Due to the Coulomb interaction $\frac{1}{\rho_{12}}$, the eigenvalue problem (2.7) does not have an exact solution and cannot be written simply as a product of one electron orbitals. As such, approximation methods are needed. The variational method is one such method, and leads to very accurate results for helium.

The variational method states that, for an approximate wavefunction Ψ^v and a known Hamiltonian H, an *energy functional* ϵ, defined as

$$\epsilon(\Psi^v) = \frac{\langle \Psi^v | \, H \, | \Psi^v \rangle}{\langle \Psi^v | \Psi^v \rangle}, \tag{2.9}$$

is stationary with respect to arbitrary functional variations in Ψ^v. Furthermore, if the spectrum is bounded from below, then $\epsilon(\Psi^v)$ is an upper bound to the exact ground-state energy. In the linear variational method, the *trial wave function* is expressed in terms of a linear combination of functions,

$$|\Psi_{tr}\rangle = \sum_{i=1}^{N} c_i \, |\phi_i\rangle \, , \tag{2.10}$$

where the c_i are linear variational coeffecients and the functions ϕ_i will form a complete basis set in the limit $N \longrightarrow \infty$. In this variational basis set, the expression (2.9) for the variational energy becomes

$$E_{tr} = \frac{\sum_{i,j} c_i^* c_j \, \langle \phi_i | \, H \, | \phi_j \rangle}{\sum_{i,j} c_i^* c_j \, \langle \phi_i | \phi_j \rangle}. \tag{2.11}$$

Since the energy functional must be stationary with respect to variations in the coefficients c_i, it follows that

$$\frac{\partial E_{tr}}{\partial c_i} = 0, \tag{2.12}$$

we are left with a system of N equations

$$\sum_{i=1}^{N} (\langle \phi_i | \, H \, | \phi_k \rangle - E_{tr} \, \langle \phi_i | \phi_k \rangle) c_i = 0. \tag{2.13}$$

This is simply an eigenvalue problem, with N eigenvalues $(E_1, E_2, ..., E_N)$, and N sets of coefficients c_i.

We next prove that the eigenvalue of the trial wave function, E_{tr}, gives an upper bound to the true ground state energy. Assuming ψ_{tr} is normalized, E_{tr} is given by

$$\begin{aligned} E_{tr} &= \langle \Psi_{tr} | \, H \, | \Psi_{tr} \rangle \\ &= c_0^2 E_0^2 + c_1^2 E_1^2 + c_2^2 E_1^2 + ... + c_N^2 E_N^2 \\ &= (1 - c_1^2 - c_2^2 - ... - c_N^2) E_0^2 + c_1^2 E_1^2 + c_2^2 E_2^2 + ... + c_N^2 E_N^2 \\ &= E_0 + c_1^2 (E_1 - E_0) + ... + c_N^2 (E_N - E_0) \\ &\geq E_0. \end{aligned} \tag{2.14}$$

This leads to a strict upper bound on E_0. In fact, $E_{tr} = E_0$ *if and only if* Ψ_{tr} is the exact ground state wave function.

2.1.3 Hylleraas-Unheim-MacDonald Theorem

As shown by (2.14), the trial eigenvalue is *always* an upper bound to the true energy. In fact, the wave function Ψ_{tr} becomes a better approximation to the real wave function Ψ as the number of parameters c_n that Ψ_{tr} depends on increases.

Since it is impossible to construct truly infinite basis sets, the general algorithm one follows is to iteratively construct larger basis sets until sufficient accuracy is reached, or a computational limit is reached. By constructing larger and larger basis sets, the trial energy eigenvalue becomes closer to the true energy. The matrix interleaving theorem states that if an extra row and column is added to a square matrix, the old eigenvalues will fall between, or *interleave*, the new eigenvalues. Furthermore, since the energy is bounded from below, as shown in 2.2 the higher-lying eigenvalues λ_i for excited states can never actually cross below the exact energies E_i. As N is systematically increased to include progressively more basis members, the new trial energy eigenvalues λ_i form upper bounds to the exact energies E_i for the excited states as well as the ground state. This is known as the Hylleraas-Undheim-Macdonald Theorem [19, 20].

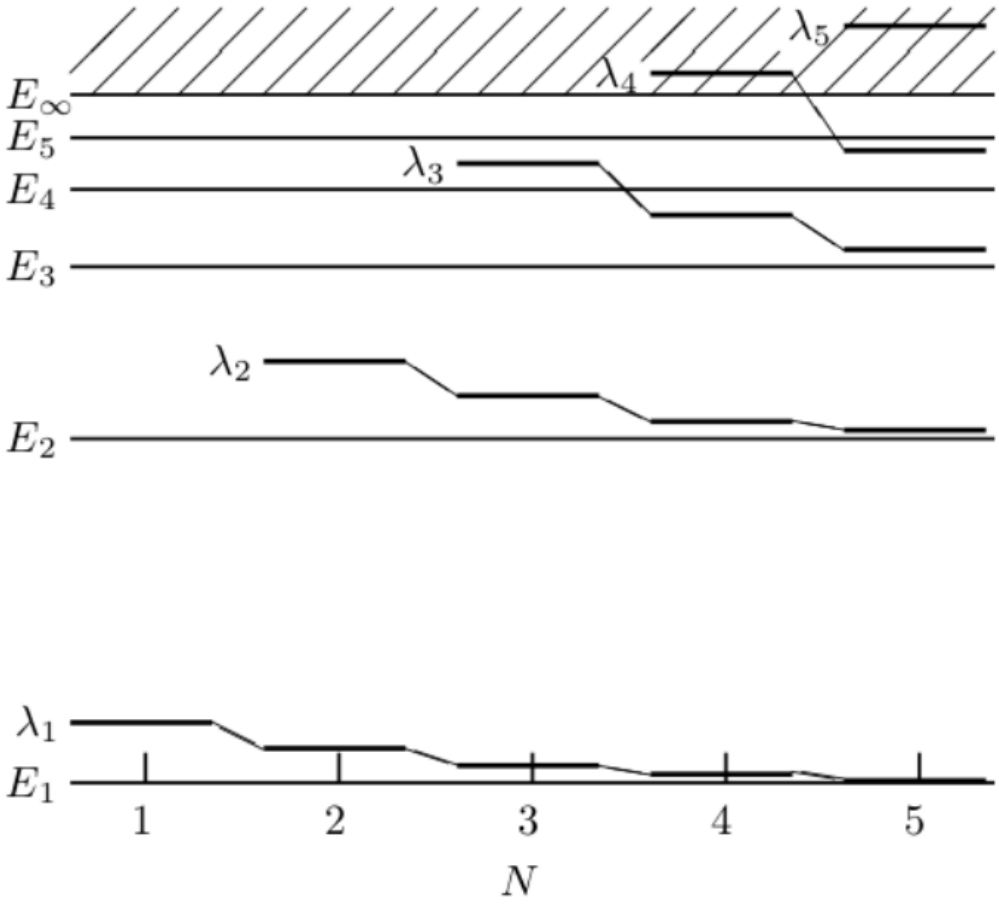

FIGURE 2.2: Illustration of the Hylleraas-Unheim-Macdonald theorem. The previous N eigenvalues lie between the new ones as N increases.

2.2 Hylleraas Coordinates and Wavefunction Construction

In 1928, Hylleraas [6] suggested to use the (r_1, r_2, r_{12}) coordinate system for the helium atom. In addition to the linear variational parameters, it is also advantageous to introduce nonlinear exponential parameters α and β that determine the distance scale for the variational wave function. The trial wave function is then constructed in the form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{i,j,k=1}^{i+j+k\leq\Omega} c_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1,l_2}^{L,M}(r_1, r_2) \pm \text{exchange}, \tag{2.15}$$

where c_{ijk} are linear variational coefficients, α and β are the nonlinear scale parameters and the "exchange" term is simply the functional with r_1 and r_2 exchanged. The energy is also minimized with respect to α and β. The parameter Ω plays a key role since it

determines the size of the basis set. The strategy is to include all powers of i, j, k such that $i + j + k \leq \Omega$. This is called a *Pekeris Shell*. Ω is then progressively increased until sufficient convergence is attained. This type of basis set is referred to as a "single basis set", as there only one set of nonlinear scale parameters α and β. The total number of terms is $N = (\Omega + 1)(\Omega + 2)(\Omega + 3)/6$.

Although this gives highly accurate results, numerical stability and computational efficiency becomes an issue as Ω increases. As shown by Drake [11–16], an effective way of addressing these problems is by introducing a second set of nonlinear scale parameters. The resulting wave function is referred to as a "double basis set", and is given by

$$\begin{aligned}\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = &\sum_{i,j,k}^{i+j+k\leq\Omega} c^{(1)}_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha_1 r_1 - \beta_1 r_2} \mathcal{Y}^{L,M}_{l_1,l_2}(r_1, r_2) \\ &+ \sum_{i,j,k}^{i+j+k\leq\Omega} c^{(2)}_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha_2 r_1 - \beta_2 r_2} \mathcal{Y}^{L,M}_{l_1,l_2}(r_1, r_2) \pm \text{exchange}. \end{aligned} \tag{2.16}$$

The total number of terms is now $N_2 = 2N_1$. There are many benefits to using this double basis set over a single basis set. (α_1, β_1) and (α_2, β_2) represent asymptotic and short-range behaviour, respectively [17]. In Z-scaled atomic units, the optimum values of α_1 and β_1 are $\alpha_1 \approx 1$ and $\beta_1 \approx 1/2n$, where n is the principle quantum number [17]. This describes the long-range asymptotic behaviour of the wave function. In contrast, the optimum values of α_2 and β_2 are much larger, and tend to increase linearly with Ω. This describes the short-range behaviour of the wave function near the nucleus where correlation effects are large. It is more numerically stable, as (α_1, β_1) and (α_2, β_2) are varied, the energy eigenvalues converge at lower Ω. This results in lower powers of r at equal total basis set size, resulting in less numerical cancellation and loss of significant figures. This loss of numerical stability is the main limiting factor in large Ω single basis sets. This also results in a much faster computational time, as the computational time is proportional to Ω^3. Constructing these *double* basis sets is now the main method used by Drake and coworkers of calculating eigenvalues of three body quantum systems [11–15].

The main focus of this work is to extend these same ideas to a triple basis set and to study the possible gains in accuracy and numerical stability. For a triple basis set, the trial

wave function is given by

$$\begin{aligned}\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = &\sum_{i,j,k}^{i+j+k\leq\Omega} c^{(1)}_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha_1 r_1-\beta_1 r_2}\mathcal{Y}^{L,M}_{l_1,l_2}(r_1,r_2)\\ &+\sum_{i,j,k}^{i+j+k\leq\Omega} c^{(2)}_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha_2 r_1-\beta_2 r_2}\mathcal{Y}^{L,M}_{l_1,l_2}(r_1,r_2)\\ &+\sum_{i,j,k}^{i+j+k\leq\Omega} c^{(3)}_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha_3 r_1-\beta_3 r_2}\mathcal{Y}^{L,M}_{l_1,l_2}(r_1,r_2) \pm \text{exchange.}\end{aligned} \tag{2.17}$$

For the same reasons that a double basis set is preferable to a single basis set, a triple basis set is preferable to a double basis set. The triple basis set was first introduced by Drake [18] for the ground state of helium, and yielded better results than a double basis set for both energy and various matrix operators for the ground states of helium, H^- and the short-lived atom consisting of two electrons and a positron, Ps^-. The three sets (α_1,β_1), (α_2,β_2) and (α_3,β_3) represent the asymptotic, intermediate and short range distance scales.

In work by other authors, [1] there has also been considerable interest in using entirely exponential basis sets, which take the form

$$\Psi(\boldsymbol{r_1},\boldsymbol{r_2}) = \sum_i^N c_i e^{-\alpha_i r_1-\beta_i r_2-\gamma_i r_{12}}\mathcal{Y}^{L,M}_{l_1,l_2}(r_1,r_2) \pm \text{exchange,} \tag{2.18}$$

where the triplets $(\alpha_i,\beta_i,\gamma_i)$ are chosen in a quasirandom fashion. This gives a result similar to a Monte Carlo calculation, with a quasirandom distribution of exponential scale factors and no radial powers of r_1, r_2, r_{12} at all. Although capable of very accurate results, calculations done in this way are very computationally intensive, often requiring up to 100 digit arithmetic and basis sets on the order of 10^4 to produce competitive results. In contrast, the double (or triple) basis set method requires only standard quadruple-precision (32 decimal digit) arithmetic to obtain results accurate to better than 1 part in 10^{20}.

2.3 Eigenvalue Calculation

The generalized energy eigenvalue problem in a nonorthogonal basis set can written in the form

$$\boldsymbol{H} - E\boldsymbol{O} = 0, \tag{2.19}$$

where $\boldsymbol{O}$ and $\boldsymbol{H}$ are the overlap matrix and Hamiltonian, respectively. The matrix elements of $\boldsymbol{O}$ and $\boldsymbol{H}$ are defined in terms of the basis set ϕ by

$$O_{mn} = \langle \phi_m | \phi_n \rangle \tag{2.20}$$

$$H_{mn} = \langle \phi_m | \, H \, | \phi_n \rangle \, , \tag{2.21}$$

where m represents a triplet of integers (i, j, k), and

$$\phi_n = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1,l_2}^{L,M}(r_1, r_2) \tag{2.22}$$

is a particular member of the basis set. For basis functions ϕ_n and $\phi_m = r_1^{i'} r_2^{j'} r_{12}^{k'} e^{-\alpha' r_1 - \beta' r_2} \mathcal{Y}_{l'_1,l'_2}^{L,M}(r_1, r_2)$, the matrix elements H_{mn} can be calculated directly from the explicit Hermitian form [17]

$$\begin{aligned} \langle \phi_m | H | \phi_n \rangle = \frac{1}{8} \sum_{\Lambda} C_\Lambda \sum_{p=0}^{2} \Big[& A_p^{(1)} I_\Lambda(i_+ - p, j_+, k_+; \alpha_+, \beta_+) \\ & + A_p^{(2)} I_\Lambda(i_+, j_+ - p, k_+; \alpha_+, \beta_+) \\ & + A_p^{(3)} I_\Lambda(i_+, j_+, k_+ - p; \alpha_+, \beta_+) \Big] \end{aligned} \tag{2.23}$$

where $i_\pm = i \pm i'$, $\alpha_\pm = \alpha \pm \alpha'$ etc., and

$$\begin{aligned}
A_0^{(1)} &= -\alpha_+^2 - \alpha_-^2 + 2\alpha_-\alpha_+(k_-/k_+)\,, \\
A_1^{(1)} &= 2\{\alpha_+(i_+ + 2) + \alpha_- i_- \\
&\quad - [\alpha_+ i_- + \alpha_-(i_+ + 2)](k_-/k_+)\} - 8Z\,, \\
A_2^{(1)} &= -i_+^2 - i_-^2 - 2i_+ + 2i_-(i_+ + 1)(k_-/k_+) \\
&\quad + 2l_1(l_1 + 1)(1 - k_-/k_+) \\
&\quad + 2l_1'(l_1' + 1)(1 + k_-/k_+)\,, \\
A_0^{(3)} &= 0\,, \qquad A_1^{(3)} = 8\,, \\
A_2^{(3)} &= 2(k_+^2 - k_-^2)\,,
\end{aligned}$$

with $(c_-/c_+) = 0$ for $c_+ = 0$. The $A_i^{(2)}$ are defined similarly to $A_i^{(1)}$ with the replacements $i \to j$, $\alpha \to \beta$, $l_1 \to l_2$. The term $\sum_\Lambda C_\Lambda$ comes from the total integration of the radial and angular components

$$\langle \mathcal{Y}^{L,M}_{l_1,l_2} \mathcal{Y}^{L,M}_{l'_1,l'_2}(r_1, r_2) r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \rangle = \sum_\Lambda C_\Lambda I_\Lambda(i, j, k; \alpha, \beta), \tag{2.24}$$

with

$$I_\Lambda(i, j, k; \alpha, \beta) = \langle r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} P_\Lambda(cos\theta) \rangle_{rad}. \tag{2.25}$$

The overlap matrix O_{mn} is calculated by

$$\langle \phi_m | \phi_n \rangle = \sum_\Lambda C_\Lambda I_\Lambda(i_+, j_+, k_+; \alpha_+, \beta_+). \tag{2.26}$$

It follows that one needs a matrix diagonalization method to calculate the eigenvalues E. There are many possible ways to do this, and one such way that will be discussed is the Power Method (and the related Inverse Power Iteration). While the Power Method does not provide a full matrix diagonalization, it does allow one to quickly calculate one

eigenvalue and the associated eigenvector. This is much faster than performing full matrix diagonalization. An additional iterative method is needed for the optimization of the nonlinear parameters α and β.

2.3.1 Power Iteration Method

This section describes an iterative method that will rapidly converge on any chosen eigenvalue in the eigenvalue spectrum. Consider the Hamiltonian, $\boldsymbol{H}$, is an n-dimensional square matrix with eigenvalues $\lambda_i (i = 1, ..., n)$ and eigenvectors $\psi_i (i - 1, ..., n)$. Assume that the eigenvalues are ordered according to $|\lambda_1| > |\lambda_2| > ... > |\lambda_n|$. λ_1 is thus called the *dominant eigenvalue*. It is always possible to expand an arbitrary starting vector ϕ_0 in terms of the eigenvectors of $\boldsymbol{H}$ as

$$\phi_0 = c_1\psi_1 + c_2\psi_2 + ... + c_n\psi_n. \tag{2.27}$$

Applying $\boldsymbol{H}$ k times to 2.27 gives

$$\begin{aligned} \boldsymbol{H}^k\phi_0 &= c_1\boldsymbol{H}^k\psi_1 + c_2\boldsymbol{H}^k\psi_2 + ... + c_n\boldsymbol{H}^k\psi_n = \boldsymbol{O}^k\phi_0 \\ &= c_1\lambda_1^k\psi_1 + c_2\lambda_2^k\psi_2 + ... + c_n\lambda_n^k\psi_n \\ &= c_1\lambda_1^k\left(\psi_1 + \frac{c_2}{c_1}\left(\frac{\lambda_2}{\lambda_1}\right)^k\psi_2 + ... + \frac{c_n}{c_1}\left(\frac{\lambda_n}{\lambda_1}\right)^k\psi_n\right). \end{aligned} \tag{2.28}$$

Since λ_1 is *dominant*, then $\left(\frac{\lambda_n}{\lambda_1}\right)^k \longrightarrow 0$ as k increases, and thus

$$\boldsymbol{H}^k\phi_0 \longrightarrow c_1\lambda_1^k\psi_1. \tag{2.29}$$

2.3.2 Inverse Power Iteration Method

While the power iteration method is useful for finding the *dominant* eigenvalue of a square matrix $\boldsymbol{H}$, it does not allow one to calculate any eigenvalue of $\boldsymbol{H}$. However, it is possible

to calculate any eigenvalue by using the inverse power iteration method, given a sufficiently accurate initial guess for a single eigenvalue. First, write the eigenvalue problem given by (2.19) as

$$(\boldsymbol{H} - \lambda_g \boldsymbol{O})\Psi = (\lambda_n - \lambda_g)\boldsymbol{O}\Psi, \tag{2.30}$$

where λ_g is the approximate guess for the eigenvalue λ_n. This can be rewritten in the form

$$\boldsymbol{H}'\Psi = \frac{1}{\lambda_n - \lambda_g}\Psi, \tag{2.31}$$

where $\boldsymbol{H}' = (\boldsymbol{H} - \lambda_g \boldsymbol{O})^{-1}\boldsymbol{O}$. By intentionally choosing λ_g close to a particular eigenvalue λ_n, then the term $\frac{1}{\lambda_n - \lambda_g}$ blows up near $\lambda_g = \lambda_n$. Thus, one can successively apply $\boldsymbol{H}'$, giving $\phi_n = \boldsymbol{H}'\phi_{n-1}$, until convergence. This sequence is equivalent to the sequence $\Gamma\phi_n = (\lambda_n - \lambda_g)^{-1}\boldsymbol{O}\phi_{n-1}$, with $\Gamma = (\boldsymbol{H} - \lambda_k)^{-1}\boldsymbol{O}$. The eigenvalue is then given by

$$\lambda_n = \frac{\langle\phi_n|\,\boldsymbol{H}\,|\phi_n\rangle}{\langle\phi_n|\phi_n\rangle} \tag{2.32}$$

This is the method used in the present work to calculate energy eigenvalues of variational wave functions.

Chapter 3

Methods

3.1 Basis Set Construction

The full trial variational wave function using a double basis set, given by (2.16), can be written as

$$\begin{aligned}\Psi(\boldsymbol{r_1},\boldsymbol{r_2}) = a_0\phi_0(Z,\boldsymbol{r_1})\phi_{nl}(Z-1,\boldsymbol{r_2}) \\ + \sum_{p=1}^{2}\sum_{i,j,k}^{i+j+k\leq\Omega} a_{i,j,k}^{(p)} r_1^i r_2^j r_{12}^k \\ \times e^{-\alpha^{(p)}r_1-\beta^{(p)}r_2}\mathcal{Y}_{l_1,l_2}^{L,M} \pm (exchange)\end{aligned} \tag{3.1}$$

where the sum over p defines the double basis set, and α^1, β^1, α^2 and β^2 represent the short and long range behaviours, respectively. The first term of (3.1) is called the screened hydrogenic term because it consists of a product of hydrogenic wave functions with an unscreened nuclear charge of Z for the inner $1s$ electron and a fully screened nuclear charge of $Z-1$ for the outer Rydberg electron with quantum numbers n and l. The full trial variational wave function using a triple basis set is given by

$$\Psi(\boldsymbol{r_1}, \boldsymbol{r_2}) = a_0\phi_0(Z, \boldsymbol{r_1})\phi_{nl}(Z-1, \boldsymbol{r_2}) + \sum_{p=1}^{3} \sum_{i,j,k}^{i+j+k\leq\Omega} a_{i,j,k}^{(p)} r_1^i r_2^j r_{12}^k \times e^{-\alpha^{(p)}r_1 - \beta^{(p)}r_2} \mathcal{Y}_{l_1,l_2}^{L,M} \pm (exchange), \tag{3.2}$$

where the sum over p covers the three sets of nonlinear parameters $\alpha^{(1)}$, $\beta^{(1)}$, $\alpha^{(2)}$, $\beta^{(2)}$, and $\alpha^{(3)}$, $\beta^{(3)}$ for the asymptotic, intermediate, and short-range sectors, respectively. If all terms in the Pekeris Shell with $i + j + k \leq \Omega$ were included for each sector, then the total number of terms in each sector would be $(\Omega+1)(\Omega+2)(\Omega+3)/6$. However, since the optimized $\alpha^{(p)}, \beta^{(p)}$ pairs are nearly equal, terms with $i < j$ can be omitted in order to avoid near-linear dependence. A second truncation, $i+j+k+|i-j| > \Omega$ is introduced. Omitted terms from this truncation eventually reappear as Ω increases. A third and final truncation $k < \kappa$ is also used, where κ is an arbitrary positive integer which adjusted iteratively until its effect on the calculation is negligible. Both of these truncation schemes were introduced by Kono and Hattori [21] in 1985, and help preserve the linear independence of the basis set.

3.2 Eigenvalue Calculation

With the basis set constructed, the principle computational step is to solve the generalized eigenvalue problem given by (2.19). Since $\boldsymbol{H}$ can be easily calculated term by term from the explicitly Hermitian form given by Eq. (11.33) of [17], the energy eigenvalue E can be solved simply by using the inverse power iteration method described in Chapter 2.

At each eigenvalue E, the non-linear scale parameters α^p and β^p must be optimized. This is done by calculating the energy derivative

$$\frac{\partial E}{\partial \alpha^{(p)}} = -2\frac{\langle\Psi|\,(\boldsymbol{H}-E)r_1|\,|\Psi^{(p)}\rangle}{\langle\Psi|\Psi\rangle}, \tag{3.3}$$

where $\Psi^{(p)}$ denotes the part of the wave function that depends explicitly on $\alpha^{(p)}$, and

similarly for $\beta^{(p)}$. The next step is then to find the next $\alpha^{(p)}$ and $\beta^{(p)}$ by using their derivatives. With the previous energy eigenvalue used as the initial guess for the energy, the eigenvalue problem can be resolved, and the zeros with respect to the non-linear scale parameters can be calculated using gradient descent.

3.3 Eigenvalue Extrapolation

Optimized energy eigenvalues are calculated at each Ω, and a ratio of successive difference $R(\Omega)$ is defined by

$$R(\Omega) = \frac{E(\Omega - 1) - E(\Omega - 2)}{E(\Omega) - E(\Omega - 1)}. \tag{3.4}$$

If the wave functions are calculated correctly, the energy will *always* decrease, and thus these ratios are used to calculate an approximate energy. If R was constant, then the series

$$\Delta E(1 + \frac{1}{R} + \frac{1}{R^2} + ...) \tag{3.5}$$

could be summed to infinity with the result

$$\Delta E_{extrap} = \frac{E}{1 - 1/R}. \tag{3.6}$$

. It turns out that $R(\Omega)$ is not constant (even in the case of no numerical instability), and decreases slightly with Ω. Thus, $R(\Omega)$ is linearized by fitting it to the functional form a/Ω^b, and and the adjusted series of differences is summed numerically to obtain the extrapolated energy. The uncertainty of the convergent value is given by the uncertainty in the fitting parameters a and b.

As discussed in Chapter 2, numerical stability becomes an issue at large basis sets, typically $N = 2200 - 2500$. Thus, the eigenvalue problem cannot be solved with larger basis without compromising numerical stability due to numerical cancellation. As such, we successively compute new basis sets until a loss of numerical stability is present. This can become apparent by observing both the behaviour of the nonlinear parameters and the

eigenvalues. As evident by (3.3), the eigenvalues will occur at a local minimum. Thus, the derivatives will be extremely small, typically of the order of 10^{-20} or smaller. When within the bounds of numerical stability, the derivatives will get smaller with increasing Ω. However, these derivatives will stop getting smaller, and will begin to behave erratically when numerical cancellation and instability is introduced. Another sign of numerical instability is the behaviour of the energies. As seen from 3.4, the energies should decrease in a regular manner, as measured by R. If these energies stop decreasing in this expected manner, or possibly even increase, then it is clear that the limit of numerical stability has been reached.

Chapter 4

Results

4.1 Tables of Nonrelativistic Energies

This section tabulates the nonrelativistic energies calculated using triple basis set wave functions for various states of helium. The tables show the the energy as a function of the basis set size N. Included is the energy eigenvalue, extrapolated using the method described in Chapter 3. In each case, the energy was found with an accuracy of 21 significant figures. The numbers in brackets following each energy value represent the calculated uncertainty in the final figure.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	375	-2.123843086496999241696		
8	492	-2.123843086497949919312	0.000000000000950035325	
9	638	-2.123843086498076495674	0.000000000000126576362	7.51
10	801	-2.123843086498097313177	0.000000000000020817503	6.08
11	996	-2.123843086498100745205	0.000000000000003432027	6.07
12	1206	-2.123843086498101257502	0.000000000000000512297	6.70
13	1450	-2.123843086498101338954	0.000000000000000081453	6.29
14	1707	-2.123843086498101354793	0.000000000000000015839	5.14
15	2000	-2.123843086498101358153	0.000000000000000003360	4.71
16	2304	-2.123843086498101358849	0.000000000000000000695	4.83
17	2646	-2.123843086498101359103	0.000000000000000000255	2.73
18	2997	-2.123843086498101359194	0.000000000000000000091	2.80
Extrap.		-2.123843086498101359241(22)		1.96

TABLE 4.1: Convergence study for the nonrelativistic energy of the $1s2p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	375	-2.133164190776373627229		
8	492	-2.133164190778993012164	0.000000000002619384936	
9	638	-2.133164190779252065061	0.000000000000259052897	10.11
10	801	-2.133164190779278833812	0.000000000000026768750	9.68
11	996	-2.133164190779282628911	0.000000000000003795100	7.05
12	1206	-2.133164190779283110708	0.000000000000000481797	7.88
13	1450	-2.133164190779283187963	0.000000000000000077255	6.24
14	1707	-2.133164190779283201692	0.000000000000000013729	5.63
15	2000	-2.133164190779283204332	0.000000000000000002640	5.20
16	2304	-2.133164190779283204885	0.000000000000000000552	4.78
17	2646	-2.133164190779283205057	0.000000000000000000172	3.20
18	2997	-2.133164190779283205113	0.000000000000000000056	3.08
Extrap.		-2.133164190779283205140(8)		2.08

TABLE 4.2: Convergence study for the nonrelativistic energy of the $1s2p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	410	-2.055144369164909224384		
8	517	-2.055144369165628371269	0.000000000000719146885	
9	649	-2.055144369165745383215	0.000000000000117011946	6.15
10	793	-2.055144369165758208024	0.000000000000012824809	9.12
11	964	-2.055144369165761443224	0.000000000000003235199	3.96
12	1145	-2.055144369165761993937	0.000000000000000550713	5.87
13	1355	-2.055144369165762128534	0.000000000000000134597	4.09
14	1573	-2.055144369165762156762	0.000000000000000028228	4.77
15	1823	-2.055144369165762166883	0.000000000000000010121	2.79
16	2081	-2.055144369165762169472	0.000000000000000002589	3.91
17	2375	-2.055144369165762170730	0.000000000000000001258	2.06
18	2677	-2.055144369165762171110	0.000000000000000000381	3.30
Extrap.		-2.055144369165762171437(74)		1.17

TABLE 4.3: Convergence study for the nonrelativistic energy of the $1s3p\ ^1P$ state of helium with finite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	410	-2.058083603515910300981		
8	517	-2.058083603517670759739	0.000000000001759058671	
9	649	-2.058083603517857231674	0.000000000000186566547	9.44
10	793	-2.058083603517884584581	0.000000000000027343623	6.82
11	964	-2.058083603517888589677	0.000000000000004026336	6.83
12	1145	-2.058083603517889189298	0.000000000000000605278	6.68
13	1355	-2.058083603517889343212	0.000000000000000138735	3.90
14	1573	-2.058083603517889372520	0.000000000000000024489	5.25
15	1823	-2.058083603517889383254	0.000000000000000006364	2.73
16	2081	-2.058083603517889386416	0.000000000000000002206	3.39
17	2375	-2.058083603517889388040	0.000000000000000000758	1.95
18	2677	-2.058083603517889388329	0.000000000000000000228	5.62
Extrap.		-2.058083603517889388575(43)		1.56

TABLE 4.4: Convergence study for the nonrelativistic energy of the $1s3p\ ^3P$ state of helium with finite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	410	-2.031069650449647689233		
8	530	-2.031069650450140110851	0.000000000000492421618	
9	667	-2.031069650450229659193	0.000000000000089548342	5.50
10	817	-2.031069650450237678503	0.000000000000008019310	11.17
11	995	-2.031069650450240212533	0.000000000000002534030	3.16
12	1184	-2.031069650450240584743	0.000000000000000372210	6.81
13	1403	-2.031069650450240687909	0.000000000000000103166	3.61
14	1631	-2.031069650450240706829	0.000000000000000018920	5.45
15	1891	-2.031069650450240712859	0.000000000000000006030	3.14
16	2159	-2.031069650450240714120	0.000000000000000001261	4.78
17	2463	-2.031069650450240714575	0.000000000000000000455	2.77
18	2775	-2.031069650450240714681	0.000000000000000000106	4.30
Extrap.		-2.031069650450240714742(22)		1.72

TABLE 4.5: Convergence study for the nonrelativistic energy of the $1s4p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	410	-2.032324354295308033413		
8	530	-2.032324354296429202979	0.000000000001121169566	
9	667	-2.032324354296610633062	0.000000000000181430082	6.18
10	817	-2.032324354296625630946	0.000000000000014997884	12.10
11	995	-2.032324354296629555289	0.000000000000003924343	3.82
12	1184	-2.032324354296630128596	0.000000000000000573308	6.85
13	1403	-2.032324354296630300245	0.000000000000000171649	3.34
14	1631	-2.032324354296630321256	0.000000000000000021011	8.17
15	1891	-2.032324354296630329931	0.000000000000000008676	2.42
16	2159	-2.032324354296630331184	0.000000000000000001253	6.92
17	2463	-2.032324354296630331775	0.000000000000000000590	2.12
18	2775	-2.032324354296630331880	0.000000000000000000106	5.59
Extrap.		-2.032324354296630331956(9)		1.40

TABLE 4.6: Convergence study for the nonrelativistic energy of the $1s4p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	410	-2.019905989900110432904		
8	530	-2.019905989900747695685	0.000000000000637262781	
9	667	-2.019905989900831440401	0.000000000000083744715	7.61
10	817	-2.019905989900843605913	0.000000000000012165512	6.88
11	995	-2.019905989900845874806	0.000000000000002268893	5.36
12	1184	-2.019905989900846296878	0.000000000000000422072	5.38
13	1403	-2.019905989900846417395	0.000000000000000120517	3.50
14	1631	-2.019905989900846442157	0.000000000000000024762	4.87
15	1891	-2.019905989900846447140	0.000000000000000004983	4.97
16	2159	-2.019905989900846448319	0.000000000000000001179	4.23
17	2463	-2.019905989900846448718	0.000000000000000000399	2.95
18	2775	-2.019905989900846448806	0.000000000000000000088	4.56
Extrap.		-2.019905989900846448848(7)		2.06

TABLE 4.7: Convergence study for the nonrelativistic energy of the $1s5p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	410	-2.020551187254302160936		
8	530	-2.020551187256086750264	0.000000000001784589329	
9	667	-2.020551187256232110004	0.000000000000145359740	12.28
10	817	-2.020551187256261731887	0.000000000000029621883	4.91
11	995	-2.020551187256266715058	0.000000000000004983171	5.94
12	1184	-2.020551187256267546587	0.000000000000000831529	5.99
13	1403	-2.020551187256267743472	0.000000000000000196885	4.22
14	1631	-2.020551187256267778115	0.000000000000000034643	5.68
15	1891	-2.020551187256267785899	0.000000000000000007784	4.45
16	2159	-2.020551187256267787545	0.000000000000000001646	4.73
17	2463	-2.020551187256267788084	0.000000000000000000539	3.05
18	2775	-2.020551187256267788192	0.000000000000000000109	4.96
Extrap.		-2.020551187256267788246(11)		2.01

TABLE 4.8: Convergence study for the nonrelativistic energy of the $1s5p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	418	-2.013833979671034576714		
8	526	-2.013833979671594030897	0.000000000000559454183	
9	657	-2.013833979671724386584	0.000000000000130355687	4.29
10	798	-2.013833979671736080303	0.000000000000011693719	11.15
11	964	-2.013833979671739485615	0.000000000000003405312	3.43
12	1138	-2.013833979671739910909	0.000000000000000425293	8.01
13	1340	-2.013833979671740069427	0.000000000000000158519	2.68
14	1550	-2.013833979671740092942	0.000000000000000023514	6.74
15	1792	-2.013833979671740099946	0.000000000000000007004	3.36
16	2042	-2.013833979671740101699	0.000000000000000001754	3.99
17	2328	-2.013833979671740102231	0.000000000000000000532	3.30
18	2622	-2.013833979671740102335	0.000000000000000000104	5.09
Extrap.		-2.013833979671740102386(9)		2.06

TABLE 4.9: Convergence study for the nonrelativistic energy of the $1s6p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	418	-2.014207958772094233002		
8	526	-2.014207958773343381265	0.000000000001249148263	
9	657	-2.014207958773709607711	0.000000000000366226446	3.41
10	798	-2.014207958773741488857	0.000000000000031881145	11.49
11	964	-2.014207958773749512614	0.000000000000008023757	3.97
12	1138	-2.014207958773750258737	0.000000000000000746123	10.75
13	1340	-2.014207958773750538042	0.000000000000000279305	2.67
14	1550	-2.014207958773750576483	0.000000000000000038441	7.27
15	1792	-2.014207958773750587889	0.000000000000000011406	3.37
16	2042	-2.014207958773750590380	0.000000000000000002491	4.58
17	2328	-2.014207958773750591083	0.000000000000000000703	3.55
18	2622	-2.014207958773750591180	0.000000000000000000098	7.19
Extrap.		-2.014207958773750591219(6)		2.56

TABLE 4.10: Convergence study for the nonrelativistic energy of the $1s6p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	444	-2.010169314527956005674		
8	582	-2.010169314529262449050	0.000000000001306443376	
9	709	-2.010169314529366079095	0.000000000000103630045	12.61
10	845	-2.010169314529385529461	0.000000000000019450365	5.33
11	1005	-2.010169314529388270369	0.000000000000002740908	7.10
12	1173	-2.010169314529388815541	0.000000000000000545172	5.03
13	1369	-2.010169314529388952278	0.000000000000000136737	3.99
14	1573	-2.010169314529388976318	0.000000000000000024040	5.69
15	1809	-2.010169314529388982818	0.000000000000000006500	3.70
16	2053	-2.010169314529388984206	0.000000000000000001388	4.68
17	2333	-2.010169314529388984719	0.000000000000000000513	2.70
18	2621	-2.010169314529388984821	0.000000000000000000102	5.04
19	2949	-2.010169314529388984877	0.000000000000000000057	1.80
Extrap.		-2.010169314529388984898(3)		2.79

TABLE 4.11: Convergence study for the nonrelativistic energy of the $1s7p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	444	-2.010405147522481641425		
8	582	-2.010405147524587923280	0.000000000002112076569	
9	709	-2.010405147524853739693	0.000000000000256211167	7.92
10	845	-2.010405147524901140106	0.000000000000047437825	5.6 1
11	1005	-2.010405147524906232451	0.000000000000005100050	9.31
12	1173	-2.010405147524907520205	0.000000000000001291946	3.95
13	1369	-2.010405147524907729551	0.000000000000000211753	6.15
14	1573	-2.010405147524907773999	0.000000000000000048171	4.71
15	1809	-2.010405147524907786189	0.000000000000000009684	3.65
16	2053	-2.010405147524907788895	0.000000000000000002253	4.51
17	2333	-2.010405147524907789826	0.000000000000000000688	2.91
18	2621	-2.010405147524907790063	0.000000000000000000152	3.93
19	2949	-2.010405147524907790142	0.000000000000000000054	3.01
Extrap.		-2.010405147524907790173(7)		2.77

TABLE 4.12: Convergence study for the nonrelativistic energy of the $1s7p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	420	-2.007789127131409726507		
8	592	-2.007789127133035062427	0.000000000001625335920	
9	684	-2.007789127133210402800	0.000000000000175340373	9.27
10	834	-2.007789127133230032618	0.000000000000019629818	8.93
11	983	-2.007789127133235015061	0.000000000000004982443	3.94
12	1140	-2.007789127133235688701	0.000000000000000673641	7.40
13	1325	-2.007789127133235857581	0.000000000000000168880	3.99
14	1518	-2.007789127133235885532	0.000000000000000027951	6.04
15	1743	-2.007789127133235893086	0.000000000000000007554	3.70
16	1976	-2.007789127133235894433	0.000000000000000001346	5.61
17	2245	-2.007789127133235894969	0.000000000000000000536	2.51
18	2522	-2.007789127133235895091	0.000000000000000000122	4.38
19	2839	-2.007789127133235895138	0.000000000000000000047	2.58
Extrap.		-2.007789127133235895156(3)		2.72

TABLE 4.13: Convergence study for the nonrelativistic energy of the $1s8p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	420	-2.007947013766997346846		
8	592	-2.007947013770867935405	0.000000000003870588559	
9	684	-2.007947013771104913502	0.000000000000236978097	16.33
10	834	-2.007947013771150116688	0.000000000000045203187	5.24
11	983	-2.007947013771159987394	0.000000000000009870705	4.58
12	1140	-2.007947013771161105624	0.000000000000001118231	8.83
13	1325	-2.007947013771161447514	0.000000000000000341889	3.27
14	1518	-2.007947013771161487525	0.000000000000000040011	8.54
15	1743	-2.007947013771161502331	0.000000000000000014806	2.70
16	1976	-2.007947013771161504230	0.000000000000000001899	7.80
17	2245	-2.007947013771161505049	0.000000000000000000820	2.32
18	2522	-2.007947013771161505198	0.000000000000000000149	5.50
19	2839	-2.007947013771161505249	0.000000000000000000051	2.92
Extrap.		-2.007947013771161505262(5)		4.10

TABLE 4.14: Convergence study for the nonrelativistic energy of the $1s8p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	420	-2.006156384650526119317		
8	592	-2.006156384652466793535	0.000000000001940674218	
9	684	-2.006156384652812475830	0.000000000000345682295	5.61
10	834	-2.006156384652846582337	0.000000000000034106507	10.14
11	1008	-2.006156384652852538057	0.000000000000005955720	5.73
12	1165	-2.006156384652853582509	0.000000000000001044452	5.70
13	1350	-2.006156384652853757765	0.000000000000000175256	5.96
14	1543	-2.006156384652853806065	0.000000000000000048300	3.63
15	1768	-2.006156384652853815263	0.000000000000000009198	5.25
16	2001	-2.006156384652853817613	0.000000000000000002349	3.92
17	2270	-2.006156384652853818145	0.000000000000000000532	4.41
18	2547	-2.006156384652853818286	0.000000000000000000141	3.78
19	2864	-2.006156384652853818327	0.000000000000000000042	3.39
Extrap.		-2.006156384652853818346(5)		2.23

TABLE 4.15: Convergence study for the nonrelativistic energy of the $1s9p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
7	420	-2.00626726736248041 7		
8	592	-2.00626726736519950378 0	0.000000000002719089743	
9	684	-2.00626726736631612220	0.000000000001116618439	2.44
10	834	-2.00626726736638347720 4	0.000000000000067354984	16.58
11	1008	-2.00626726736640739094 3	0.000000000000023913739	2.82
12	1165	-2.00626726736640863544 6	0.000000000000001244504	19.22
13	1350	-2.00626726736640892543 4	0.000000000000000289988	4.29
14	1543	-2.00626726736640901385 3	0.000000000000000088419	3.28
15	1768	-2.00626726736640902704 1	0.000000000000000013188	6.70
16	2001	-2.00626726736640903143 4	0.000000000000000004393	3.00
17	2270	-2.00626726736640903224 1	0.000000000000000000806	5.45
18	2547	-2.00626726736640903250 8	0.000000000000000000267	3.02
19	2864	-2.00626726736640903255 4	0.000000000000000000047	5.72
Extrap.		-2.006267267366409032580(14)		1.83

TABLE 4.16: Convergence study for the nonrelativistic energy of the $1s9p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
8	592	-2.004987983801743131746		
9	684	-2.004987983802092548384	0.000000000000349416639	
10	834	-2.004987983802206932983	0.000000000000114384598	3.05
11	1008	-2.004987983802215874007	0.000000000000008941025	12.79
12	1190	-2.004987983802217921624	0.000000000000002047616	4.37
13	1375	-2.004987983802218170507	0.000000000000000248883	8.23
14	1568	-2.004987983802218219422	0.000000000000000048916	5.09
15	1793	-2.004987983802218235586	0.000000000000000016164	3.03
16	2026	-2.004987983802218238272	0.000000000000000002686	6.02
17	2295	-2.004987983802218239212	0.000000000000000000940	2.86
18	2572	-2.004987983802218239378	0.000000000000000000166	5.66
19	2889	-2.004987983802218239436	0.000000000000000000058	2.86
Extrap.		-2.004987983802218239451(2)		3.93

TABLE 4.17: Convergence study for the nonrelativistic energy of the $1s10p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
8	592	-2.005068805494138260697		
9	684	-2.005068805497475010895	0.000000000003336750198	
10	834	-2.005068805497675575143	0.000000000000200564248	16.64
11	1008	-2.005068805497700641212	0.000000000000025066069	8.00
12	1190	-2.005068805497706644749	0.000000000000006003536	4.18
13	1375	-2.005068805497707096699	0.000000000000000451951	13.28
14	1568	-2.005068805497707294122	0.000000000000000197423	2.29
15	1793	-2.005068805497707310577	0.000000000000000016456	12.00
16	2026	-2.005068805497707314551	0.000000000000000003974	4.14
17	2295	-2.005068805497707316086	0.000000000000000001535	2.59
18	2572	-2.005068805497707316307	0.000000000000000000221	6.94
19	2889	-2.005068805497707316415	0.000000000000000000108	2.04
Extrap.		-2.005068805497707316465(65)		2.19

TABLE 4.18: Convergence study for the nonrelativistic energy of the $1s10p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
10	834	-2.004123191922286548493		
11	1008	-2.004123191922329618119	0.000000000000043069626	
12	1190	-2.004123191922331558479	0.000000000000001940359	22.20
13	1400	-2.004123191922332575721	0.000000000000001017242	1.91
14	1593	-2.004123191922332630358	0.000000000000000054637	18.62
15	1818	-2.004123191922332647436	0.000000000000000017078	3.20
16	2051	-2.004123191922332651148	0.000000000000000003712	4.60
17	2320	-2.004123191922332652120	0.000000000000000000971	3.82
18	2597	-2.004123191922332652410	0.000000000000000000290	3.35
19	2914	-2.004123191922332652496	0.000000000000000000086	3.38
Extrap.		-2.004123191922332652537(30)		2.06

TABLE 4.19: Convergence study for the nonrelativistic energy of the $1s11p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
10	834	-2.004183903199324561972		
11	1008	-2.004183903199580958836	0.000000000000256396863	
12	1190	-2.004183903199587340805	0.000000000000006381969	40.18
13	1400	-2.004183903199590408157	0.000000000000003067352	2.08
14	1593	-2.004183903199590558568	0.000000000000000150411	20.39
15	1818	-2.004183903199590634006	0.000000000000000075438	1.99
16	2051	-2.004183903199590638931	0.000000000000000004925	15.32
17	2320	-2.004183903199590641922	0.000000000000000002991	1.65
18	2597	-2.004183903199590642233	0.000000000000000000311	9.62
19	2914	-2.004183903199590642311	0.000000000000000000079	3.95
Extrap.		-2.004183903199590642324(3)		6.06

TABLE 4.20: Convergence study for the nonrelativistic energy of the $1s11p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
11	1008	-2.003465252704870274536		
12	1190	-2.003465252704884496368	0.000000000000014221832	
13	1400	-2.003465252704885475960	0.000000000000000979592	14.52
14	1618	-2.003465252704885765054	0.000000000000000289093	3.39
15	1843	-2.003465252704885786418	0.000000000000000021365	13.53
16	2076	-2.003465252704885796768	0.000000000000000010349	2.06
17	2345	-2.003465252704885797821	0.000000000000000001054	9.82
18	2622	-2.003465252704885798118	0.000000000000000000296	3.55
19	2939	-2.003465252704885798213	0.000000000000000000096	3.10
Extrap.		-2.003465252704885798265(21)		1.85

TABLE 4.21: Convergence study for the nonrelativistic energy of the $1s12p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
11	1008	-2.003512006535115329475		
12	1190	-2.003512006535138729298	0.000000000000023399823	
13	1400	-2.003512006535141941334	0.000000000000003212036	7.29
14	1618	-2.003512006535142646735	0.000000000000000705401	4.55
15	1843	-2.003512006535142715030	0.000000000000000068295	10.33
16	2076	-2.003512006535142741381	0.000000000000000026351	2.59
17	2345	-2.003512006535142744044	0.000000000000000002664	9.89
18	2622	-2.003512006535142745396	0.000000000000000001352	1.97
19	2939	-2.003512006535142745468	0.000000000000000000071	18.92
Extrap.		-2.003512006535142745516(2)		1.49

TABLE 4.22: Convergence study for the nonrelativistic energy of the $1s12p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
12	1060	-2.002953093958142725038		
13	1252	-2.002953093958149299712	0.000000000000006574675	
14	1452	-2.002953093958149619857	0.000000000000000320145	20.54
15	1684	-2.002953093958149768491	0.000000000000000148635	2.15
16	1908	-2.002953093958149778568	0.000000000000000010077	14.75
17	2168	-2.002953093958149784140	0.000000000000000005572	1.81
18	2436	-2.002953093958149784555	0.000000000000000000415	13.42
19	2744	-2.002953093958149784805	0.000000000000000000250	1.66
20	3060	-2.002953093958149784839	0.000000000000000000034	7.40
Extrap.		-2.002953093958149784866(2)		1.26

TABLE 4.23: Convergence study for the nonrelativistic energy of the $1s13p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
12	1060	-2.002989859764895217805		
13	1252	-2.002989859764907277442	0.000000000000012059637	
14	1452	-2.002989859764908459134	0.000000000000001181692	10.21
15	1684	-2.002989859764908772888	0.000000000000000313754	3.77
16	1908	-2.002989859764908799763	0.000000000000000026875	11.67
17	2168	-2.002989859764908814155	0.000000000000000014392	1.87
18	2436	-2.002989859764908815479	0.000000000000000001324	10.87
19	2744	-2.002989859764908816203	0.000000000000000000724	1.83
20	3060	-2.002989859764908816268	0.000000000000000000065	11.14
Extrap.		-2.0029898597649088163 19(11)		1.26

TABLE 4.24: Convergence study for the nonrelativistic energy of the $1s13p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
12	1060	-2.002546625370179429564		
13	1252	-2.002546625370187318703	0.000000000000007889139	
14	1452	-2.002546625370190752244	0.000000000000003433541	2.30
15	1684	-2.002546625370190903723	0.000000000000000151479	22.67
16	1924	-2.002546625370190960465	0.000000000000000056742	2.67
17	2184	-2.002546625370190965007	0.000000000000000004542	12.49
18	2452	-2.002546625370190967606	0.000000000000000002599	1.75
19	2760	-2.002546625370190967839	0.000000000000000000233	11.14
20	3076	-2.002546625370190967979	0.000000000000000000140	1.67
Extrap.		-2.0025466253701909680 07(8)		5.01

TABLE 4.25: Convergence study for the nonrelativistic energy of the $1s14p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
12	1060	-2.002576056426603710105		
13	1252	-2.002576056426621195780	0.00000000000017485676	
14	1452	-2.002576056426625033078	0.00000000000003837298	4.56
15	1684	-2.002576056426625589744	0.00000000000000556666	6.89
16	1924	-2.002576056426625745668	0.00000000000000155924	3.57
17	2184	-2.002576056426625761590	0.00000000000000015922	9.79
18	2452	-2.002576056426625767722	0.00000000000000006132	2.60
19	2760	-2.002576056426625768562	0.00000000000000000839	7.31
20	3076	-2.002576056426625768918	0.00000000000000000357	2.35
Extrap.		-2.002576056426625768993(13)		4.75

TABLE 4.26: Convergence study for the nonrelativistic energy of the $1s14p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
13	1252	-2.002218647104084119604		
14	1452	-2.002218647104087101093	0.00000000000002981489	
15	1684	-2.002218647104088204197	0.00000000000001103104	2.70
16	1924	-2.002218647104088271772	0.00000000000000067574	16.32
17	2200	-2.002218647104088298072	0.00000000000000026300	2.57
18	2468	-2.002218647104088300117	0.00000000000000002046	12.86
19	2776	-2.002218647104088301381	0.00000000000000001264	1.62
20	3092	-2.002218647104088301500	0.00000000000000000118	10.68
Extrap.		-2.002218647104088301583(29)		1.42

TABLE 4.27: Convergence study for the nonrelativistic energy of the $1s15p\ ^1P$ state of helium with infinite nuclear mass using a triple basis set.

Ω	N	$E(\Omega)$	ΔE	Ratio
13	1252	-2.00224257122200609863		
14	1452	-2.00224257122214817530 3	0.00000000000142165439	
15	1684	-2.00224257122214995243 7	0.00000000000001777134	80.00
16	1924	-2.00224257122215026028 6	0.00000000000000307849	5.77
17	2200	-2.00224257122215031613 0	0.00000000000000055844	5.51
18	2468	-2.00224257122215032265 3	0.00000000000000006523	8.56
19	2776	-2.00224257122215032563 6	0.00000000000000002983	2.19
20	3092	-2.00224257122215032620 1	0.00000000000000000565	5.28
Extrap.		-2.002242571222150326733(53)		1.06

TABLE 4.28: Convergence study for the nonrelativistic energy of the $1s15p\ ^3P$ state of helium with infinite nuclear mass using a triple basis set.

4.2 Behaviour of Nonlinear Parameters

The behaviour of α_1, β_1, α_2, β_2, α_3, and β_3 were analyzed as a function of Ω for the $1s2s\ ^1S$ (finite nuclear mass), $1s2p\ ^1P$ (infinite nuclear mass) and $1s3p\ ^1P$ (infinite nuclear mass) states of helium. As expected, α_1 and β_1 remain approximately constant, with a value near 1. α_2 and β_2 increase slowly, while α_3, and β_3 increase approximately linearly with Ω.

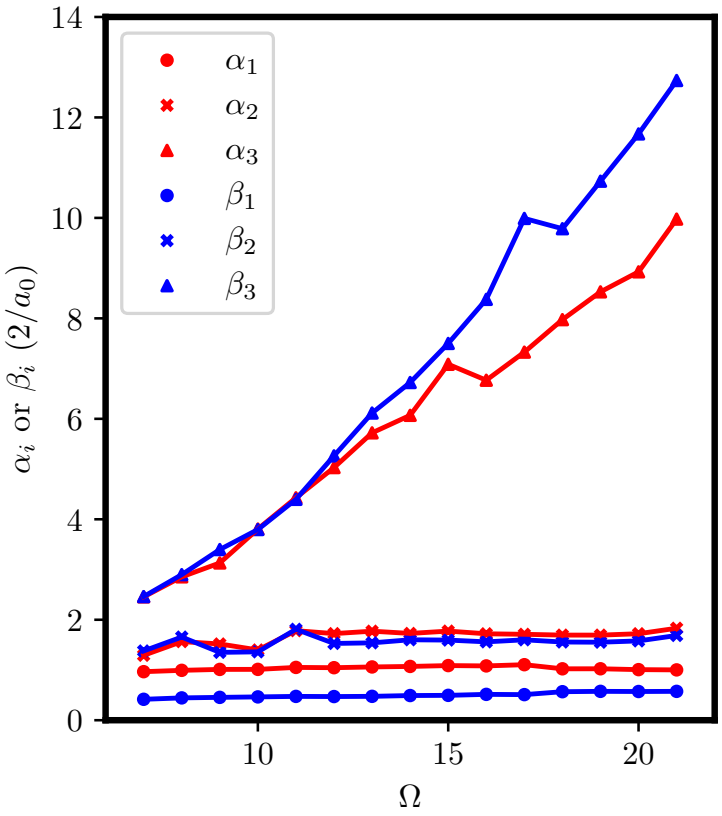

FIGURE 4.1: Behaviour of nonlinear scale parameters α_i and β_i vs. Ω for the $1s2s\ ^1S$ state of helium with finite nuclear mass.

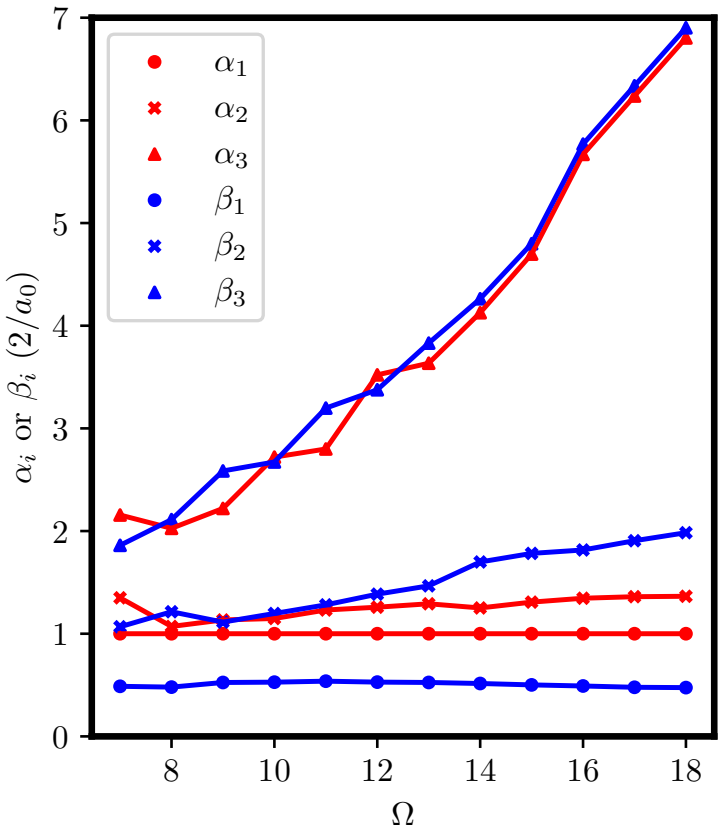

FIGURE 4.2: Behaviour of nonlinear scale parameters α_i and β_i vs. Ω for the $1s2p\ ^1P$ state of helium with infinite nuclear mass.

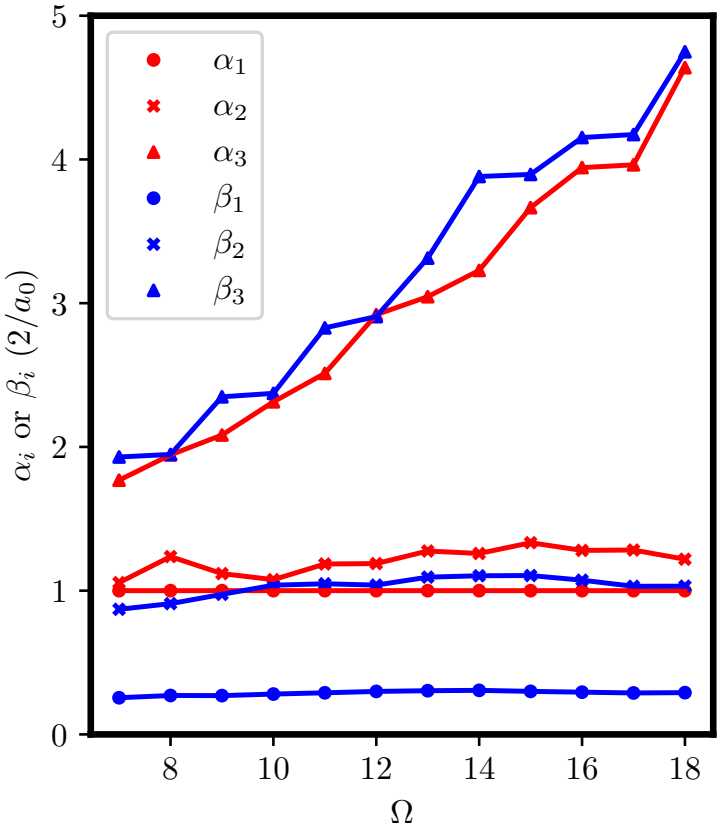

FIGURE 4.3: Behaviour of nonlinear scale parameters α_i and β_i vs. Ω for the $1s3p\ ^1P$ state of helium with infinite nuclear mass.

4.3 Matrix Operator Elements

The expectation value of various matrix operator elements were calculated for the $1s2s\ ^1S$ (infinite nuclear mass), $1s2p\ ^1P$ (finite nuclear mass) and $1s3p\ ^1P$ (finite nuclear mass) states of helium.

Operator	Expectation value
$\langle 1/r_1^2 \rangle$	2.07346950990163(36)
$\langle 1/r_1^1 \rangle$	1.135407686125600537(63)
$\langle r_1 \rangle$	11.89224453755795513(85)
$\langle r_1^2 \rangle$	128.7138659523239542(43)
$\langle 1/r_{12}^2 \rangle$	0.07186240699880(11)
$\langle 1/r_{12}^1 \rangle$	0.2496826523935671 32(11)
$\langle r_{12} \rangle$	21.0787848093672076(17)
$\langle r_{12}^2 \rangle$	258.4190429749951480(85)
$\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$	-0.4956555351736184967(49)
$\langle 1/r_1 r_2 \rangle$	0.17031692293005115(89)
$\langle 1/r_1 r_{12} \rangle$	0.28093073372999001(21)
$\langle \delta(r_1) \rangle$	0.02844809194925(22)
$\langle \delta(r_{12}) \rangle$	0.0033962319271(23)

TABLE 4.29: Expectation values of various operators of the $1s2s\ ^1S$ state of helium with infinite nuclear mass using a triple basis set. Units are Z-scaled atomic units.

Operator	Expectation value
$\langle 1/r_1^2 \rangle$	2.02152079061545(27)
$\langle 1/r_1^1 \rangle$	1.123169234785106 6501(14)
$\langle r_1 \rangle$	11.64342539668621453(51)
$\langle r_1^2 \rangle$	126.140699887077589(28)
$\langle 1/r_{12}^2 \rangle$	0.0428896830160720(62)
$\langle 1/r_{12}^1 \rangle$	0.24500338288695 16230(26)
$\langle r_{12} \rangle$	20.55461924315095018(95)
$\langle r_{12}^2 \rangle$	252.817578792563576(54)
$\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$	-0.2680895092041986(16)
$\langle 1/r_1 r_2 \rangle$	0.142666081066556910(72)
$\langle 1/r_1 r_{12} \rangle$	0.245602449922093 7060(82)
$\langle \delta(r_1) \rangle$	0.000910073952683(65)
$\langle \delta(r_{12}) \rangle$	0.000288514161130(31)

TABLE 4.30: Expectation values of various operators of the $1s2p\ ^1P$ state of Helium with finite nuclear mass using a triple set. Units are Z-scaled atomic units.

Operator	Expectation value
$\langle 1/r_1^2 \rangle$	2.02151752198509(62)
$\langle 1/r_1^1 \rangle$	1.12317751033175510146(15)
$\langle r_1 \rangle$	11.64273736977213438(68)
$\langle r_1^2 \rangle$	126.125239538902477(71)
$\langle 1/r_{12}^2 \rangle$	0.0428988854070915(43)
$\langle 1/r_{12}^1 \rangle$	0.24502386827400133364(18)
$\langle r_{12} \rangle$	20.5533134884828305(16)
$\langle r_{12}^2 \rangle$	252.78812796966035(17)
$\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$	-0.268824445927702(13)
$\langle 1/r_1 r_2 \rangle$	0.142679931186051263(39)
$\langle 1/r_1 r_{12} \rangle$	0.245622471307052062 1(29)
$\langle \delta(r_1) \rangle$	0.00090583237036(16)
$\langle \delta(r_{12}) \rangle$	0.000288700144531(85)

TABLE 4.31: Expectation values of various operators of the $1s3p\ ^1P$ state of helium with finite nuclear mass using a triple basis set. Units are Z-scaled atomic units.

4.4 Comparison With Double Basis Sets

The purpose of this section is to compare the accuracy that can be obtained from a triple basis set relative to that for a double basis set for basis sets of approximately the same size. The rates of convergence for both the energy and other matrix elements are considered for the states $1s2s\ ^1S$, $1s2p\ ^1P$ and $1s3p\ ^1P$. Figures 4.4, 4.5, 4.6 compare the convergence of the $1s2s\ ^1S$, $1s2p\ ^1P$ and $1s3p\ ^1P$ states of helium as a function of Ω for a double basis set and triple basis set, respectively. Tables 4.36 and 4.40 show the energy interpolated at $N = 2000$ using both a double basis set and triple basis set for the $1s2p\ ^1P$ and $1s3p\ ^1P$ states, respectively.

Ω	N	$E(\Omega)$	$\Delta(E)$	Ratio
4	44	-2.145973621067592416858		
5	67	-2.145973998079224422468	0.000000377011632005610	
6	98	-2.145974035712226872302	0.000000037633002449834	10.02
7	135	-2.145974044712458511138	0.000000009000231638836	4.18
8	182	-2.145974045793237178562	0.000000001080778667424	8.33
9	236	-2.145974045999170144190	0.000000000205932965628	5.25
10	301	-2.145974046042856586608	0.000000000043686442418	4.71
11	373	-2.145974046050579960226	0.000000000007723373618	5.66
12	457	-2.145974046053435382676	0.000000000002855422450	2.70
13	548	-2.145974046054069906588	0.000000000000634523912	4.50
14	652	-2.145974046054312612750	0.000000000000242706162	2.61
15	763	-2.145974046054381802328	0.000000000000069189578	3.51
16	888	-2.145974046054404649954	0.000000000000022847626	3.03
17	1020	-2.145974046054413025170	0.000000000000008375216	2.73
18	1167	-2.145974046054415659229	0.000000000000002634059	3.18
19	1321	-2.145974046054416763798	0.000000000000001104570	2.38
20	1491	-2.145974046054417142418	0.000000000000000378620	2.92
21	1668	-2.145974046054417299916	0.000000000000000157498	2.40
22	1862	-2.145974046054417362425	0.000000000000000062509	2.52
23	2063	-2.145974046054417389499	0.000000000000000027075	2.31
Extrap.		-2.145974046054417411 6(74)		1.22

TABLE 4.32: Convergence study for the nonrelativistic energy of the $1s2s\ ^1S$ state of helium with infinite nuclear mass using a double basis set.

Ω	N	$E(\Omega)$	$\Delta(E)$	Ratio
7	200	-2.145974045980449430111		
8	268	-2.145974046043587345202	0.000000000063137915091	
9	344	-2.145974046053282510051	0.000000000009695164849	6.51
10	436	-2.145974046054226783262	0.000000000000944273211	10.27
11	536	-2.145974046054331326000	0.000000000000104542737	9.03
12	654	-2.145974046054408996536	0.000000000000077670536	1.35
13	780	-2.145974046054415939213	0.000000000000006942678	11.19
14	926	-2.145974046054416807174	0.000000000000000867960	8.00
15	1080	-2.145974046054417280634	0.000000000000000473460	1.83
16	1256	-2.145974046054417354532	0.000000000000000073898	6.41
17	1440	-2.145974046054417399066	0.000000000000000044533	1.66
18	1648	-2.145974046054417408305	0.000000000000000009239	4.82
19	1864	-2.145974046054417413185	0.000000000000000004880	1.89
20	2106	-2.145974046054417414616	0.000000000000000001431	3.41
21	2356	-2.145974046054417415262	0.000000000000000000647	2.21
Extrap.		-2.145974046054417415 64(26)		1.70

TABLE 4.33: Convergence study for the nonrelativistic energy of the $1s2s\ ^1S$ state of helium with infinite nuclear mass using a triple basis set.

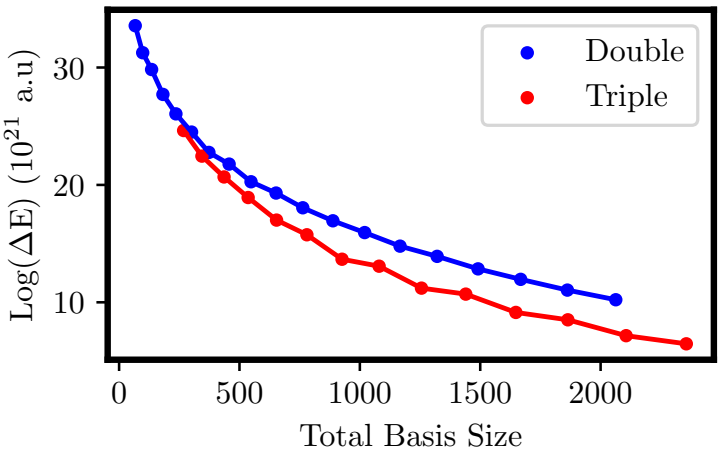

FIGURE 4.4: Comparison of energy difference vs total basis set size using a double and triple basis set for the $1s2s\ ^1S$ state of helium with infinite nuclear mass.

Operator	Expectation value
$\langle 1/r_1^2 \rangle$	2.07346950989979(69)
$\langle 1/r_1^1 \rangle$	1.135407686125600548(53)
$\langle r_1 \rangle$	11.8922445375579569(49)
$\langle r_1^2 \rangle$	128.7138659523247(12)
$\langle 1/r_{12}^2 \rangle$	0.0718624070019(11)
$\langle 1/r_{12}^1 \rangle$	0.2496826523935670722(93)
$\langle r_{12} \rangle$	21.078784809367210(10)
$\langle r_{12}^2 \rangle$	258.4190429749966(23)
$\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$	-0.49565535173624796(13)
$\langle 1/r_1 r_2 \rangle$	0.170316922930076(30)
$\langle 1/r_1 r_{12} \rangle$	0.2809307337299796(21)
$\langle \delta(r_1) \rangle$	0.02844809194749(69)
$\langle \delta(r_{12}) \rangle$	0.003396231958(24)

TABLE 4.34: Expectation values of various operators of the $1s2s\ ^1S$ state of helium using a double basis set. Units are Z-scaled atomic units.

Ω	N	$E(\Omega)$	$\Delta(E)$	Ratio
4	104	-2.123843081178558472994		
5	145	-2.123843085794947765847	0.000000004616389292852	
6	197	-2.123843086401389877840	0.000000000606442111993	7.61
7	265	-2.123843086482872697094	0.000000000081482819255	7.44
8	346	-2.123843086495445271167	0.000000000012572574073	6.48
9	446	-2.123843086497537797326	0.000000000002092526159	4.72
10	559	-2.123843086497981006816	0.000000000000443209490	4.72
11	692	-2.123843086498069657236	0.000000000000088650421	5.00
12	836	-2.123843086498092666100	0.000000000000023008863	3.85
13	1000	-2.123843086498098442369	0.000000000000005776270	3.98
14	1173	-2.123843086498100195198	0.000000000000001752829	3.30
15	1366	-2.123843086498100943184	0.000000000000000747986	2.34
16	1566	-2.123843086498101190697	0.000000000000000247513	3.02
17	1786	-2.123843086498101292500	0.000000000000000101803	2.43
18	2011	-2.123843086498101330933	0.000000000000000038434	2.65
19	2256	-2.123843086498101343429	0.000000000000000012496	3.08
20	2505	-2.123843086498101353621	0.000000000000000010192	1.23
Extrap.		-2.123843086498101363 8(54)		0.99

TABLE 4.35: Convergence study for the nonrelativistic energy of the $1s2p\ ^1P$ state of helium with infinite nuclear mass using a double basis set. Ω is the highest power in the basis set, and N is the total number of terms. Units are atomic units.

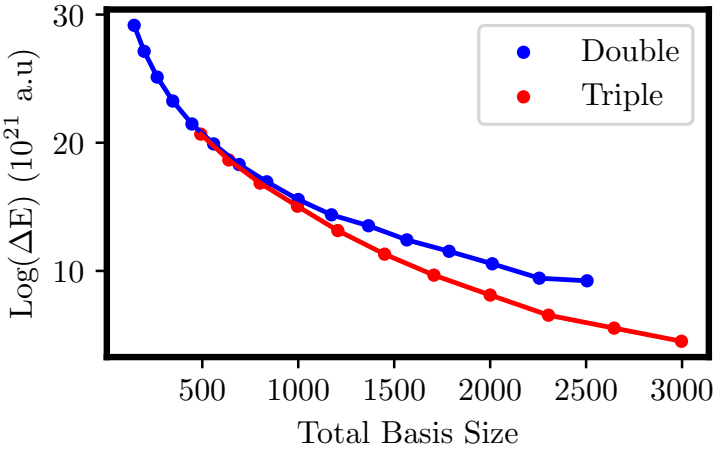

FIGURE 4.5: Comparison of energy difference vs total basis set size using a double and triple basis set for the $1s2p\ ^1P$ state of helium with infinite nuclear mass.

Basis Set	Nuclear Mass	Energy
Double	Infinite	-2.123843086498101329(19)
Triple	Infinite	-2.1238430864981013 5815(34)
Double	Finite	-2.123836778126737428(33)
Triple	Finite	-2.123836778126737 48657(63)

TABLE 4.36: Energy of the $1s2p\ ^1P$ state of helium interpolated at N = 2000 total basis set size using a double and triple basis set. Units are atomic units.

TABLE 4.37: Expectation values of various operators of the $1s2p\ ^1P$ state of helium with finite nuclear mass using a double basis set. Units are Z-scaled atomic units.

Operator	Expectation value
$\langle 1/r_1^2 \rangle$	2.0215207906062(78)
$\langle 1/r_1^1 \rangle$	1.12316923478510668 6(21)
$\langle r_1 \rangle$	11.6434253966862056(82)
$\langle r_1^2 \rangle$	126.14069988707708(41)
$\langle 1/r_{12}^2 \rangle$	0.042889683016052(60)
$\langle 1/r_{12}^1 \rangle$	0.245003382886951677(54)
$\langle r_{12} \rangle$	20.554619243150928(20)
$\langle r_{12}^2 \rangle$	252.8175787925621(12)
$\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$	-0.26808950920396(23)
$\langle 1/r_1 r_2 \rangle$	0.14266608106655786(41)
$\langle 1/r_1 r_{12} \rangle$	0.245602449922093798(61)
$\langle \delta(r_1) \rangle$	0.000910074136(16)
$\langle \delta(r_{12}) \rangle$	0.0002885142010(19)

TABLE 4.38: Expectation values of various operators of the $1s2p\ ^1P$ state of helium with finite nuclear mass using a double basis set. Units are Z-scaled atomic units.

Ω	N	E(Ω)	$\Delta(E)$	Ratio
4	104	-2.055144358563399820312		
5	164	-2.055144368105483849868	0.000000009542084029555	
6	238	-2.055144369009065542027	0.000000000903581692159	10.56
7	300	-2.055144369136423216614	0.000000000127357674587	7.09
8	371	-2.055144369159036177266	0.000000000022612960651	5.63
9	457	-2.055144369164551984074	0.000000000005515806808	4.10
10	551	-2.055144369165431990994	0.000000000000880006920	6.27
11	660	-2.055144369165684081207	0.000000000000252090214	3.49
12	775	-2.055144369165731290283	0.000000000000047209076	5.34
13	905	-2.055144369165750517509	0.000000000000019227226	2.46
14	1039	-2.055144369165756127937	0.000000000000005610428	3.43
15	1189	-2.055144369165759439576	0.000000000000003311639	1.69
16	1343	-2.055144369165760722501	0.000000000000001282925	2.58
17	1515	-2.055144369165761443526	0.000000000000000721026	1.78
18	1691	-2.055144369165761759158	0.000000000000000315632	2.28
19	1887	-2.055144369165761950328	0.000000000000000191170	1.65
20	2087	-2.055144369165762033572	0.000000000000000083244	2.30
21	2309	-2.055144369165762099251	0.000000000000000065679	1.27
Extrap.		-2.055144369165762192(32)		0.70

TABLE 4.39: Convergence study for the nonrelativistic energy of the $1s3p\ ^1P$ state of helium with finite nuclear mass using a double basis set.

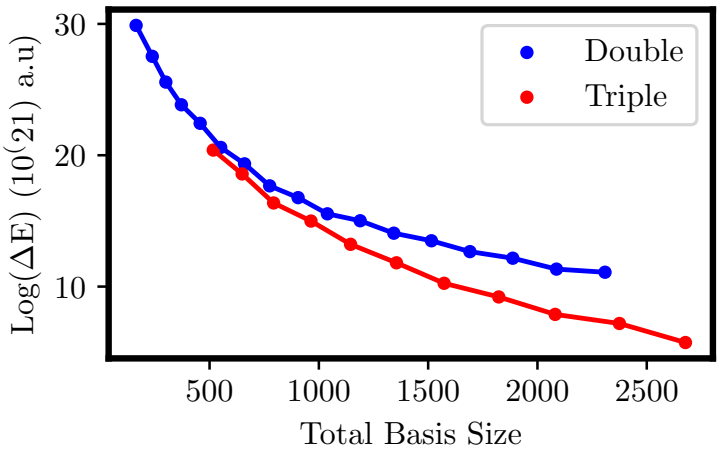

FIGURE 4.6: Comparison of energy difference vs total basis set size using a double and triple basis set for the $1s3p\ ^1P$ state of Helium with finite nuclear mass.

Basis Set	Nuclear Mass	Energy
Double	Infinite	-2.055146362091943434(19)
Triple	Infinite	-2.0551463620919435353(89)
Double	Finite	-2.055144369165761997(41)
Triple	Finite	-2.0551443691657621686(13)

TABLE 4.40: Energy of the $1s3p\ ^1P$ state of helium interpolated at N = 2000 total basis set size using a double and triple basis set. Units are atomic units.

Operator	Expectation value
$\langle 1/r_1^2 \rangle$	2.0215175220275(78)
$\langle 1/r_1^1 \rangle$	1.12317751031755134(77)
$\langle r_1 \rangle$	11.642737369772144(33)
$\langle r_1^2 \rangle$	126.1252395389017(12)
$\langle 1/r_{12}^2 \rangle$	0.0428988854061(14)
$\langle 1/r_{12}^1 \rangle$	0.24502386827400136(12)
$\langle r_{12} \rangle$	20.5533134884828171(92)
$\langle r_{12}^2 \rangle$	252.7881279696608(36)
$\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle$	-0.26882444592751(49)
$\langle 1/r_1 r_2 \rangle$	0.14267993118605151(80)
$\langle 1/r_1 r_{12} \rangle$	0.245622471307052079(61)
$\langle \delta(r_1) \rangle$	0.000905832378(11)
$\langle \delta(r_{12}) \rangle$	0.000288700135(11)

TABLE 4.41: Expectation values of various operators of the $1s3p\ ^1P$ state of helium with finite nuclear mass using a double basis set. Units are Z-scaled atomic units.

4.5 Discussion

In general, eigenvalues were obtained to an accuracy of 21 significant figures for all P states from $n = 2$ to $n = 15$, as well as the $1s2s\ ^1S$ state of helium. In the states that were computed, there did not seem to be a loss of accuracy when reaching larger n, indicating a robust variational schema. For the $1s2s\ ^1S$, $1s3p\ ^1P$ and $1s2p\ ^1P$ states of helium, this was an improvement of *at least* two orders of magnitude for both the energy and other matrix elements of other operators when compared with those calculated using a double basis set wave function. The behaviour of the nonlinear parameters for the $1s2s\ ^1S$, $1s3p\ ^1P$ and $1s2p\ ^1P$ states of helium followed the expected convergence pattern, which was observed by Drake [18].

It was observed that the convergence followed the same pseudo-logarithmic pattern that is observed when using double basis sets (see Figures 4.4, 4.5, 4.6). However, it was true that at any total basis set N, $\Delta(E_{triple}) << \Delta(E_{double})$. Thus, at any N, the energy eigenvalue

of the triple basis set wave function was *closer* to convergence than it was for the double basis set wave function. This is further emphasized in Tables 4.36 and 4.40, which show that the energy of a triple basis set wave function is both lower *and* more accurate than the corresponding double basis set wave function at $N = 2000$.

It is generally true that matrix elements of other operators can be calculated to about half as many figures as the energy. For the $1s2s\ ^1S$, $1s3p\ ^1P$ and $1s2p\ ^1P$ of helium, operator expectation values were determined to anywhere from 8 ($\delta(r_{12})$) to 16 ($1/r_1 r_{12}$) figures. In each case, the accuracy obtained was *at least* as good, any in many cases the accuracy when using a triple basis set was more accurate by up to 2 orders of magnitude than the same value calculated using a double basis set.

4.5.1 Comparison with Other Works

Using a single basis set, Pekeris et al. [9], [10] were able to achieve convergence in the energy to 12 significant figures for states up to $n = 2$. However, it was very difficult for them to compute higher-lying states. Pekeris [22] was able to compute eigenvalues for the S states up to $n = 9$, only being able to obtain 7 or 8 significant figures for all excited states past $n = 2$. For example, the energy of the $1s9s\ ^1S$ state could only be calculated to 7 significant figures. More accurate calculations of excited S Rydberg states were performed by Nakashmia et al. [23], who were able to compute $1sns\ ^1S$ and $1sns\ ^3S$ up to $n = 24$, obtaining energy values to 19 significant figures.

Accad, Pekeris and Schiff [24] were able to compute P states up to $n = 5$, with limited, diminishing accuracy with increasing n. They obtained 9 significant figures for $n = 1$, however were only able to obtain 7 significant figures for $n = 5$. It is important to note that the first several figures of the energy come from the screened hydrogenic energy, given by $E_n = -2 - 1/(2n^2)$. For $n = 9$, $E_n = -2.0061728$, and comparing with Table 4.15, accounts for the first 5 figures of the energy. A triple basis set, in comparison, is shown to be stable for higher-lying Rydberg states up to $n = 15$, with impressive 22 figure accuracy for the energy.

Using a double basis set, Drake et al. [14], [15] calculated energy eigenvalues for the P states up to $n = 10$ in 1992, and the S states up to $n = 10$ in 1994. In these analyses,

the energy for these states was determined to up to 19 significant figures. However, the author points out that with higher-lying Rydberg states past $n = 10$, numerical stability becomes an issue. This was not noticed in this present work, as P states up to $n = 15$ were calculated with no limitation of numerical stability, and to even further accuracy of 22 figures by using a triple basis set. Table 4.42 gives a comparison of energy values for P states up to $n = 10$ calculated by a variety of authors. In each case, using a triple basis set indeed gives the most accurate results.

State	Author	Energy
$1s2p\ ^1P$	Schiff *et al.* [25]	-2.1238430858
	Kono and Hattori [26]	-2.1238430862
	Morgan and Baker [27]	-2.1238430864025
	Drake (extrap.) [27]	-2.123843086498093(10)
	This work.	-2.12384308649810135924(22)
$1s2p\ ^3P$	Schiff *et al.* [25]	-2.1331641905
	Kono and Hattori [26]	-2.1331641906
	Schwartz	[28] -2.133164190626
	Morgan and Baker [27]	-2.1331641906735
	Drake (extrap.) [27]	-2.133164190779274(9)
	This work.	-2.13316419077928320514(8)
$1s3p\ ^1P$	Schiff *et al.* [25]	-2.0551463554
	Kono and Hattori [26]	-2.0551463621
	Drake (extrap.) [27]	-2.055146362091944(31)
	This work.	-2.05514636209194353692(34)
$1s3p\ ^3P$	Schiff *et al.* [25]	-2.0580810816
	Kono and Hattori [26]	-2.0580810844
	Drake (extrap.) [27]	-2.058081084274274(34)
	This work.	-2.05808360351788938857(43)
$1s4p\ ^1P$	Accad *et al.* [24]	-2.031069591
	Kono and Hattori [26]	-2.0310696503
	Drake (extrap.) [27]	-2.031069650450235(24)
	This work.	-2.03106965045024071474(22)

$1s4p\ ^3P$	Accad *et al.* [24]	-2.032324325
	Kono and Hattori [26]	-2.0323243540
	Drake (extrap.) [27]	-2.032324354296619(16)
	This work.	-2.0323243542966303319 56(9)
$1s5p\ ^1P$	Accad *et al.* [24]	-2.01990572
	Kono and Hattori [26]	-2.0199059897
	Drake (extrap.) [27]	-2.019905989900825(22)
	This work.	-2.0199059899008464488 48(7)
$1s5p\ ^3P$	Accad *et al.* [24]	-2.02055103
	Kono and Hattori [26]	-2.0205511870
	Drake (extrap.) [27]	-2.020551187256247(23)
	This work.	-2.0205511872562677882 46(11)
$1s6p\ ^1P$	Kono and Hattori [26]	-2.0138339802
	Drake (extrap.) [27]	-2.013833979671734(23)
	This work.	-2.0138339796717401023 86(9)
$1s6p\ ^3P$	Kono and Hattori [26]	-2.0142079589
	Drake (extrap.) [27]	-2.014207958773734(12)
	This work.	-2.0142079587737505912 19(6)
$1s7p\ ^1P$	Kono and Hattori [26]	-2.0101693149
	Drake (extrap.) [27]	-2.010169314529353(20)
	This work.	-2.0101693145293889848 98(3)
$1s7p\ ^3P$	Kono and Hattori [26]]	-2.0104049599
	Drake (extrap.) [27]	-2.0104049560007936(21)
	This work.	-2.0104051475249077901 73(7)
$1s8p\ ^1P$	Kono and Hattori [26]	-2.0077891270
	Drake (extrap.) [27]	-2.007789127133214(18)
	This work.	-2.0077891271332358951 56(3)
$1s8p\ ^3P$	Kono and Hattori [26]	-2.0079470137
	Drake (extrap.) [27]	-2.007947013771117(13)
	This work.	-2.0079470137711615052 62(5)

TABLE 4.42: Energy of various and P states of helium up to $n = 8$.

Aznabaev et al. [1] were able to calculate energies for states up to $n = 4$, and with accuracy of up to 35 significant figures. However, computation time was significant, due to the large number of calculations required with pseudo Monte Carlo basis sets, such as those with wave functions given by 2.18. Due to the large number of terms required for these entirely exponential basis sets, the computation utilized a *duodecimal arithmetic* (100 digits), which further slowed down the computation by a factor of about 100 compared to standard quadruple precision. Since such a large number of terms is generated randomly in the wave function construction, random coincidences in the exponential factors are present, increasing the redundancy of the wave function and slowing down computation time by a factor of 100. The same duodecimal arithmetic must then be used for all subsequent calculations using the generated wave functions to avoid serious numerical cancellation and loss of significance in the calculation of matrix elements. By comparison, the present work was able to achieve 22 significant figures of accuracy whilst only requiring the commonly used quadruple arithmetic (approximately 32 decimal digits). Remembering that relativistic corrections are accurate to only about half as many significant figures, this level of accuracy is just past what is currently achievable by experimental accuracy for helium, which currently is able to perform spectroscopic measurements to about 12 significant figures [29], [30], [31], [32].

Recent high precision calculations by Aznabaev et al. provide an important test of the uncertainty estimates obtained in the present work. A comparison of the energy obtained in this work and by Aznabaev et al. [1] for helium states up to $n = 4$ is tabulated in Table 4.43. In each case, the energy obtained using a triple basis set was within the uncertainty estimations given, and thus agrees with the work by Aznabaev et al. Since the results agree within the estimated uncertainty for the present work, this gives confidence that the uncertainty estimates for the higher-lying states up to n = 15 are well founded and realistic. The results for the higher-lying Rydberg states are the most accurate in the literature.

State	Author	Energy
$1s2s\ ^1S$	Aznabaev [1]	-2.145974046054417415805028975461921
	This work.	-2.14597404605441741564(26)
	Difference	0.000000000000000000016(26)
$1s2p\ ^1P$	Aznabaev [1]	-2.123843086498101359247333142374
	This work.	-2.12384308649810135924(22)
	Difference	0.000000000000000000006(22)
$1s2p\ ^3P$	Aznabaev [1]	-2.133164190779283205146992763806
	This work.	-2.1331641907792832051(8)
	Difference	0.000000000000000000006(8)
$1s3p\ ^1P$	Aznabaev [1]	-2.055146362091943536928341092 1
	This work.	-2.0551463620919435369(34)
	Difference	0.000000000000000000001(34)
$1s4p\ ^1P$	Aznabaev [1]	-2.031069650450240714758931436 0941
	This work.	-2.0310696504502407147(22)
	Difference	0.000000000000000000016(22)

TABLE 4.43: Energy of various S and P states of helium.

Chapter 5

Conclusion

In conclusion, it was discovered that it is possible to construct wave functions in Hylleraas coordinates with three sets of nonlinear scale parameters for higher-lying Rydberg states of helium. The accuracy of the eigenvalues themselves was found to be very high, giving energy eigenvalues with 21 significant figures, and matrix elements of other operators up to 16 significant figures. Furthermore, the wave function construction scheme used was found to be very robust, with no loss of accuracy or computational stability up to $n = 15$.

Comparisons of calculations using a double basis set and triple basis set were carried out for the $1s2s\ ^1S$, $1s2p\ ^1P$ and $1s3p\ ^1P$ states of helium, and it was found that the energy eigenvalues and all matrix operator elements could be determined with significantly higher accuracy when using a triple basis set for basis sets of comparable size. Specifically, it was found that using a triple basis set yielded an improvement in energy accuracy of two significant figures. This improvement was noted in every state considered, and thus it is concluded that using a triple basis set is up to *100 times* more accurate than using a double basis set. Furthermore, at each total basis set size N, the corresponding energy eigenvalue was calculated with more accuracy with a triple basis set, indicating a stronger convergence scheme.

The general schema using a triple basis set was proven to be more effective than a double basis set for high precision calculations of helium. Using a triple basis set offered more numerical stability and less computational time, whilst giving significantly more accurate

energy eigenvalues and matrix operator elements. Since the computation can be carried out on any workstation and does not require parallel or multithreaded computation or calculations requiring more than 32 decimal digit arithmetic, this method proves to be more efficient and useful than constructing exponential quasi-random exponential trial wave functions, as per Aznabaev et al.[1]. Furthermore, due to current experimental limitations in the field of high precision atomic physics, the extra precision obtained by constructing exponential quasi-random exponential trial wave functions does not warrant the computation time.

Chapter 6

Future Work

This work opens numerous opportunities for future work in the field of high precision atomic physics. The triple basis set method extends the accuracy of the double basis set method, without needing parallel or multi-threaded computational capabilities or precision beyond 32 decimal digit arithmetic.

Firstly, the triple basis set method can be applied to other states of helium. It is possible to extend these calculations to states beyond $n = 15$, and since using double basis sets becomes difficult with higher n, the triple basis set method is a viable alternative when higher-lying Rydberg states are needed. This can also be applied to other three-body quantum systems, such as Li^+ and Be^{2+}.

Secondly, in the search for physics beyond the standard model, it is imperative that high precision theory be able to keep up with experimental accuracy. Many atomic physics phenomena, such as two photon processes, as well as relativistic and QED corrections, rely on the ability to accurately and efficiently model the three-body wave functions. QED corrections are calculated by comparing the total energy, $E_{Total} = E_{Relativistic} + E_{Nonrelativistic} + E_{QED}$ with experimental transition frequencies. Using the nonrelativistic energies tabulated in Chapter 4, relativistic and QED corrections should be performed up to α^5 for all states up to $n = 15$. Meaningful results can then be obtained and compared to experiment, which is currently accurate to approximately 12 significant figures.

Finally, it would be wise to investigate the possibility of constructing wavefunctions

using $n - order$ basis sets, with $n > 3$. Since using a triple basis set offers such significant accuracy, stability and computational improvements over a double basis sets, it would be interesting to discover if even further improvements could be made by extending the number of nonlinear parameters even further.

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