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Amirreza Moini
University of Windsor

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CRITICAL NUCLEAR CHARGE OF QUANTUM MECHANICAL THREE-BODY PROBLEM

by

Amirreza Moini

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by

Amirreza Moini

APPROVED BY:

Dr. Richard J. Caron
Department of Mathematics and Statistics

Dr. Eugene H. Kim
Department of Physics

Dr. Gordon W. F. Drake, Advisor
Department of Physics

20 December 2013

Author's Declaration of Originality

I certify that I am the sole author of this thesis and that no part of this project has been taken from any other work.

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Abstract

The critical nuclear charge Z_c for a three-body quantum mechanical system consisting of positive and negative charges is the minimum charge for the system to remain in a bound state. This work presents a study of the critical nuclear charge for heliumlike systems with infinite nuclear mass, and also a range of the reduced mass up to $\frac{\mu}{M} = 0.5$. The results help us to resolve a discrepancy in the literature for the infinite mass case, and they are the first to study the dependence on $\frac{\mu}{M}$.

It is found that Z_c has a maximum at $\frac{\mu}{M} = 3525$, which is intermediate between the atomic structure of helium, and the molecular structure of H_2^+. Z_c for the infinite mass case is found to be 0.911028267. This value is compatible with the result of Baker, et al, who found the upper bound for Z_c to be 0.91103. However, it does not agree with other results in the literature.

The understanding of the critical charge will bring us a deeper appreciation of the stability of a three-body system as a function of the reduced mass, correlation effects of coulombic potential and more importantly, the physics of a three-body quantum mechanical system.

To my parents.

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Chapter 1

INTRODUCTION

The twentieth century started with the discovery of two of the greatest scientific theories of history, quantum mechanics and Einstein general theory of relativity. The former explains the world at the smallest scale, whereas the latter explains the universe in the largest scale, strong gravitational fields and velocities comparable to the speed of light. Both theories have proved incredibly successful in their own realm, even though their predictions can drastically conflict with classical physics predictions. These two theories provide the framework for all branches of modern physics. This thesis focuses on application of quantum mechanics to atomic systems.

Initially applied to the simplest physical systems such as free particles, simple harmonic oscillators and the hydrogen atom, quantum mechanics proved to be accurate in calculating all the physical quantities of these systems, such as energy levels, angular momentum, transition probabilities and so on. Helium, being the simplest system after the aforementioned systems, containing a positively charged nucleus and two electrons orbiting around it, has also been studied in great detail. It consists of three particles and as we know, three-body systems are not analytically solvable, neither classically nor quantum mechanically. Nevertheless, its eigenstates and eigenvalues have been calculated to great precision using various approximation methods

1.1 HELIUM AND CRITICAL NUCLEAR CHARGE

The total energy of any physical system is calculated by its Hamiltonian. It is expressed as the sum of the kinetic energgy and the potential energy of the system.

$$H = T + V, \tag{1.1}$$

where T and V denote the kinetic and potential energy, respectively.

The potential energy in the Hamiltonian of helium is coulombic, consisting of an attractive potential between the nucleus and each of the two electrons, but is repulsive between electrons. Consequently, the interaction of these three particles through these three potentials results in a stable system that has an infinite number of bound states (identified by a set of quantum numbers such as n, l, s, j, etc) or any linear combination of them.

What would happen to helium if its nuclear charge were to be continuously decreased? Although this hypothetical process is physically impossible due to quantum nature of charge, as we will see, it will give us a deeper insight into the coulombic potential and $\frac{1}{Z}$ expansion (defined in 1.2).

As we decrease the nuclear charge, the attractive forces between the nucleus and the electrons weaken while the repulsive force between the two electrons remains unchanged. As a result, one electron starts moving further away from the nucleus. Eventually at a specific Z, the binding energy of the outer electron becomes zero, and the energy of the entire system will be $-1/2$ [1, 2]. We call this nuclear charge 'critical charge' and denote it by Z_c. This is the minimum amount of nuclear charge required to keep the atom in a bound state. One might think that at this point the outer electron is free and the atom is ionized. However, it is shown by Reinhardt [2] and explained by the table 4.4 that the outer electron will be in a resonance state.

1.2 $\frac{1}{Z}$ EXPANSION AND CRITICAL CHARGE

As mentioned before, helium is a three-body system that can not be described analytically, so it requires numerical methods and approximations. One of the most versatile methods of approximation in quantum mechanics is perturbation theory. We will see that critical charge of helium plays a crucial role in perturbation series of helium.

As will be explained in the section 3.1, the Hamiltonian for helium (neglecting the mass polarization term) can be scaled and written in the form [3, 4]

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z}\frac{1}{r_{12}}. \tag{1.2}$$

We can split this Hamiltonian into two parts:

$$\begin{aligned} H_0 &= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} && (1.3) \\ \lambda H_1 &= \frac{1}{Z}\frac{1}{r_{12}}, && (1.4) \end{aligned}$$

where $\lambda = \frac{1}{Z}$ plays the role of a perturbation parameter.

The solutions for H_0 are just two hydrogenic wave functions. H_1 can be treated as a small perturbative Hamiltonian, thus it is possible to write a perturbation series for eigenstates and eigenvalues of H, based on the complete and orthonormal set of H_0 eigenstates. Specifically, the expansion for the energy is [5]

$$E(\lambda) = \sum_{i=0}^{\infty} E_i \lambda^i, \tag{1.5}$$

where $\lambda = \frac{1}{Z}$ and E_i is the energy correction of the order i. This perturbation expansion is one the most essential tools in atomic physics. It is used for calculations of energy levels of highly-charged ions [6], the correlation energies [7], calculations of autoionisation rate [8], accurate energy and oscillator strength calculation [9], negative-energy contributions to transition amplitudes [10] and the calculations of double photoeffect [11], and for many other problems.

However, the radius of convergence of such a series is thought to be controlled by the critical charge of the nucleus [12]. The radius of convergence for this perturbation series is $(Z_{critical})^{-1}$, therefore finding the critical charge gives us a deeper understanding of perturbative solutions of helium.

1.3 POSITRONIUM MINUS

Positronium minus is an exotic ion that contains two electrons, and a positron as its nucleus. Its structure is similar to helium except for the fact that positronium minus nucleus is much lighter than helium nucleus. Dealing with crtitical charge of positronium needs much more carefull consideration because its Hamiltonian has a term called 'Mass Polarization', which is much smaller for helium and can be neglected to a first approximation.

Mass polarization changes the Hamiltonian of positronium minus to the form (see sect. 3.1)

$$-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z}\frac{1}{r_{12}} - \frac{\mu}{M}\nabla_1 \cdot \nabla_2 \tag{1.6}$$

where $\frac{\mu}{M}$ is negligible for helium (≈ 0.000136), unless we are dealing with high-precision calculations. However, for positronium minus $\frac{\mu}{M}$ is 0.5, making mass polarization term non-negligible.

1.4 THE PUISEUX EXPANSION

A Puiseux expansion [13] is the generalization of power series expansion to negative and fractional powers. It may be written as

$$y = \sum_{i=m}^{\infty} a_i x^{\frac{i}{n}}, \tag{1.7}$$

where m and n are fixed integers (m can be $-\infty$), and a_i is the coefficient. It is clear that for $t = x^{\frac{1}{n}}$, the Puiseux series is

$$y = \sum_{i=m}^{\infty} a_i t^i, \tag{1.8}$$

which is a Laurent series.

The Puiseux expansion for the energy of heliumlike atoms can be written as [6]:

$$E = -\frac{1}{2}Z_{cr}^2 + \sum_{n=1}^{N_{max}} P_n (Z - Z_{cr})^{\frac{n}{2}}. \tag{1.9}$$

By fitting the values of energy versus nuclear charge, we can evaluate the coefficients P_n and also Z_{cr}. This will be done for different values of reduced mass, starting from zero (corresponding to helium with infinitely heavy nucleus) all the way up to 0.5 (for positronium minus).

Although the upper limit of the Puiseux expansion should be infinity, it was truncated at N_{max} for two reasons. Firstly, for this series to converge, there is a necessary condition that $\lim_{n\to\infty} P_n = 0$. Secondly, we will calculate P_n's by fitting the data to the Puiseux expansion, and the limited number of data points of finite accuracy cannot support an infinite number of coefficients. Therefore, the point at which the series is truncated depends on the number and quality of data points.

Chapter 2

LITERATURE REVIEW

The motivation for this work is twofold. First because a general three-body problem is not analytically solvable. Therefore, knowing the numerical value of the critical nuclear charge will give us a better understanding of such a system.

Second, there is a discrepancy in the literature for the critical nuclear charge of helium, in the infinite mass case. This made us delve into this problem and try to find a more accurate and comprehensive solution for this problem.

Quantum mechanical investigations of helium, which is the most important three-body atomic system, started immediately after Schroedinger proposed his wave equation. As mentioned previously, the Schroedinger equation is solvable for hydrogen but not for helium. Hylleraas [14] introduced the first variational wave function for helium, which was in the form

$$\psi_{tr}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i+j+k \leq \Omega} a_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2) \pm \text{exchange}. \tag{2.1}$$

The majority of calculations on heliumlike sequence are either based on this wave function, or based on extended versions of this wave function, such as introducing a second or third set of nonlinear parameters done by Drake [15], or only exponential function with nonlinear coefficients which are generated in a random manner over a finite interval [16].

In 2011, N. L Guevara and A. V. Turbiner [13] used wave function of the form

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{i=1}^{N} A_i[\exp(-\beta_i r_1 - \gamma_i r_2) + \text{exchange}] \exp(-\alpha_i r_{12}) \tag{2.2}$$

and calculated the ground state energy for Z range from 0.95 to 1.35 with the increment of 0.05. By extrapolating the binding energy of the outer electron, they calculated the critical charge of 0.910850. Their value is about 0.02 % less than our value for Z_c (0.9110282679). The reason is partly because their energies have 12 significant digits (the energy values that we used has 20 significant digits). Also because their trial wave function does not converge fast enough as $Z \to Z_c$, so they had to keep the nuclear charge Z over 0.95, which is relatively far from the critical charge, and increases the error of extrapolation. Also the error of their final result is not addressed, which makes it hard to realize how accurate their result is.

Frank H. Stillinger [17] treated electron-electron interaction as a perturbation and expanded the energy as a power series expansion

$$E = \sum_{n=0}^{\infty} E_n \lambda^n, \tag{2.3}$$

where $\lambda = 1/Z$ is the parameter that controls the perturbation. For heavy ions in helium isoelectric series (large Z, or small λ), this series converges rapidly. However, for small Z it doesn't converge rapidly, and in fact it has a a radius of convergence that is related to $Z_{critical}$. Stillinger calculated $\lambda_{critical} = Z_{critical}^{-1} = 1.1184$ and therefore, $Z_{critical}$ is approximately 0.89413, which is almost 2% off the real value. He used the ratio $r_n = \frac{E_n}{E_{n-1}}$ to calculate Z_c as $n \to \infty$. However, the coefficients of perturbation series are known with a good accuracy only for the first few terms, which is the reason for poor accuracy of the result.

Gustavo A. Arteca,Francisco M. Fernandez, and Eduardo A. Castro [18] also did the same calculation as Stillinger did and found 0.9045 ± 0.0035 for $Z_{critical}$, which is still not compatible with Z_c even considering the error.

Baker [12] found the upper bound for the critical charge which is in complete agreement with Z_c. They found the upper bound of 0.91103, which is correct. They also proved that the radius of convergence is equal to $\lambda_c = (Z_c)^{-1}$ and the fact that λ_c is the closest singularity on the complex plane to the origin.

For the case of excited states, we have $Z_c \geq 1$, because H^- has only one excited states [19, 20]. However, the calculations of Katriel, Puchalski and Pachucki [21] shows that for $1s2s\ ^{1,3}S$ and $1s2p\ ^{1,3}P$, the critical charge is exactly equal to one.

The table 2.1 shows the previously calculated values of critical charge in the literature

Table 2.1: The previously calculated values of the critical charge

Name and reference	the critical charge
N. L Guevara and A. V. Turbiner [13]	0.910850
Frank H. Stillinger, JR. [17]	0.89413
Gustavo A. Arteca,Francisco M. Fernandez, and Eduardo A. Castro [18]	0.9045 ± 0.0035
Jonathan D. Baker, David E. Freund, Robert Nyden Hill and John D. Morgan III [12]	0.91103 (upper bound)
Katriel, Puchalski and Pachucki [21] (the excited states)	1.0

All these values, except Katriel, Puchalski and Pachucki [21], are calculated for infinite mass limit, whereas the values proposed in this thesis are for both infinite and finite nuclear mass ($\frac{\mu}{M}$ ranges from 0 to 0.5).

Chapter 3

THEORY AND CALCULATION

Before dealing with critical charge, we need to know the wave function of three-body systems, specifically helium-like atomic systems. After finding the Hamiltonian and fixing the notation, different approximation methods, numerical analysis and error analysis will be introduced.

3.1 HAMILTONIAN

The following notation is adopted for writing the Hamiltonian

M = mass of nucleus
m = mass of electron
$\boldsymbol{R}$ = position vector of nucleus
$\boldsymbol{r}_1$ = position vector of 1st electron
$\boldsymbol{r}_2$ = position vector of 2nd electron

∇_{R} = gradient operator that acts on the nucleus coordinate

∇_{r_1} = gradient operator that acts on the 1st electron coordinate

∇_{r_2} = gradient operator that acts on the 2st electron coordinate

Z = nuclear charge.

Although indices 1 and 2 are used to label electrons, they are not meant to identify them, due to the fact that electrons are identical particles (so the cannot be distinguished). Therefore, those indices are only used to address the coordinate of each electron as well as the differentiation with respect to their coordinate.

The Hamiltonian can be written in the form

$$H = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\sum_{i=1}^{2}\nabla_{r_i}^2 - \sum_{i=1}^{2}\frac{Ze^2}{|r_i - R|} + \frac{e^2}{|r_1 - r_2|}. \tag{3.1}$$

In order to further simplify this Hamiltonian, we transform from the laboratory coordinate to the centre of mass coordinate

$$\begin{aligned} \boldsymbol{\rho}_i &= \boldsymbol{r}_i - \boldsymbol{R} \qquad i = 1,2 \\ \boldsymbol{R}_{CM} &= \frac{M\boldsymbol{R} + m(\boldsymbol{r}_1 + \boldsymbol{r}_2)}{M + 2m}. \end{aligned} \tag{3.2}$$

Differential operators in these new coordinates are described by

$$\begin{aligned} \nabla_{r_i} &= \nabla_{\rho_i} + \frac{m}{M+2m}\nabla_{R_{CM}} \qquad i = 1,2 \\ \nabla_R &= -\nabla_{\rho_1} - \nabla_{\rho_2} + \frac{M}{M+2m}\nabla_{R_{CM}}. \end{aligned} \tag{3.3}$$

Eventually the Hamiltonian will look like

$$-\frac{\hbar^2}{2}\left\{\frac{1}{M+2m}\right\}\nabla_{R_{CM}}^2 - \frac{\hbar^2}{2}\left\{\frac{1}{m} + \frac{1}{M}\right\}\sum_{i=1}^{2}\nabla_{\rho_i}^2 - \sum_{i=1}^{2}\frac{Ze^2}{|\rho_i|} + \frac{e^2}{|\rho_1 - \rho_2|} + \frac{\hbar^2}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2}. \tag{3.4}$$

Further simplification will be achieved by definition of the reduced mass of the electron μ

$$\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m} \tag{3.5}$$

therefore

$$-\frac{\hbar^2}{2}\left\{\frac{1}{M+2m}\right\}\nabla^2_{R_{CM}} - \frac{\hbar^2}{2\mu}\sum_{i=1}^{2}\nabla^2_{\rho_i} - \sum_{i=1}^{2}\frac{Ze^2}{|\rho_i|} + \frac{e^2}{|\rho_1-\rho_2|} + \frac{\hbar^2}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2}. \tag{3.6}$$

It is clear that the Hamiltonian is seperable for the center of mass and relative motion of the electrons with respect to centre of mass

$$\begin{aligned} H &= H_{CM} + H(\rho_1,\rho_2) &(3.7)\\ H_{CM} &= -\frac{\hbar^2}{2}\left\{\frac{1}{M+2m}\right\}\nabla^2_{R_{CM}} &(3.8)\\ H(\rho_1,\rho_2) &= -\frac{\hbar^2}{2\mu}\sum_{i=1}^{2}\nabla^2_{\rho_i} - \sum_{i=1}^{2}\frac{Ze^2}{|\rho_i|} + \frac{e^2}{|\rho_1-\rho_2|} + \frac{\hbar^2}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2}. &(3.9)\end{aligned}$$

Hence, the wave function can be written as a product

$$\psi(R_{CM},\rho_1,\rho_2) = \psi_{CM}(R_{CM})\psi(\rho_1,\rho_2). \tag{3.10}$$

Substituting this ansatz in to the Schroedinger equation results in

$$\begin{aligned} H_{CM}\psi_{CM}(R_{CM}) &= E_{CM}\psi_{CM}(R_{CM}) &(3.11)\\ H(\rho_1,\rho_2)\psi(\rho_1,\rho_2) &= E\psi(\rho_1,\rho_2) &(3.12)\\ E_{total} &= E_{CM} + E. &(3.13)\end{aligned}$$

Equation (3.11) describes a free particle of mass $M + 2m$. Its solutions are

$$\psi_{CM}(R_{CM}) = \sum_{nlm} R_{E,l}(|R_{CM}|)Y_l^m(\theta,\phi), \tag{3.14}$$

where $R_{E,l}$ is a linear combination of spherical Bessel functions and spherical Neumann functions. This is nothing but the spherical wave expansion of $e^{i\boldsymbol{k}_{CM}\cdot\boldsymbol{R}_{CM}}$.

The centre of mass wave function describes the general motion of the entire system in space-time, while the information about the internal structure of our system is contained in the relative part of the wave function $[\psi(\rho_1, \rho_2)]$. One can make a transformation to a coordinate system in which the centre of mass is not moving ($\boldsymbol{k}_{CM} = 0$) and focus entirely on the relative part of the wave function. Hence, we turn our attention to the relative wave function from now on. The term 'wave function' will be used for $[\psi(\rho_1, \rho_2)]$ instead of 'relative wave function', without any confusion.

The wave function satisfies the Schroedinger equation

$$\begin{aligned} H(\rho_1, \rho_2)\psi(\rho_1, \rho_2) &= \Big\{ -\frac{\hbar^2}{2\mu}\sum_{i=1}^{2}\nabla^2_{\rho_i} - \sum_{i=1}^{2}\frac{Ze^2}{|\rho_i|} + \frac{e^2}{|\rho_1 - \rho_2|} \\ &\quad + \frac{\hbar^2}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2}\Big\}\psi(\rho_1, \rho_2) = E\psi(\rho_1, \rho_2). \end{aligned}$$

Using the following units, called 'Atomic Units', the equations will be simplified even more

$$\begin{aligned} \hbar &= 1 \\ e &= 1 \\ m &= 1, \end{aligned} \tag{3.15}$$

then the Schroedinger equation will be

$$\left\{ -\frac{1}{2\mu}\sum_{i=1}^{2}\nabla^2_{\rho_i} - \sum_{i=1}^{2}\frac{Z}{|\rho_i|} + \frac{1}{|\rho_1 - \rho_2|} + \frac{1}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2} \right\}\psi(\rho_1, \rho_2) = E\psi(\rho_1, \rho_2). \tag{3.16}$$

To put the Schroedinger equation in its simplest form, we scale all the lengths by Z

$$\begin{aligned} \rho_i &\rightarrow \frac{\rho_i}{Z}, \\ \nabla_{\rho_i} &\rightarrow Z\nabla_{\rho_i}, \\ \nabla^2_{\rho_i} &\rightarrow Z^2\nabla^2_{\rho_i}. \end{aligned}$$

Therefore

$$Z^2\left\{-\frac{1}{2\mu}\sum_{i=1}^{2}\nabla^2_{\rho_i}-\sum_{i=1}^{2}\frac{1}{|\rho_i|}+\frac{1}{Z}\frac{1}{|\rho_1-\rho_2|}+\frac{1}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2}\right\}\psi(\rho_1,\rho_2)=E\psi(\rho_1,\rho_2), \quad (3.17)$$

we then divide the entire equation by Z^2

$$\left\{-\frac{1}{2\mu}\sum_{i=1}^{2}\nabla^2_{\rho_i}-\sum_{i=1}^{2}\frac{1}{|\rho_i|}+\frac{1}{Z}\frac{1}{|\rho_1-\rho_2|}+\frac{1}{M}\nabla_{\rho_1}\cdot\nabla_{\rho_2}\right\}\psi(\rho_1,\rho_2)=E\psi(\rho_1,\rho_2), \quad (3.18)$$

where in the last equation, $\frac{E}{Z^2}$ is replaced by E.

This Hamiltonian is not seperable any further because of the terms $\nabla_{\rho_1}\cdot\nabla_{\rho_2}$ and $\frac{1}{|\rho_1-\rho_2|}$, and the only way to investigate it, is to approximate the eigenfunctions and the eigenvalues.

3.2 THE VARIATIONAL METHOD

The variational method is a powerful method to approximate the eigenvalues and eigenfunctions of the Schroedinger equation. It works specifically on the Schroedinger equation because the spectrum of Schroedinger equation is bounded from below. As we will prove in the appendix, this method provides an upper bound for the exact eigenvalues. This method has been used in this thesis to calculate the energy of a two-electron atomic system for various values of Z.

Let's assume that the desired wave function is ϕ, then

$$H|\phi\rangle = E|\phi\rangle \quad (3.19)$$

and multiply it by $\langle\phi|$ from the right

$$\langle\phi|H|\phi\rangle = \langle\phi|E|\phi\rangle = E\langle\phi|\phi\rangle, \quad (3.20)$$

therefore

$$E=\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}. \quad (3.21)$$

This is an exact equality. However, one can prove that (see appendix)

$$E_{tr} \geq E, \tag{3.22}$$

where E_{tr} is the energy corresponding to a trial (guessed) wave function.

Our wave function ϕ that satisfies equation 3.19, can be expanded in terms of a complete and orthogonal set of eigenfunctions ψ_i in the form of

$$|\phi\rangle = \sum_{i=0}^{\infty} a_i |\psi_i\rangle. \tag{3.23}$$

Substituting it into equation (3.21) yields

$$E = \frac{\sum_{ij=0}^{\infty} a_j^* a_i \langle\psi_j|H|\psi_i\rangle}{\sum_{ij=0}^{\infty} a_j^* a_i \langle\psi_j|\psi_i\rangle} = \frac{\sum_{i=0}^{\infty} |a_i|^2 E_i}{\sum_{i=0}^{\infty} |a_i|^2}. \tag{3.24}$$

If E_{tr} is calculated for a trial wave function ϕ_{tr} that is a finite linear combination of arbitrary functions χ_i (not necessarily orthogonal)

$$|\phi\rangle = \sum_{i=1}^{N} a_i |\chi_i\rangle, \tag{3.25}$$

then

$$E_{tr} = \frac{\sum_{ij=1}^{N} a_j^* a_i H_{ij}}{\sum_{ij=1}^{N} a_j^* a_i A_{ij}}, \tag{3.26}$$

where

$$\begin{aligned} H_{ij} &= \langle\chi_i|H|\chi_j\rangle \\ A_{ij} &= \langle\chi_i|\chi_j\rangle. \end{aligned}$$

Minimizing E_{tr} in terms of a_k

$$\frac{\partial E_{tr}}{\partial a_k} = 0. \tag{3.27}$$

differentiating explicitly and equating the derivatives to zero yields

$$\begin{aligned}\frac{\partial E_{tr}}{\partial a_k} &= \frac{\Big(\sum_{j=1}^{N} a_j^* H_{kj}\Big)\Big(\sum_{ij=1}^{N} a_j^* a_i A_{ij}\Big) - \Big(\sum_{ij=1}^{N} a_j^* a_i H_{ij}\Big)\Big(\sum_{j=1}^{N} a_j^* A_{kj}\Big)}{\Big(\sum_{ij=1}^{N} a_j^* a_i A_{ij}\Big)^2} \\ &= \frac{\Big(\sum_{j=1}^{N} a_j^* H_{kj}\Big) - E_{tr}\Big(\sum_{j=1}^{N} a_j^* A_{kj}\Big)}{\Big(\sum_{ij=1}^{N} a_j^* a_i A_{ij}\Big)} = 0, \qquad (3.28)\end{aligned}$$

which means

$$\sum_{j=1}^{N} a_j^* H_{kj} = E_{tr} \sum_{j=1}^{N} a_j^* A_{kj}. \qquad (3.29)$$

Taking the complex conjugate of this equation and assuming that H_{ij} is real

$$\sum_{j=1}^{N} a_j H_{kj} = E_{tr} \sum_{j=1}^{N} a_j A_{kj}, \qquad (3.30)$$

which is equivalent to the following matrix equation

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} = E_{tr} \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1N} \\ A_{21} & A_{22} & \cdots & A_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ A_{N1} & A_{N2} & \cdots & A_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}. \qquad (3.31)$$

Therefore

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} - E_{tr} \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1N} \\ A_{21} & A_{22} & \cdots & A_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ A_{N1} & A_{N2} & \cdots & A_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} = 0. \qquad (3.32)$$

This means we need to diagonalize $\boldsymbol{H} - E_{tr}\boldsymbol{A}$ to get N eigenvalues and N eigenvectors.

This is a powerful method since the accuracy can be increased by improving our guessed (trial) wave functions and attempting to include a complete set of function in the trial wave function. Unfortunately, improving the trial wave function results in rapid increase in computing time since it increases in proportion to N^3.

There are two main theorems that ensure that our trial eigenvalues will converge monotonically to the real eigenvalues as we increase the size of our basis: Hylleraas-Undheim-Macdonald theorem and the matrix interleaving theorem. These are discussed in the appendix.

3.3 THE TRIAL WAVEFUNCTION

The Hylleraas variational wave function for S states has the form

$$\psi_{tr}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i+j+k \leq \Omega} a_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2) \pm \text{exchange}, \tag{3.33}$$

where $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$, the a_{ijk} are linear variational coefficients and α and β are nonliear parameters that will be found by variational principle that was mentioned (eq 3.27). The exchage term is the same as the first term but with r_1 and r_2 interchanged. This term exploits the exchange symmetry of the system, and therefore brings about a better accuracy with the same number of terms (for a given Ω).

The total wave function is the direct product of spatial wave function $\psi_{tr}(\mathbf{r}_1, \mathbf{r}_2)$ and spin wave function of the two electrons $|\chi_1, \chi_2\rangle$.

This wave function does not explicitly depend on angular coordinates since our system is in the ground state and the ground state is spherically symmetric. The wave functions of higher angular momentum are dependant on angular coordinates.

The wave function introduced here is referred to as a 'single basis' wave function, which works very well and could have been used to calculate the variational energy. However, adding more nonlinear parameters could improve our wave function further.

This new wave function, called double basis wave function, can be written as

$$\begin{aligned}\psi_{tr}(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{i+j+k \leq \Omega} a_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha_1 r_1 - \beta_1 r_2) \\ &+ \sum_{i+j+k \leq \Omega} b_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha_2 r_1 - \beta_2 r_2) \pm \text{exchange},\end{aligned} \tag{3.34}$$

this double-basis wave function has some advantages over the single-basis wave function. Most importantly, the series converges faster due to the existence of second set of nonlinear parameters, provided that the energy is minimized with respect to all four nonlinear parameters $\alpha_1, \beta_1, \alpha_2, \beta_2$, and it can be truncated at smaller Ω. This means that numerical cancellation is less severe because the highest power of r will be smaller due to the smaller Ω.

One could still take another step forward and add another set of nonlinear parameters. The 'triple-basis' wave function then will have the form

$$\begin{aligned}\psi_{tr}(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{i+j+k\leq\Omega} a_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha_1 r_1 - \beta_1 r_2) \\ &+ \sum_{i+j+k\leq\Omega} b_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha_2 r_1 - \beta_2 r_2) \\ &+ \sum_{i+j+k\leq\Omega} c_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha_3 r_1 - \beta_3 r_2) \pm \text{exchange}. \end{aligned} \tag{3.35}$$

This could reduce the number of terms required for a certain precision even further for large Ω. Nevertheless, we stick to double-basis in this case because it brings about the desired accuracy for calculating the critical charge.

The truncation condition still needs to be defined. Ω is defined to be the maximum number of $i + j + k$, and all the other terms will be neglected. The relation between Ω and the number of terms in the wave function for $\Omega \in [8, 20]$ is listed in the table below

Table 3.1: The number of terms in the wave function in terms of Ω

Ω	Number of terms in the wave function
8	189
9	248
10	317
11	398
12	490
13	596
14	714
15	848
16	995
17	1160
18	1339
19	1538
20	1752

3.4 THE GENERALIZED EIGENVALUE PROBLEM

Having a suitable wave function in hand, we turn our attention to solving the eigenvalue problem, equation (3.29), which can be written in a simple form

$$\boldsymbol{H} a_j = E_j \boldsymbol{A} a_j, \tag{3.36}$$

as mentioned before, $\boldsymbol{H}$ is the Hamiltonian matrix, and $\boldsymbol{A}$ is the overlap matrix, each built from matrix elements of different terms in the trial wave function according to

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \tag{3.37}$$

$$A_{ij} = \langle \phi_i | \phi_j \rangle, \tag{3.38}$$

where j stands for a triplet of integers ijk.

There is a variety of methods to find the eigenvalues E_j and eigenvectors a_j. We will use the inverse power method to diagonalize the Hamiltonian. Here I explain the power method and the inverse power method to diagonalize a matrix

3.4.1 THE POWER METHOD

If $\boldsymbol{H}$ is a n-dimensinal square matrix with the eigenvalues λ_j $(j = 1, ...n)$ and eigenvectors $\psi_j (j = 1, ..., n)$, under the condition that $|\lambda_1| > |\lambda_2| > |\lambda_3| > ... > |\lambda_n|$, then we can choose an arbitrary vector and expand it in term of the finite number of exact(unknown) eigenvectors of $\boldsymbol{H}$

$$\phi_0 = \sum_{i=1}^{N} a_i \psi_i. \tag{3.39}$$

Now we apply the Hamiltonian on ϕ n times

$$\begin{aligned}
\phi_1 &= H\phi_0 = \sum_{i=1}^{N} a_i \lambda_i \psi_i, \\
\phi_2 &= H\phi_1 = \sum_{i=1}^{N} a_i \lambda_i^2 \psi_i, \\
&\vdots \\
\phi_n &= H\phi_{n-1} = \sum_{i=1}^{N} a_i \lambda_i^n \psi_i.
\end{aligned}$$

It should already be clear that if n is sufficiently large, the first term in the summation dominates. To show it more clearly, we divide the last equation by λ_1^n

$$\frac{\phi_n}{\lambda_1^n} = \sum_{i=1}^{N} a_i \frac{\lambda_i^n}{\lambda_1^n} \psi_i = a_1 \psi_1 + \sum_{i=2}^{N} a_i \left(\frac{\lambda_i}{\lambda_1} \right)^n \psi_i, \tag{3.40}$$

It can be seen, the sum term will vanish as n becomes large enough, because $\left(\frac{\lambda_i}{\lambda_1}\right)^n \to 0$. Hence

$$\begin{aligned}
\phi_n &= a_1\lambda_1^n\psi_1 + O\left(\frac{\lambda_i}{\lambda_1}\right)^n \qquad a_1 \neq 0 \\
H\phi_n &= a_1\lambda_1^{n+1}\psi_1 + O\left(\frac{\lambda_i}{\lambda_1}\right)^n = \lambda_1\phi_n + O\left(\frac{\lambda_i}{\lambda_1}\right)^n, \qquad (3.41)
\end{aligned}$$

The power method provides us with the largest eigenvalue and corresponding eigenvector, as long as the initial (guessed) vector does not have zero projection on the eigenvector corresponding to the largest eigenvalue. The most important downside of power method is that we can not find any other eigenvalue for our Hamiltonian. However, we can manipulate this method to make it able to converge to any eigenvalue, by a method called 'inverse power method', as described in the following section.

3.4.2 THE INVERSE POWER METHOD

Now we know how to find the largest eigenvalue of a matrix. By changing the last procedure slightly, we can obtain a power method that will converge on any eigenvalue that is closest to an initial guess E_g.

$$\begin{aligned}
\boldsymbol{H}a_j &= E_j\boldsymbol{A}a_j & (3.42)\\
(\boldsymbol{H} - E_g\boldsymbol{A})\,a_j &= (E_j - E_g)\,\boldsymbol{A}a_j & (3.43)\\
(\boldsymbol{H} - E_g\boldsymbol{A})^{-1}\,\boldsymbol{A}a_j &= \frac{1}{E_j - E_g}a_j & (3.44)\\
\boldsymbol{H'}a_j &= E'_j a_j, & (3.45)
\end{aligned}$$

where $\boldsymbol{H'}$ is $(\boldsymbol{H} - E_g\boldsymbol{A})^{-1}\,\boldsymbol{A}$ and E'_j is $\frac{1}{E_j - E_g}$. By choosing E_g close enough to E_j, we can make E'_j as large as we would like, thus making the power method converge to the desired eigenvalue and eigenvector.

So far, we know how to write the Hamiltonian, how to write our trial wave function, and how to find our eigenvalues. Knowing this, we can find the energy of the two-electron system for different Z, and then find the Z for which the binding energy of the outer electron is zero. Two important steps are still required; they are least square fitting and error analysis. They are explained in the two following sections.

3.5 LEAST SQUARE FITTING

In order to calculate the critical charge, we calculated the energy of the outer electron for different values of nuclear charge. Then we extrapolated the nuclear charge to find the value for which the energy of the second electron is zero, which corresponds to critical charge of the system. Extrapolating the energy requires a knowledge of the energy of the outer electron as a function of nuclear charge. We fit the data to different polynomial functions, and chose the one that reduced our error (error analysis is discussed in the following section).

The least square fitting is based on choosing a certain polynomial with unknown coefficients, and then trying to find the unknown coefficients such that the sum of the squares of the distances between the fit and the data points is minimum. Here we choose a polynomial of order m

$$y = \sum_{i=0}^{m} A_i x^i, \tag{3.46}$$

The A_n are the unknown coefficients. Then the sum of squares of distances is a function called Δ^2.

$$\Delta^2 = \sum_{j=1}^{n} (y(x_j) - y_j)^2 \tag{3.47}$$

where n is the number of data points that we have.

The next step is fixing the values of the coefficients A_i in such a way that Δ^2 becomes minimum. This can be easily done by setting the derivatives of Δ^2 equal to zero

$$\frac{\partial \Delta^2}{\partial A_k} = 0, \qquad k = 0, 1, ..., m \tag{3.48}$$

in a more explicit form

$$\begin{cases} \dfrac{\partial \Delta^2}{\partial A_0} = 0 \\ \dfrac{\partial \Delta^2}{\partial A_1} = 0 \\ \dfrac{\partial \Delta^2}{\partial A_2} = 0 \\ \vdots \\ \dfrac{\partial \Delta^2}{\partial A_m} = 0, \end{cases} \tag{3.49}$$

calculating the derivatives explicitly gives

$$\begin{cases} 2\sum_{j=1}^{n}(y(x_j) - y_j) = 0 \\ 2\sum_{j=1}^{n}(y(x_j) - y_j)x_j = 0 \\ 2\sum_{j=1}^{n}(y(x_j) - y_j)x_j^2 = 0 \\ \vdots \\ 2\sum_{j=1}^{n}(y(x_j) - y_j)x_j^m = 0, \end{cases} \tag{3.50}$$

this is equivalent to

$$\begin{cases} A_0 n + A_1 \sum_{j=1}^{n} x_j + A_2 \sum_{j=1}^{n} x_j^2 + \cdots + A_m \sum_{j=1}^{n} x_j^m = \sum_{j=1}^{n} y_j \\ A_0 \sum_{j=1}^{n} x_j + A_1 \sum_{j=1}^{n} x_j^2 + A_2 \sum_{j=1}^{n} x_j^3 + \cdots + A_m \sum_{j=1}^{n} x_j^{m+1} = \sum_{j=1}^{n} x_j y_j \\ A_0 \sum_{j=1}^{n} x_j^2 + A_1 \sum_{j=1}^{n} x_j^3 + A_2 \sum_{j=1}^{n} x_j^4 + \cdots + A_m \sum_{j=1}^{n} x_j^{m+2} = \sum_{j=1}^{n} x_j^2 y_j \\ \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ A_0 \sum_{j=1}^{n} x_j^m + A_1 \sum_{j=1}^{n} x_j^{m+1} + A_2 \sum_{j=1}^{n} x_j^{m+2} + \cdots + A_m \sum_{j=1}^{n} x_j^{2m} = \sum_{j=1}^{n} x_j^m y_j, \end{cases} \tag{3.51}$$

or in matrix form

$$\begin{pmatrix} n & \sum_{j=1}^n x_j & \sum_{j=1}^n x_j^2 & \cdots & \sum_{j=1}^n x_j^m \\ \sum_{j=1}^n x_j & \sum_{j=1}^n x_j^2 & \sum_{j=1}^n x_j^3 & \cdots & \sum_{j=1}^n x_j^{m+1} \\ \sum_{j=1}^n x_j^2 & \sum_{j=1}^n x_j^3 & \sum_{j=1}^n x_j^4 & \cdots & \sum_{j=1}^n x_j^{m+2} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \sum_{j=1}^n x_j^m & \sum_{j=1}^n x_j^{m+1} & \sum_{j=1}^n x_j^{m+2} & \cdots & \sum_{j=1}^n x_j^{2m} \end{pmatrix} \begin{pmatrix} A_0 \\ A_1 \\ A_2 \\ \vdots \\ A_m \end{pmatrix} = \begin{pmatrix} \sum_{j=1}^n y_j \\ \sum_{j=1}^n x_j y_j \\ \sum_{j=1}^n x_j^2 y_j \\ \vdots \\ \sum_{j=1}^n x_j^m y_j \end{pmatrix}, \tag{3.52}$$

putting it in a compact form, we will get

$$\boldsymbol{X} A = Y, \tag{3.53}$$

X is invertible, and the solution is

$$A = \boldsymbol{X}^{-1} Y, \tag{3.54}$$

This is the general linear regression for finding the best fit to our data. The only unknown parameter is m (the power of the polynomial), which will be settled by error analysis.

Comparing our fit to the Puiseux expansion (defined in section 1.4), we will immediately find that the right choice for x and y is $(Z - Z_{critical})^{1/2}$ and $(E + 1/2Z^2)$, respectively.

3.6 CRITICAL CHARGE

The critical charge is related to the smallest root of the Puiseux expansion whose coefficients were found in the previous section. As we know from equation 1.5, the Puiseux expansion is

$$E + \frac{1}{2} Z_{cr}^2 = \sum_{n=1}^{N_{max}} P_n (Z - Z_{cr})^{\frac{n}{2}}. \tag{3.55}$$

We have already found the coefficients of this series (P_n). Using the substitution $y = E + \frac{1}{2} Z_{cr}^2$ and $x = (Z - Z_{cr})^{\frac{1}{2}}$

$$y = \sum_{n=1}^{N_{max}} P_n x^n, \tag{3.56}$$

Which is a polynomial of order n.

There are two simple methods to find the root of this polynomial that we will discuss in the next two sections.

3.6.1 NEWTON'S METHOD

Newton's method is an iterative method for finding the roots of functions (that are continuous and differentiable on a open interval containing the root). The function can be approximated by its tangent line, and the root of the tangent line can be easily obtained. Then the function is again approximated by its tangent line at the root of the previous tangent line, and this process is done many times until the desired accuracy is reached.

The equation of the tangent line of a function f at the point x_0 is given by

$$y = f'(x_0)(x - x_0) + f(x_0), \tag{3.57}$$

setting $y = 0$

$$x = x_0 - \frac{f(x_0)}{f'(x_0)}, \tag{3.58}$$

here x_0 is the initial guess and x is the zero of the tangent line of f. We can do the same process, starting at x, and find another approximation for the root of f. Changing the notation, We will have

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}, \tag{3.59}$$

as n is increased, the difference between x_n and x_{n+1} will approach zero. This process is stopped when the desired accuracy is obtained.

3.6.2 THE BISECTION METHOD

Another way of solving the equation $f(x) = 0$ for a continuous function is choosing two arbitrary points such that $f(x_1)$ and $f(x_2)$ have different sign. It is guaranteed (by the continuity of f) that the root of the function f lies between x_1 and x_2. Then x_3 is chosen

$$x_3 = \frac{x_1 + x_2}{2}. \tag{3.60}$$

if the sign of $f(x_3)$ is the same as $f(x_1)$, then x_1 is replaced by x_3, otherwise x_2 is replaced by x_3. Let's say that x_3 and x_1 have the same sign, so x_1 is replaced by x_3, and the root of the function f lies between x_2 and x_3. Then

$$x_4 = \frac{x_3 + x_2}{2}. \tag{3.61}$$

Now if the sign of x_4 and x_3 are the same, then x_3 is replaced by x_4, otherwise x_2 is replaces by x_4. This procedure keeps narrowing down the range which contains the root of the function. In this case we performed 30 iterations to narrow down the range to machine accuracy.

The advantage of bisection method is that it can be used to find the roots of functions that are not differentiable, but continuous.

3.7 THE ERROR ANALYSIS

Here we use a simple, yet powerful, method for finding the error in any sort of linear regression, which is called ‘bootstrap’.

3.7.1 THE BOOTSTRAP

The bootstrap method [22] is based on calculating the difference between the real value of the data and the fit (which are called ‘residuals’), adding them to our data points with random mixing, doing the regression again, calculating the desired value from the fit, and repeating the this process many times.

Let's say our data points are a set of (x_i, y_i) for $i = 1, \cdots, n$ and $y = f(x)$ represents the regression which is built by least square fitting. The residuals are

$$\delta y_i = y_i - f(x_i), \tag{3.62}$$

now we randomly choose an integer, j, and

$$y_i := y_i + \delta y_j, \tag{3.63}$$

for all data points. We can do the fitting again and calculate the critical charge, and repeat the same process. Eventually we will have a set of critical charges, each coming from one round of bootstrap, on which we can define the average values, variance and standard deviation. The standard deviation of this set around the average value is the precision of the calculation. The codes for the bootstrap is given in the appendix.

It has been shown [22] that 200 or 300 repetitions is sufficient to calculate a reliable data to calculate the standard deviation (error). Doing the bootstrap procedure more than that will produce a set whose standard deviation is almost the same as the bootstrap set with around 200 samples.

Chapter 4

RESULTS

In this chapter, the critical charge for different values of reduced mass is presented, based on the methods discussed in the third chapter. The infinite nuclear mass case is explained separately, due to the significance of helium, and then the finite mass cased is investigated in the subsequent section.

4.1 THE INFINITE NUCLEAR MASS MASS CASE

For the infinite mass case ($\frac{\mu}{M} = 0$), the energy of helium has been calculated for nuclear charge in the Z interval [0.9115,0.9250] with the increment of 0.0005, using the program called 'DPOLDLZ' that is written by Drake. The trial wave function that was used is the double basis wave function (3.34). The Tables 4.1 and 4.2 show the energies as a function of Z for $\Omega = 10$ and $\Omega = 20$, respectively. All the energies in all tables are scaled by Z^2, so that the critical charge corresponds to $E = -0.5$ exactly. The errors in the tables are computational error from the inverse power method, not convergence error.

Table 4.1: Energy as a function of Z, for $\Omega = 10$ (infinite mass case)

Nuclear charge	Energy	Error
0.9115	-0.500139549435461	2.92×10^{-21}
0.9120	-0.500287823136685	1.21×10^{-21}
0.9125	-0.500436461591967	4.23×10^{-21}
0.9130	-0.500585445609739	4.78×10^{-22}
0.9135	-0.500734757971090	2.64×10^{-21}
0.9140	-0.500884383076883	8.40×10^{-19}
0.9145	-0.501034306684361	1.18×10^{-20}
0.9150	-0.501184515703259	1.24×10^{-19}
0.9155	-0.501334998041360	2.65×10^{-21}
0.9160	-0.501485742465492	4.23×10^{-19}
0.9165	-0.501636738507309	1.82×10^{-21}
0.9170	-0.501787976370523	2.82×10^{-21}
0.9175	-0.501939446859550	3.98×10^{-22}
0.9180	-0.502091141317567	2.46×10^{-19}
0.9185	-0.502243051573658	2.65×10^{-21}
0.9190	-0.502395169897371	1.17×10^{-21}
0.9195	-0.502547488959232	4.33×10^{-21}
0.9200	-0.502700001796167	5.71×10^{-20}
0.9205	-0.502852701781304	1.91×10^{-21}
0.9210	-0.503005582597039	7.84×10^{-20}
0.9215	-0.503158638211385	9.79×10^{-21}
0.9220	-0.503311862856699	5.21×10^{-20}
0.9225	-0.503465251010695	7.58×10^{-21}
0.9230	-0.503618797379388	3.08×10^{-22}
0.9235	-0.503772496881681	3.45×10^{-21}
0.9240	-0.503926344635429	1.12×10^{-21}
0.9245	-0.504080335944774	5.72×10^{-21}
0.9250	-0.504234466288623	1.18×10^{-20}

Table 4.2: Energy as a function of Z, for $\Omega = 20$ (infinite mass case)

Nuclear charge	Energy	Error
0.9115	-0.500139549945404	2.10×10^{-19}
0.9120	-0.500287823584977	4.42×10^{-19}
0.9125	-0.500436461994085	3.45×10^{-19}
0.9130	-0.500585445975776	2.22×10^{-18}
0.9135	-0.500734758308171	1.65×10^{-18}
0.9140	-0.500884383390220	4.88×10^{-19}
0.9145	-0.501034306977815	1.15×10^{-18}
0.9150	-0.501184515980867	4.95×10^{-19}
0.9155	-0.501334998303364	6.81×10^{-19}
0.9160	-0.501485742714850	9.25×10^{-19}
0.9165	-0.501636738745395	9.97×10^{-19}
0.9170	-0.501787976598599	1.17×10^{-19}
0.9175	-0.501939447078642	1.59×10^{-19}
0.9180	-0.502091141528508	4.03×10^{-19}
0.9185	-0.502243051777159	1.52×10^{-19}
0.9190	-0.502395170094042	6.12×10^{-19}
0.9195	-0.502547489149554	8.16×10^{-18}
0.9200	-0.502700001980633	2.18×10^{-19}
0.9205	-0.502852701960252	4.52×10^{-19}
0.9210	-0.503005582770816	7.01×10^{-19}
0.9215	-0.503158638380277	1.39×10^{-18}
0.9220	-0.503311863020954	9.28×10^{-19}
0.9225	-0.503465251170534	2.28×10^{-16}
0.9230	-0.503618797535001	6.96×10^{-18}
0.9235	-0.503772497033234	3.69×10^{-18}
0.9240	-0.503926344783061	5.11×10^{-18}
0.9245	-0.504080336088605	3.11×10^{-18}
0.9250	-0.504234466428755	3.72×10^{-19}

These values for the energy of the outer electron (the ionization energy) were used for linear fitting, in the range $\Omega \in [10, 20]$. The results are shown in the table 4.3. The critical charges in the table 4.3 are calculated by the bisection method. As equation 3.57 suggests, the constant term in the Puiseax expansion for fitting y versus x is zero. We chose two different Z_c for which the corresponding constant terms had opposite signs, and then used the bisection method to find the Z_c that made the constant term as small as possible. The bootstrap method was used to find the error for each Ω afterwards.

Table 4.3: Critical charge values for different Ω

Ω	Critical Charge	Error
10	0.911028195245228596366	5×10^{-22}
11	0.911028193450693205189	4×10^{-22}
12	0.911028194757463381332	5×10^{-22}
13	0.911028192532756319668	6×10^{-22}
14	0.911028192606744256861	6×10^{-22}
15	0.911028192523750668681	5×10^{-22}
16	0.911028192539144253753	4×10^{-22}
17	0.911028192494349041185	7×10^{-22}
18	0.911028192375722594482	4×10^{-22}
19	0.911028192497349491141	7×10^{-22}
20	0.911028192481446474436	5×10^{-22}

Extrapolating critical charge for $\Omega = \infty$ yields

$$\text{critical charge} = 0.9110282679 \pm 4 \times 10^{-10}. \tag{4.1}$$

This is the critical charge for the infinite mass case. The final error is calculated by using the bootstrap method (residuals) instead of using the error bars on each Ω because the error bars are relatively small (notice that the error bars are so small, so using residuals is more realistic than error bars).

The table and the graph on the next page shows β_1 versus Z. We see that the value of β_1 does not tend to zero as $Z \to Z_c$. This means that the second electron will not be absolutely free at the critical charge, because its wave function is localized and tends to zero at infinity, as opposed to the wave function of a free electron. So we can conclude that for $Z \leq Z_c$, the second electron is in a resonance state, which might be because of the long-range attraction between this electron and the ion which is now polarized due to the electrostatic potential of the second electron. Understanding the state of this electron at $Z = Z_{critical}$ is interesting and will be investigated in future works.

Table 4.4: β_1 as a function of Z, for $\Omega = 20$ and $\frac{\mu}{M} = 0$

Nuclear charge	β_1
0.9110	0.14655
0.9115	0.16577
0.9120	0.17908
0.9125	0.18884
0.9130	0.19550
0.9135	0.21179
0.9140	0.21802
0.9145	0.22583
0.9150	0.22943
0.9155	0.23804
0.9160	0.24219
0.9165	0.24872
0.9170	0.25482
0.9175	0.26300
0.9180	0.26697

4.2 THE FINITE MASS CASE

In this section, we investigate the critical charge of a quantum mechanical three-body system for nonzero reduced mass. Z_c was found in the range [0,0.5] with 0.05 increment. Finally the results was fit to a nonlinear polynomial, and the maximum value of Z_c is found.

The process of finding the critical charge for $\frac{\mu}{M} = 0.20$ is explained in detail. The critical charge for other values of $\frac{\mu}{M}$ was found in the exact same way. Only energies for 20 different nuclear charges were used in the case of finite nuclear mass, because in the case of infinite mass case, we noticed that having more than 20 data point does not increase the accuracy of the fitting (unless the maximum power of the Puiseux fit, N_{max}, is close to or more than 20). The maximum power of the Puiseux expansion (N_{max}) for this case is set to six since it gives us the best accuracy and a stable answer compared to other values (see equation 1.7).

The Tables 4.5 to 4.8 show the energies as a function of Z for the finite mass case $\frac{\mu}{M} = 0.20$ and $\Omega = 8, 12, 16, 20$, respectively. All the energies in all tables are scaled by Z^2, so that the critical charge corresponds to $E = -0.5$.

Table 4.5: Energy as a function of Z, for $\Omega = 8$ and $\frac{\mu}{M} = 0.2$

Nuclear charge	Energy	Error
0.922	–0.500054676686963	1.90×10^{-21}
0.923	–0.500333089847785	7.76×10^{-23}
0.924	–0.500613231121681	4.91×10^{-21}
0.925	–0.500894925182759	7.63×10^{-24}
0.926	–0.501178030541077	1.67×10^{-21}
0.927	–0.501462429161003	6.90×10^{-24}
0.928	–0.501748020273198	8.87×10^{-22}
0.929	–0.502034716331382	3.62×10^{-23}
0.930	–0.502322440257180	4.57×10^{-23}
0.931	–0.502611123430672	4.75×10^{-21}
0.932	–0.502900704216900	5.41×10^{-23}
0.933	–0.503191126828770	7.54×10^{-22}
0.934	–0.503482340449626	7.60×10^{-24}
0.935	–0.503774298521624	7.57×10^{-23}
0.936	–0.504066958183491	6.56×10^{-23}
0.937	–0.504360279811276	1.87×10^{-22}
0.938	–0.504654226619019	1.59×10^{-22}
0.939	–0.504948764350659	5.04×10^{-21}
0.940	–0.505243860991616	1.42×10^{-22}
0.941	–0.505539486575898	2.77×10^{-23}

For the $\Omega = 12$

Table 4.6: Energy as a function of Z, for $\Omega = 12$ and $\frac{\mu}{M} = 0.2$

Nuclear charge	Energy	Error
0.922	–0.500054682967957	1.47×10^{-17}
0.923	–0.500333095105228	4.33×10^{-18}
0.924	–0.500613235736934	2.94×10^{-18}
0.925	–0.500894929349761	3.05×10^{-19}
0.926	–0.501178034373335	7.36×10^{-19}
0.927	–0.501462432733876	4.90×10^{-19}
0.928	–0.501748023634776	2.72×10^{-18}
0.929	–0.502034719520620	1.80×10^{-19}
0.930	–0.502322443299543	1.26×10^{-18}
0.931	–0.502611126347159	4.28×10^{-18}
0.932	–0.502900707022658	5.77×10^{-19}
0.933	–0.503191129536543	1.49×10^{-19}
0.934	–0.503482343066445	1.00×10^{-19}
0.935	–0.503774301054500	9.16×10^{-20}
0.936	–0.504066960639350	4.29×10^{-20}
0.937	–0.504360282191610	4.10×10^{-21}
0.938	–0.504654228928545	3.19×10^{-20}
0.939	–0.504948766591530	1.75×10^{-20}
0.940	–0.505243863173418	7.73×10^{-21}
0.941	–0.505539488686168	1.89×10^{-22}

For the $\Omega = 16$

Table 4.7: Energy as a function of Z, for $\Omega = 16$ and $\frac{\mu}{M} = 0.2$

Nuclear charge	Energy	Error
0.922	–0.500054683074367	1.28×10^{-17}
0.923	–0.500333095182418	1.10×10^{-17}
0.924	–0.500613235797793	3.98×10^{-17}
0.925	–0.500894929400014	2.68×10^{-17}
0.926	–0.501178034416190	6.49×10^{-17}
0.927	–0.501462432771282	5.52×10^{-17}
0.928	–0.501748023667993	1.67×10^{-16}
0.929	–0.502034719550468	5.09×10^{-17}
0.930	–0.502322443326638	6.80×10^{-17}
0.931	–0.502611126371852	3.28×10^{-17}
0.932	–0.502900707045290	3.20×10^{-18}
0.933	–0.503191129557349	3.42×10^{-17}
0.934	–0.503482343085643	2.47×10^{-17}
0.935	–0.503774301072185	1.07×10^{-18}
0.936	–0.504066960655693	3.12×10^{-18}
0.937	–0.504360282206741	8.02×10^{-18}
0.938	–0.504654228942573	4.39×10^{-18}
0.939	–0.504948766604559	2.99×10^{-19}
0.940	–0.505243863185544	1.02×10^{-18}
0.941	–0.505539488697473	9.28×10^{-19}

For the $\Omega = 20$

Table 4.8: Energy as a function of Z, for $\Omega = 20$ and $\frac{\mu}{M} = 0.2$

Nuclear charge	Energy	Error
0.922	–0.500054683077891	1.85×10^{-17}
0.923	–0.500333095184595	1.50×10^{-17}
0.924	–0.500613235799370	2.22×10^{-17}
0.925	–0.500894929401268	9.85×10^{-18}
0.926	–0.501178034417207	6.09×10^{-18}
0.927	–0.501462432772122	1.37×10^{-17}
0.928	–0.501748023668683	1.96×10^{-17}
0.929	–0.502034719551054	1.72×10^{-17}
0.930	–0.502322443327136	8.85×10^{-18}
0.931	–0.502611126372278	4.20×10^{-17}
0.932	–0.502900707045659	3.37×10^{-17}
0.933	–0.503191129557669	2.22×10^{-17}
0.934	–0.503482343085922	7.66×10^{-18}
0.935	–0.503774301072433	5.45×10^{-18}
0.936	–0.504066960655912	2.42×10^{-18}
0.937	–0.504360282206936	5.83×10^{-18}
0.938	–0.504654228942748	4.07×10^{-18}
0.939	–0.504948766604715	4.36×10^{-18}
0.940	–0.505243863185686	4.03×10^{-18}
0.941	–0.505539488697601	2.94×10^{-18}

The critical charge corresponding each Ω is

Table 4.9: The critical Charge corresponding to each Ω

Ω	the critical charge
8	$0.9218044442404086848644083044 \pm 7 \times 10^{-28}$
9	$0.9218044301126528180524047758 \pm 5 \times 10^{-28}$
10	$0.921804419991431563316142945 \pm 7 \times 10^{-28}$
11	$0.921804420117847513268876567 \pm 5 \times 10^{-28}$
12	$0.921804419378172531484077942 \pm 6 \times 10^{-28}$
13	$0.921804419126854790568569224 \pm 6 \times 10^{-28}$
14	$0.921804418979931331395977979 \pm 7 \times 10^{-28}$
15	$0.921804418957264966158018009 \pm 5 \times 10^{-28}$
16	$0.921804418949345289744637204 \pm 9 \times 10^{-28}$
17	$0.921804418981228838620014405 \pm 9 \times 10^{-28}$
18	$0.921804418931807204602580348 \pm 7 \times 10^{-28}$
19	$0.921804418927810516991060236 \pm 6 \times 10^{-28}$
20	$0.921804418920502403965940553 \pm 4 \times 10^{-28}$

It is again obvious that the error bars are extremely small. Hence, for extrapolating to $\Omega = \infty$, residuals must be used. The critical charge for $\frac{\mu}{M} = 0.2$ and $\Omega = \infty$ is

$$\text{critical charge} = 0.921804403 \pm 5 \times 10^{-9} \tag{4.2}$$

In the following table, the critical charge values are shown for different $\frac{\mu}{M}$ ratio in the interval [0,0.55] with 0.05 increment

Table 4.10: The critical charge corresponding to each $\frac{\mu}{M}$

$\frac{\mu}{M}$	the critical charge	Error
0	0.9110282679	4×10^{-10}
0.05	0.91457055	8×10^{-8}
0.10	0.917522575	3×10^{-9}
0.15	0.919929005	4×10^{-9}
0.20	0.921804403	5×10^{-9}
0.25	0.923153656	5×10^{-9}
0.30	0.923978177	6×10^{-9}
0.35	0.924271380	4×10^{-9}
0.40	0.92402294	2×10^{-8}
0.45	0.9232117	2×10^{-7}
0.50	0.92180704	4×10^{-8}
0.55	0.9197618	2×10^{-7}

The critical charge for $\frac{\mu}{M} = 0.55$, which is not in the mentioned range (0 to 0.5), was also calculated. However, this value of reduced mass means that our system is not an atomic system anymore, it is gradually going into a molecular regime. So the atomic wave function must be replaced by a molecular wave function to obtain more reliable energies and critical charges.

We fit these values to a polynomial of power eight. The power of eight was chosen because it gives the closest value of B_0 to the critical charge for infinite mass, without blowing up the coefficients of the fit. Here is the fitting function

$$Z_c\Big(\frac{\mu}{M}\Big) = \sum_{i=0}^{8} B_i \Big(\frac{\mu}{M}\Big)^i. \tag{4.3}$$

The coefficients (B_i) are

$$
\begin{aligned}
B_0 &= 0.91102827 \\
B_1 &= 7.734 \times 10^{-2} \\
B_2 &= -0.139 \\
B_3 &= 0.224 \\
B_4 &= -0.966 \\
B_5 &= 2.725 \\
B_6 &= -4.73 \\
B_7 &= 4.509 \\
B_8 &= -1.934
\end{aligned}
$$

This function has a maximum at $\frac{\mu}{M} = 0.3525$, which means that Z_c for this reduced mass is the largest. In other words, this is the least stable system among all other Z_c, which as an intermiediate between an atomic system and a molecular one.

The graph on the page illustrates Z_c versus $\frac{\mu}{M}$

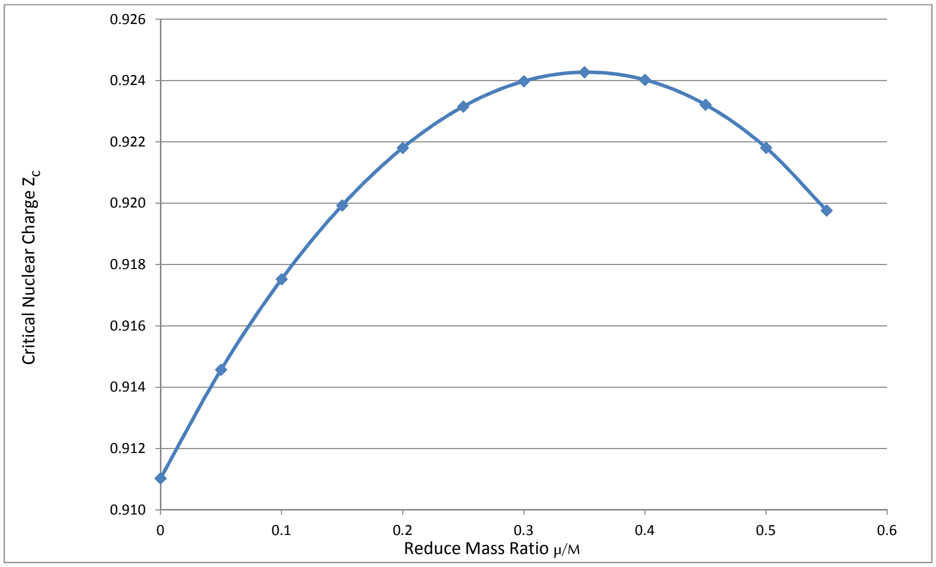

Figure 4.1: Plot of critical charge Z_c versus reduced mass ratio $\frac{\mu}{M}$ for $0.0 \leq \frac{\mu}{M} \leq 0.55$

Chapter 5

CONCLUSION

The critical charge for different values of reduced mass is shown in the table 4.10. The error for the range 0 to 0.5 is of the order of 10^{-7} to 10^{-10}. We have much better accuracy for the infinite mass case which clarifies the discrepancy in the literature, and also provides the value of Z_c for a broad range of $0.0 \leq \frac{\mu}{M} \leq 0.55$. This range includes two familiar atoms, helium ($\frac{\mu}{M} = 0.000136$) and positronium minus ($\frac{\mu}{M} = 0.5$).

The maximum value of the critical charge corresponds to $\mu = 0.3525$, which makes it the most unstable three-body atomic system in this range. That is the consequence of dynamical destabilization since all three particles are in motion, as opposed to $\mu = 0$. There must be interesting physics in the correlation states of a three-body quantum mechanical system that explain this fact and is a fascinating topic to work on in the future.

For $\frac{\mu}{M} \geq 0.5$, the orbiting electrons are in fact heavier that the positively charged particle. Therefore, in a classical picture, the orbiting electrons are moving more slowly than the positively charged particle, and the system resembles the structure of H_2^+, the atom is transiting into a molecular system. It is not reasonable to use an atomic wave function to calculate the energies of a molecular system. Therefore, further investigation of this case ($\frac{\mu}{M} > 0.5$) needs a molecular wave function, such as the wave function has been investigated in [23].

Chapter 6

FUTURE WORK

There are multiple potential ways to either make these results more accurate or use method to answer several other problems. The first question concerns the state of the atom if the nuclear charge is exactly equal to the critical charge. One might guess that at this point the atom will split into a free electron and an ion. This would be the right answer if the value of $\beta_1 \to 0$ az $Z \to Z_{critical}$. The table 4.4 , however, shows that the this is not the case. The value of β_1 stays nonzero even if $Z < Z_{critical}$. Therefore, the outer electron is not a free particle at $Z = Z_{critical}$, and its wave function drops to zero at infinity. Its wave function reduces to $\frac{1}{e}$ at $r_1 = \frac{1}{\beta_1}$, and the system is in a resonance-like state. The reason for this might be the fact that the outer electron can polarize the ion as it is getting farther, and this electron-dipole attraction might almost balances the initial repulsive force of the second electron and the ion. This question has not been answered yet and it needs a deeper inspection.

Another possible way of extending this research is to take one step even further and treat nuclear charge Z as a complex variable, and find the energy as a complex function of Z. It is known that $(Z_c)^{-1}$ is the closest singularity to the origin [12]. However, there might be some other singularities on the complex plane further from that. The analyticity of this function will provide us with a much deeper grasp of energy function, its poles, other singularities, and their natures, branch cuts, radius of convergence perturbation series and so forth.

The accuracy of this work can also be increased by considering all other effects that have been neglected here. Relativistic corrections shift the energy by terms of the order $(Z\alpha)^2$. The spin-orbit interaction won't have any effect on the ground state ($l = 0$), but its effects on excited states are of the order $(Z\alpha)^2$. Even more accurate results are obtainable by considering the energy shift due to the other terms in the Breit interaction, hyperfine interaction (due to the interaction of electronic magnetic moment and nuclear magnetic moment), electron self energy and vacuum polarization.

Chapter 7

APPENDIX

7.1 HYLLERAAS-UNDHEIM-MACDONALD THEOREM

This theorem states that variational eigenvalues are upper bounds to real eigenvalues [24]. In other words, a trial wave function that results in a lower energy eigenvalue is more accurate than other variational eigenvalues.

To prove this, lets expand our trial wave function in terms of the complete set of exact orthonormal eigenfunctions of H, so that

$$|\phi_{tr}\rangle = \sum_{i=0}^{\infty} a_i |\psi_i\rangle, \tag{7.1}$$

where

$$H|\psi_i\rangle = E_i|\psi_i\rangle. \tag{7.2}$$

Then according to 3.21

$$\begin{aligned}
E_{tr} &= \frac{\langle \phi_{tr} | H | \phi_{tr} \rangle}{\langle \phi_{tr} | \phi_{tr} \rangle} \\
&= \frac{\sum_{ij} \langle c_i \psi_i | H | c_j \psi_j \rangle}{\sum_{ij} \langle c_i \psi_i | c_j \psi_j \rangle} \\
&= \frac{\sum_{ij} c_j^* c_i E_i \langle \psi_i | \psi_j \rangle}{\sum_{ij} c_j^* c_i \langle \psi_i | \psi_j \rangle},
\end{aligned} \tag{7.3}$$

assuming that ϕ_{tr} is normalized,

$$\begin{aligned}
E_{tr} &= \frac{\sum_{ij} c_j^* c_i E_i \delta_{ij}}{\sum_{ij} c_j^* c_i \delta_{ij}} \\
&= \frac{\sum_i |c_i|^2 E_i}{\sum_i |c_i|^2} \\
&= \sum_i |c_i|^2 E_i \\
&= |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \dots
\end{aligned}$$

here we will use the normalization condition

$$\sum_i |c_i|^2 = |c_0|^2 + |c_1|^2 + |c_2|^2 + \dots = 1 \tag{7.4}$$

$$|c_0|^2 = 1 - |c_1|^2 - |c_2|^2 - \dots$$

therefore

$$\begin{aligned}
E_{tr} &= |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \dots \\
&= (1 - |c_1|^2 - |c_2|^2 - \dots) E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \dots \qquad (7.5) \\
&= E_0 + |c_1|^2 (E_1 - E_0) + |c_2|^2 (E_2 - E_0) + \dots \qquad (7.6)
\end{aligned}$$

$E_i - E_0$ for $i = 1, 2, 3 \dots$. Thus, all terms on the right hand side are non-negative and

$$E_{tr} \geq E_0, \tag{7.7}$$

which proves the theorem.

Now that we know that lower variational energies are more accurate, let's see where the old variational energies lie with respect to new variational energies, as we increase the size of our basis. The matrix interleaving theorem explains this, as discussed in the following section.

7.2 THE MATRIX INTERLEAVING THEOREM

Since any $N \times N$ matrix has exactly N eigenvalues, therefore, finding the energy eigenvalue for $N + 1$ and any higher state is impossible by diagonalizing a $N \times N$ matrix. Therefore, increasing the size of basis set is the only way of getting higher eigenvalues.

What would be the relation between the new eigenvalues and the old ones as the size of basis is increased? The matrix interleaving theorem helps us to answer this question [25]. It states that if we increase the number of rows and columns of a matrix by one, then the old N eigenvalues fall between new $N + 1$ eigenvalues.

In other words, not only do we get an upper limit for $(N + 1)$th state, but also the previous N eigenvalues decrease, therefore, will be more accurate since they are the upper limit for the corresponding real eigenvalues, or in other words, they are bounded from below.

7.3 THE BOOTSTRAP FORTRAN CODE

Here is the Fortran code that was used for the bootstrap and bisection method.

```
Module Newtons_Method

implicit none

REAL*16, ALLOCATABLE :: B(:,:)

REAL*16, ALLOCATABLE :: B1(:)

Contains

real*16 function f(t)

real*16 :: t

integer :: n, k

COMMON n

f=0

do k=0,n

f=f+B1(k)*(t**k)

enddo

return

end function f

real*16 function Df(t)

real*16 :: t

integer :: n, k

COMMON n

Df=0

do k=0,n

Df=Df+K*B1(k)*(t**(k-1))

enddo

return

end function Df
```

```
end module Newtons_Method
!------------------------------------------------------------------------
c This program finds the the n-th degree fitting
c to a set of datapoints(E versus Z) and then finds
c the root of the fit and finds the Zcritical!
PROGRAM Fitting
USE Newtons_Method
IMPLICIT NONE
REAL*16, ALLOCATABLE, DIMENSION(:,:) :: Matrix, invMatrix
REAL*16, ALLOCATABLE, DIMENSION(:) :: sumx, Syx
REAL*16, ALLOCATABLE, DIMENSION(:) :: sumyx
REAL*16, ALLOCATABLE, DIMENSION(:) :: Z, E, Res
REAL*16, ALLOCATABLE, DIMENSION(:) :: x
REAL*16, ALLOCATABLE, DIMENSION(:) :: y
INTEGER :: i, j, n, n2, ErrorFlag
integer :: k, l, ndata, nboot
c B is the coefficients of the polynomial
c n is the degree of fitting
c nboot id the number of bootstrap sample
c ndata is the number of datapoints
c sumyx(i,j) is sum(y*x**j) for i-th bootstrap sample
REAL*16 :: Zcr1, Zcr2, Zcr3
real*16 :: epsilon, eps
real*16 :: x0, x1
real*16 :: ZcrMAX, ZcrMIN, ERROR
```

```
real :: r

COMMON n

INTEGER, ALLOCATABLE, DIMENSION(:) :: NZcr ! number of Zcrs in each interval

INTEGER m !number of intervals in Zcritical Range!

REAL*16 d

REAL*16, ALLOCATABLE, DIMENSION(:) :: A, C, G

REAL*16 signn

INTEGER NZcritical

REAL*16, ALLOCATABLE, DIMENSION(:) :: Zcr

REAL*16, ALLOCATABLE, DIMENSION(:) :: B0

REAL*16, ALLOCATABLE, DIMENSION(:) :: sumZcr

REAL*16, ALLOCATABLE, DIMENSION(:) :: sumB0Zcr

REAL*16, ALLOCATABLE, DIMENSION(:,:) :: Mat, invMat

REAL*16, ALLOCATABLE, DIMENSION(:,:) :: bsumB0Zcr

REAL*16, ALLOCATABLE, DIMENSION(:,:) :: bB0

REAL*16, ALLOCATABLE, DIMENSION(:) :: Zcritical

real*16 :: Z_critical

open(1,file='input.dat')

READ(1,*) n,ndata,NZcritical,Zcr1,Zcr2,epsilon

ALLOCATE(Matrix(0:n,0:n))

ALLOCATE(invMatrix(0:n,0:n))

ALLOCATE(sumx(0:2*n))

ALLOCATE(sumyx(0:n))

ALLOCATE(B1(0:n))

ALLOCATE(A(0:n))
```

```
ALLOCATE(C(0:n))
ALLOCATE(G(0:n))
ALLOCATE(Z(ndata))
ALLOCATE(E(ndata))
ALLOCATE(x(ndata))
ALLOCATE(Res(ndata))
ALLOCATE(y(ndata))
ALLOCATE(Syx(0:n))
ALLOCATE(Zcr(NZcritical))
ALLOCATE(B0(NZcritical))
ALLOCATE(sumZcr(0:2*n2))
ALLOCATE(sumB0Zcr(0:n2))
ALLOCATE(Mat(0:n2,0:n2))
ALLOCATE(invMat(0:n2,0:n2))
ALLOCATE(bsumB0Zcr(nboot,0:n2))
ALLOCATE(bB0(nboot,NZcritical))
ALLOCATE(Zcritical(nboot))
c sumx(i)=sum(x**i)
c sumyx(i)=sum(y*x**i)
open(1,file='input.dat')
open(2,file='result.dat')
do i=1,ndata
read(1,*) Z(i), E(i)
enddo
ccc NZcritical is the number of B(0)s we will produce to do bootstrapping
```

```
do k=1,NZcritical

do

sumx(0)=ndata

do i=1,2*n

sumx(i)=0

enddo

do i=0,n

sumyx(i)=0

enddo

C x and y are actually x=(z-zcr)^1/2 and y=E+1/2*Z^2,

do i=1,ndata

x(i)=sqrt(Z(i)-Zcr1)

y(i)=E(i)+0.5*(Z(i)**2)

do j=1,2*n

sumx(j)=sumx(j)+x(i)**j

enddo

do j=0,n

sumyx(j)=sumyx(j)+y(i)*(x(i)**j)

enddo

enddo

do i=0,n

do j=0,n

Matrix(i,j)=sumx(i+j)

enddo

enddo
```

```
c Matrix inversion happenes here

CALL FindInv(Matrix, invMatrix, n+1, ErrorFlag)

B1=MATMUL(invMatrix,sumyx)

A=B1

ccc doing the same thing for another Zcrit(guess)

do i=1,2*n

sumx(i)=0

enddo

do i=0,n

sumyx(i)=0

enddo

do i=1,ndata

x(i)=sqrt(Z(i)-Zcr2)

do j=1,2*n

sumx(j)=sumx(j)+x(i)**j

enddo

do j=0,n

sumyx(j)=sumyx(j)+y(i)*(x(i)**j)

enddo

enddo

do i=0,n

do j=0,n

Matrix(i,j)=sumx(i+j)

enddo

enddo
```

```
c Matrix inversion happenes here
CALL FindInv(Matrix, invMatrix, n+1, ErrorFlag)
B1=MATMUL(invMatrix,sumyx)
C=B1
if ((A(0)*C(0)) .GT. 0) then
write(*,*) "zeroth coefficients have the same sign"
endif
ccc doing the same thing for Zcr3=(Zcr1+Zcr2)/2
Zcr3=(Zcr1+Zcr2)/2
do i=1,2*n
sumx(i)=0
enddo
do i=0,n
sumyx(i)=0
enddo
do i=1,ndata
x(i)=sqrt(Z(i)-Zcr3)
do j=1,2*n
sumx(j)=sumx(j)+x(i)**j
enddo
do j=0,n
sumyx(j)=sumyx(j)+y(i)*(x(i)**j)
enddo
enddo
do i=0,n
```

```
do j=0,n

Matrix(i,j)=sumx(i+j)

enddo

enddo

c Matrix inversion happenes here

CALL FindInv(Matrix, invMatrix, n+1, ErrorFlag)

B1=MATMUL(invMatrix,sumyx)

G=B1

if ((Zcr1-Zcr2) < epsilon .AND. (Zcr2-Zcr1) < epsilon) then

Zcr(k)=Zcr3

B0(k)=G(0)

write(2,*) 'Zcritical=', Zcr(k)

write(2,*) 'B(0)=', B0(k)

write(2,*) '----------------------------------------------'

Zcr1=Zcr1 * 0.99999

Zcr2=Zcr2 * 1.00001

exit

endif

if (A(0)*G(0) .GT. 0) then

Zcr1=Zcr3

Zcr2=Zcr2

else

Zcr1=Zcr1

Zcr2=Zcr3

endif
```

```
enddo
enddo
write(2,*) '--------------------------------------------------'
write(2,*) '--------------------------------------------------'
do i=0,n
write(2,*) 'B(',i,')=',G(i)
enddo
write(2,*) '--------------------------------------------------'
write(2,*) '--------------------------------------------------'
Z_critical = sum(Zcr)/(NZcritical)
ERROR = (MAXVAL(Zcr) - MINVAL(Zcr))/2
write(2,*) 'Z_critical=', Z_critical
write(2,*) 'Error=', ERROR
END PROGRAM Fitting
!Subroutine comes here
!-----------------------------------------------------
!Subroutine to find the inverse of a square matrix
!Author : Louisda16th a.k.a Ashwith J. Rego
!Reference : Algorithm has been well explained in:
!http://math.uww.edu/~mcfarlat/inverse.htm
!http://www.tutor.ms.unimelb.edu.au/matrix/matrix_inverse.html
SUBROUTINE FINDInv(matrix, inverse, n, errorflag)
IMPLICIT NONE
!Declarations
INTEGER, INTENT(IN) :: n
```

```
INTEGER, INTENT(OUT) :: errorflag !Return error status. -1 for error, 0 for normal

REAL*16, INTENT(IN), DIMENSION(n,n) :: matrix !Input matrix

REAL*16, INTENT(OUT), DIMENSION(n,n) :: inverse !Inverted matrix

LOGICAL :: FLAG = .TRUE.

INTEGER :: i, j, k, l

REAL*16 :: m

REAL*16, DIMENSION(n,2*n) :: augmatrix !augmented matrix

!Augment input matrix with an identity matrix

DO i = 1, n

DO j = 1, 2*n

IF (j <= n ) THEN

augmatrix(i,j) = matrix(i,j)

ELSE IF ((i+n) == j) THEN

augmatrix(i,j) = 1

Else

augmatrix(i,j) = 0

ENDIF

END DO

END DO

!Reduce augmented matrix to upper traingular form

DO k =1, n-1

IF (augmatrix(k,k) == 0) THEN

FLAG = .FALSE.

DO i = k+1, n

IF (augmatrix(i,k) /= 0) THEN
```

```
DO j = 1,2*n

augmatrix(k,j) = augmatrix(k,j)+augmatrix(i,j)

END DO

FLAG = .TRUE.

EXIT

ENDIF

IF (FLAG .EQV. .FALSE.) THEN

PRINT*, "Matrix is non - invertible"

inverse = 0

errorflag = -1

return

ENDIF

END DO

ENDIF

DO j = k+1, n

m = augmatrix(j,k)/augmatrix(k,k)

DO i = k, 2*n

augmatrix(j,i) = augmatrix(j,i) - m*augmatrix(k,i)

END DO

END DO

END DO

!Test for invertibility

DO i = 1, n

IF (augmatrix(i,i) == 0) THEN

PRINT*, "Matrix is non - invertible"
```

```
inverse = 0

errorflag = -1

return

ENDIF

END DO

!Make diagonal elements as 1

DO i = 1 , n

m = augmatrix(i,i)

DO j = i , (2 * n)

augmatrix(i,j) = (augmatrix(i,j) / m)

END DO

END DO

!Reduced right side half of augmented matrix to identity matrix

DO k = n-1, 1, -1

DO i =1, k

m = augmatrix(i,k+1)

DO j = k, (2*n)

augmatrix(i,j) = augmatrix(i,j) -augmatrix(k+1,j) * m

END DO

END DO

END DO

!store answer

DO i =1, n

DO j = 1, n

inverse(i,j) = augmatrix(i,j+n)
```

```
END DO
END DO
errorflag = 0
END SUBROUTINE FINDinv
```

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VITA AUCTORIS

Amirreza Moini was born in 1988, in Mashhad, Iran. He graduated from NODET high school (National Organization for Development of Exceptional Talents) in 2007. He started pharmacology in Mashhad University of Medical Science in 2007, and then switched to physics in 2008. He received his bachelor degree in 2011 and moved to Canada. He entered Masters of Science in physics at the University of Windsor in 2012, under the supervision of Dr. Drake. He expects to graduate in January 2014.