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# Variational calculations for the lithium isoelectronic sequence.

Mauro. Tambasco  
*University of Windsor*

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**VARIATIONAL CALCULATIONS FOR THE LITHIUM  
ISOELECTRONIC SEQUENCE**

**By**

**Mauro Tambasco**

**A Thesis**

**Submitted to the Faculty of Graduate Studies and Research  
through the Department of Physics  
in Partial Fulfillment of the Requirements for  
the Degree of Master of Science at the  
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## ABSTRACT

Variational eigenvalues for the  $1s^22s\ ^2S$  and  $1s^22p\ ^2P$  states of the lithium isoelectronic sequence ( $3 \leq Z \leq 15$ ) are calculated using multiple basis sets in Hylleraas coordinates. A systematic convergence pattern for each of these nonrelativistic energies is established, and extrapolated values are determined to within an accuracy of several parts in  $10^{10}$  to  $10^{11}$ . An analytical calculation to determine the first two coefficients  $\varepsilon^{(0)}$  and  $\varepsilon^{(1)}$  of the  $Z$ -expansion for the above states of the lithium isoelectronic sequence is also presented. Using improved electron-pair energies, the third coefficient  $\varepsilon^{(2)}$  for the above states is determined to twelve significant figures, and the next several coefficients of the expansion are found by applying the linear least squares fit method to the extrapolated variational eigenvalues. Finally, first order relativistic and mass polarization corrections from [8], and [40] are added to the nonrelativistic energies obtained, and the resulting  $1s^22s\ ^2S - 1s^22p\ ^2P$  transition energies are compared with experiment to determine the “experimental” QED corrections.

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# Chapter 1

## Introduction

The lithium isoelectronic sequence comprises lithium and all other atoms of higher nuclear charge which have been stripped of all their electrons except for the three innermost. The nonrelativistic description of such three electron systems includes an interaction between each electron and the nucleus as well as an interaction between each of the electrons. It is this interaction between each of the electrons which prevents one from obtaining exact analytic solutions to these systems. However, despite this complication, a particular theoretical technique known as the variational method has been used since the late 1920's to obtain approximate solutions for several electron atoms. The basic idea of this method, as explained in detail in the first chapter, is to choose a trial wavefunction  $\Psi$  that depends on a number of parameters  $(\alpha_1, \alpha_2, \dots)$ , and minimize  $\langle \Psi | H | \Psi \rangle$  with respect to these parameters to obtain an upper bound to the energy being calculated. This seems simple enough, however, there are many details about the form of the trial wavefunction which must be considered if one is to obtain very accurate solutions for the several electron systems. Some of these details include:

1. the size of the basis set,
2. the explicit inclusion of correlation effects by incorporating powers of the interelectronic coordinates  $r_{ij}$  (Hylleraas coordinates), where  $i, j = 1, 2$ , and  $3$ ,

3. the usage of multiple basis sets (i.e. the explicit inclusion of multiple distance scales),
4. the inclusion of nonlinear as well as linear variational parameters,
5. the optimization of the nonlinear parameters for improved numerical stability, and
6. the inclusion of all terms which yield a systematic convergence pattern for increasing basis set size.

With the incorporation of all these details to form the optimum trial wavefunction, time becomes an important factor for the lithium calculation. This is mainly due to the very slow convergence of integrals with several interelectronic distances  $r_{ij}$  in the integrand. The solution to this problem as well as the particulars of an optimum trial wavefunction have been addressed by many atomic theorists over the last 60 years. Much of the success in dealing with these problems has come in the last 10 years as a result of significant increases in computational power and the application of new mathematical techniques. The most recent progress has been made by Drake and Yan [11] who have succeeded in dramatically decreasing the time required for the calculation of three electron integrals in Hylleraas coordinates. This development along with improved methods for obtaining an optimum trial wavefunction have led Drake and Yan to obtain the most accurate results for the lithium calculation to date [38]. One of the purposes of this thesis is to present these recent methods for the lithium calculation.

These methods have been used in this work to determine the nonrelativistic upper bound energies for the  $1s^22s\ ^2S$  and  $1s^22p\ ^2P$  states of the lithium isoelectronic sequence for up to  $Z = 15$ . These energies may also be determined from the  $Z$ -expansions for these states, namely,

$$E(Z) = \varepsilon^{(0)} Z^2 + \varepsilon^{(1)} Z + \varepsilon^{(2)} + \varepsilon^{(3)} Z^{-1} + \varepsilon^{(4)} Z^{-2} + \dots, \quad (1.1)$$

where the leading terms  $\varepsilon^{(0)}$  and  $\varepsilon^{(1)}$  can easily be evaluated exactly. Equation (1.1) arises by treating the electron-electron interactions as an entire perturbation term and expanding the resultant total energy. In this thesis,  $\varepsilon^{(0)}$  and  $\varepsilon^{(1)}$  are calculated analytically, an improved value for  $\varepsilon^{(2)}$  is obtained as a weighted sum of electron-pair energies and single-electron energies [7], [5], and the next several terms  $\varepsilon^{(3)}, \varepsilon^{(4)}, \dots$  of the expansion are found by performing a least squares fit using the nonrelativistic energies obtained from extrapolations of the three electron computer calculations.

A meaningful comparison with experiment can only be made once the mass polarization and relativistic corrections have been added to the nonrelativistic energies. In this thesis, these corrections have been obtained from Chung et al. [8], [40] for both the  $S$  and  $P$ -states of the lithium isoelectronic sequence up to  $Z = 10$ . The QED corrections may then be extracted from the difference between theory and experiment and the results may be compared to directly calculated QED results.

## 1.1 Historical Survey

The first variational calculation for lithium was done in 1930 by Eckhart [13]. He used the following screened type radial wavefunctions

$$u(r) = \exp(-\alpha r), \tag{1.2}$$

and

$$v(r) = (1 - \gamma r) \exp(-\gamma r), \tag{1.3}$$

for the  $1s$  and  $2s$  orbitals, respectively, where  $\alpha$  and  $\gamma$  are the variational parameters. Using these analytic functions he also calculated the ground state energies for the low  $Z$  members of the lithium isoelectronic sequence. All his values except for lithium itself were accurate to within a few percent. The calculation for lithium turned out to be in error, and it was later corrected by Wilson [12].

The ground state calculation for lithium was improved upon in that same year by Guillemin and Zener [17] who introduced a third parameter in place of the non-exponential parameter  $\gamma$  in Eq. (1.3). With this new three parameter wavefunction they obtained an improved value of  $-7.4183$  a.u. for the ground state of lithium. Calculations such as these, containing simple analytic wavefunctions, continued throughout the early 1930's. However, the accuracy in the energies obtainable from using these simple separate orbital wavefunctions was limited.

In 1936, important breakthroughs were made by James and Coolidge [21] with their introduction of more elaborate wavefunctions. In an effort to improve upon previous trial functions, they made three different types of adjustments to their wavefunctions, and examined which of these adjustments resulted in significant improvements for the bound states and ionization potential of lithium. The first of these adjustments was the addition of new linear and nonlinear parameters to the radial function representing the  $2s$  orbital. This change was made for the purpose of improving the representation of the  $2s$  orbital, however, the resultant four-term function yielded an improvement of less than  $1 \times 10^{-4}$  a.u. for the ground state energy. The second adjustment that they made was intended to improve the core representation. Previously, the core had been represented by a product of two separate orbital functions,  $u(r_1) u(r_2)$ . In the place of this product, James and Coolidge tried using a single function  $u(r_1, r_2)$ , which explicitly included the first two powers of the interelectronic coordinates, i.e.,  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  and  $r_{12}^2$ . The use of such coordinates was first introduced, with great success, by Hylleraas [19] [20] for the helium calculation in 1928. As such, it seemed very likely that similar success could be achieved for the lithium calculation since the interelectronic coordinates would improve the core representation by allowing correlation effects within the core to be taken into account. This, in fact, turned out to be the case. With the inclusion of  $r_{12}$  and  $r_{12}^2$ , a value of  $-7.47268$  a.u. was obtained for the ground state energy of lithium. This dramatic improvement was obtained with just a six-term core and a single term valence orbital function. The success indicated that correlation effects within the core have a



significant impact on the variational energies of lithium.

The final adjustment made by James and Coolidge was to abandon the separate orbital concept altogether by including the interelectronic coordinates  $r_{13}$  and  $r_{23}$  in their wavefunction. This change allowed correlation effects between the valence orbital and the core to be taken into account, and with a new ten term wavefunction, they improved the ground state energy of lithium by a few parts in  $10^3$ . Hence, the importance of polarization effects between the core and the outer electron in determining energy levels for three electron systems was also demonstrated.

At this point, one may wonder why the use of interelectronic coordinates in the trial wavefunction for lithium had not been introduced sooner. Eight years had gone by since Hylleraas had first introduced and shown the importance of using such coordinates in calculations for few electron systems. The reason they were not introduced sooner is probably because the inclusion of these coordinates for three electron systems enormously complicates the calculation of the radial integrals. With the inclusion of the interelectronic coordinates, these integrals turn out to be of the general form,

$$I(j_1, j_2, j_3, j_{12}, j_{23}, j_{31}; \alpha, \beta, \gamma) = \int d^3v r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}. \quad (1.4)$$

This integral may be evaluated by expanding powers of  $r_{ij}$  in terms of a series of Legendre functions. However, a numerical summation of an infinite series is required if all three powers  $j_{12}$ ,  $j_{23}$ , and  $j_{31}$  are odd. James and Coolidge got around this problem by including only one nonzero power of  $r_{ij}$  in each of their terms constituting the wavefunction.

Due to the difficulty of solving radial integrals of the form (1.4), improvements over the James and Coolidge results using Hylleraas type trial wavefunctions did not come until almost thirty years later. In 1963, Berggren and Wood [2] extended the wavefunction of James and Coolidge by adding terms alternating between the inclusion of coordinates  $r_{23}$  and  $r_{13}$  up to the third power. The addition of these terms allowed for an improved description of the core-valence correlation, and their 14 term wavefunction led to an improved value of  $-7.47631$  a.u. for the ground state energy of lithium. In the same year,

a similar extension was also made by Burke [4] who obtained a slightly better value of  $-7.47695$  a.u. Although these extensions by Burke, and Berggren and Wood yielded some improvement in the ground state energy of lithium, it was clear that even more elaborate extensions were necessary if any further improvements were to be made. Such extensions became possible that same year with the discovery of a reasonably efficient algorithm for dealing with the case mentioned above where all three powers of the interelectronic coordinates are odd. In addition to this discovery made by Öhrn and Nordling [28], a computationally useful expansion for arbitrary powers of the interelectronic coordinates was introduced by Sack [34] a year later. Perkins [30], in 1968, also provided a similar expansion but for only the integral powers of the coordinates  $r_{ij}$ . With the introduction of these powerful computational tools, the door was now open for calculations with more complex Hylleraas type wavefunctions.

In 1968, Larsson [24] made use of the new computational tools for his lithium calculation which involved the most complex Hylleraas type wavefunctions anyone had ever used up until then. He performed calculations for various basis set sizes up to a size which included 60 different radial terms. The terms he used were selected on the basis of their ability to improve the ground state energy, and with these trial and error selection processes he obtained a final energy of  $-7.478025$  a.u.

While various Hylleraas type variational calculations were being studied during the 1960's, the usefulness of  $Z$ -expansions for predicting atomic properties, such as the correlation energy, were also being explored [7][5][39]. To make meaningful predictions for the atomic properties, the expansions were carried up to second-order. The second-order coefficient  $\epsilon^{(2)}$  of the  $Z$ -expansion (1.1) was derived from electron-pair eigenfunctions. This method for calculating  $\epsilon^{(2)}$  appears to have been first pointed out by Bacher and Goudsmit [1] in 1934. However, it wasn't until almost three decades later that the method was used to extend the  $Z$ -expansions for the lithium isoelectronic sequence.

In 1960, Sinanoğlu [37] showed that the first order wavefunction  $\Psi^{(1)}$ , [see Eqs. (3.11) and (3.15)], can be obtained rigorously in terms of the first order wavefunctions of in-

dependent two-electron systems. For example, if  $\phi^{(1)}(1s^2 \ ^1S)$ ,  $\phi^{(1)}(1s2s \ ^3S_0)$ ,  $\phi^{(1)}(1s2s \ ^3S_1)$ , and  $\phi^{(1)}(1s2s \ ^1S)$  are first-order corrections to the two-electron states, then the first-order wavefunction for the lithium ground state can be written as

$$\begin{aligned} \Psi^{(1)}(1s^2 2s \ ^2S) &= 2^{-(1/2)} \mathcal{A} \left\{ \phi_{12}^{(1)}(1s^2 \ ^1S) c_3 + 2^{-(1/2)} \right. \\ &\quad \left. \times \left[ \phi_{12}^{(1)}(1s2s \ ^3S_0) - \phi_{12}^{(1)}(1s2s \ ^1S) \right] a_3 + \phi_{12}^{(1)}(1s2s \ ^3S_1) b_3 \right\}, \end{aligned} \quad (1.5)$$

where  $a = 1s\alpha$ ,  $b = 1s\beta$ , and  $c = 2s\alpha$  are one electron hydrogenic solutions for nuclear charge  $Z$ , the subscripts denote electrons, and  $\alpha$  and  $\beta$  represent spin up and spin down, respectively.  $\mathcal{A}$  is the three particle antisymmetrizer (2.11). The first-order corrections to the two-electron states can be obtained individually by variational or other methods.

With the first-order wavefunction  $\Psi^{(1)}$ , the nonrelativistic energies can be calculated to third order, with second and third-order energies  $\varepsilon^{(2)}$  and  $\varepsilon^{(3)}$  written as a weighted sum of electron-pair energies and certain single-electron energies. In 1965, such a calculation was carried out to second-order by Chisholm and Dalgarno [7] for the ground state lithium isoelectronic sequence. They obtained the pair energies from direct two-electron variational calculations, and presented a method for evaluating the single-electron energies exactly. With this work, they concluded that the nonrelativistic eigenvalues of the  $1s^2 2s \ ^2S$  states of the lithium sequence were given by

$$E_{(2S)}(Z) = -1.125Z^2 + 1.02280521Z - 0.40814899 + O(Z^{-1}). \quad (1.6)$$

Several years later, a similar calculation was done by Chisholm *et al.* for the  $1s^2 2p \ ^2P$  state of the lithium isoelectronic sequence [5] with the result

$$E_{(2P)}(Z) = -1.125Z^2 + 1.02280521Z - 0.52717136 + O(Z^{-1}). \quad (1.7)$$

It turned out, however, that the calculated second order energies in (1.6) and (1.7) were slightly off. In 1969, an improved value for the pair energy  $\varepsilon^{(2)}(1s2s \ ^1S)$  had been used

by Horak *et al.* [39], and this led to a slightly more accurate value for  $\varepsilon^{(2)}(1s^2 2s \ ^2S)$  than that of Chisholm and Dalgarno. They also made a correction to one of the single-electron energy terms used in the calculation of the second order coefficient  $\varepsilon^{(2)}(1s^2 2p \ ^2P)$  of Eq. (1.7). With these adjustments they obtained  $\varepsilon^{(2)}(1s^2 2s \ ^2S) = 0.4081652$  and  $\varepsilon^{(2)}(1s^2 2p \ ^2P) = 0.5285786$  for the  $1s^2 2s \ ^2S$  and  $1s^2 2p \ ^2P$  state expansion, respectively.

A few years later, Seung and Wilson [36] carried out a similar calculation for the  $1s^2 2s \ ^2S$  state up to the third order. Their work led to the result that the nonrelativistic energy for this state is given by

$$E_{(2S)}(Z) = -1.125Z^2 + 1.022805Z - 0.4083 \\ -0.0230(1/Z) + O(Z^{-2}). \quad (1.8)$$

To obtain this result, they used the same pair energies as Chisholm and Dalgarno, however, their calculation for the single-electron terms was less extensive. These terms were evaluated only approximately using variationally determined representations of the two-electron pair functions. From Table 1.1 below, we see how the second and third order  $Z$ -expansions compared to some of the variational calculations for the lithium ground state.

During the 1970's, Larsson's work was extended with Hylleraas type variational calculations for various states of lithium, and for the ground state of the lithium isoelectronic sequence [31]. Despite this progress, however, the next significant gains with these types of calculations did not come until 1986 with the ground state lithium calculation by King and Shoup [23]. The importance of the King and Shoup calculation was their employment of a more systematic method for extending the basis set size. Instead of increasing the size of the basis by using trial and error techniques, they simply included all possible permutations of the powers of the coordinates that added to a fixed sum. This unbiased approach of extending the basis set later proved useful for convergence studies.

In 1989, King extended his calculation to the ground state lithium isoelectronic se-

Table 1.1: Comparison of a few lithium ground state calculations.

Method	Author	Energy (a.u.)
Variational	James and Coolidge <sup>a</sup>	-7.47607
Variational	Burke <sup>b</sup>	-7.47695
Variational	Larsson <sup>c</sup>	-7.478025
Perturbation	Horak <i>et al.</i> <sup>d</sup>	-7.46461
Perturbation	Seung and Wilson <sup>e</sup>	-7.47262

<sup>a</sup>Reference [21].

<sup>b</sup>Reference [4].

<sup>c</sup>Reference [24].

<sup>d</sup>Reference [39].

<sup>e</sup>Reference [36].

quence and to some excited  $S$  states [22]. With a total of 602 terms, they obtained the nonrelativistic ground state energy with an accuracy of a few parts in  $10^6$ . A few years later, another dramatic improvement was made by McKenzie and Drake [25]. The main difference between their wavefunction and previous wavefunctions was the use of a multiple basis set, that is, their basis set was divided into sectors with different scale factors  $\alpha$ ,  $\beta$ , and  $\gamma$ . Using up to 1134 terms in their basis set, the result they obtained for the ground state energy of lithium was two orders of magnitude more accurate than previously obtained values. This result remained to be one of the most accurate until the recent calculation by Yan and Drake in 1995 [38]. They improved upon the multiple basis set method by using a better partitioning of the different sectors, and they also discovered an asymptotic expansion method which they used to deal with the slowly convergent integrals [11]. This latter improvement allowed them to carry out computationally efficient calculations with significantly larger basis set sizes. Their nonrelativistic calculations for the  $1s^2 2s \ ^2S$ ,  $1s^2 2p \ ^2P$ , and  $1s^2 3d \ ^2D$  states of lithium converged to a few parts in  $10^{10} - 10^{11}$ . These are the most accurate values to date.

# Chapter 2

## The Lithium Calculation

In order to determine the energies and states of lithium and other three electron systems, we must first determine the form of the Hamiltonian. Once this is done, we may proceed to solve the Schrödinger equation to find nonrelativistic solutions of our system. However, as we shall see below, no exact analytic solutions are possible for three electron systems. As a result, we shall turn to the variational method in Hylleraas coordinates as a means of obtaining approximate high precision solutions for these systems.

### 2.1 The Hamiltonian

Assuming infinite nuclear mass, the nonrelativistic Hamiltonian (in atomic units with  $e = \hbar = 1$ ) for three electrons in a Coulomb potential is given by

$$H = -\frac{1}{2} \sum_{i=1}^3 \nabla_{R_i}^2 - Z \sum_{i=1}^3 \frac{1}{R_i} + \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{R_{ij}}, \quad (2.1)$$

where  $Z$  is the nuclear charge. Now substituting  $r = R/Z$ , we obtain

$$H = -\frac{1}{2} \sum_{i=1}^3 \nabla_i^2 - \sum_{i=1}^3 \frac{1}{r_i} + \frac{1}{Z} \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}}, \quad (2.2)$$

the Hamiltonian in  $Z$ -scaled atomic units. The form of the  $\nabla_i^2$  operators is derived in Appendix A.

From Eq. (2.2), we see that the eigenvalue equation,  $H\Psi = E\Psi$ , cannot be solved exactly. This is due to the fact that the interelectron interaction terms,  $r_{ij}$ , cause the equation to be nonseparable. As a result, we resort to the variational method for finding solutions.

## 2.2 The Variational Method

The variational method is one of the principal methods used to obtain approximate energy levels and wave functions of a system for which no exact analytic solution exists. The general form of the variational principle is stated as follows:

**Theorem 1** *The mean value of the Hamiltonian  $H$ ,*

$$\langle H \rangle = E(\Psi) = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.3)$$

*is stationary if and only if the state vector  $|\Psi\rangle$  to which it corresponds is an eigenvector of  $H$ , and the stationary values of  $\langle H \rangle$  are eigenvalues of  $H$ .*

A proof of this theorem may be found in many quantum mechanics books (for example, Messiah [26]). In essence, the theorem allows us to apply the variational method in lieu of solving Schrödinger's equation. In doing so, it creates a means for setting up approximate solutions of Schrödinger's equation.

The main idea behind the method is to choose a wavefunction  $\Psi_{tr}$ , which may be expressed in terms of a finite linear combination of linearly independent functions whose coefficients are the parameters with respect to which  $\langle H \rangle_{tr} = E_{tr}$  is minimized. That is,  $\Psi_{tr}$  is expanded as

$$\Psi_{tr} = \sum_{i=0}^M c_i \Phi_i \quad (2.4)$$

and the coefficients are determined from the condition  $\partial E_{tr}/\partial c_i = 0$ , for  $i = 0, \dots, M$ . This procedure is equivalent to solving the following generalized eigenvalue equation

$$\mathbf{H}\mathbf{c} = \lambda\mathbf{O}\mathbf{c}, \quad (2.5)$$

where  $\mathbf{H}$  is the Hamiltonian matrix with matrix elements given by  $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$ ,  $\mathbf{O}$  is the overlap matrix with matrix elements  $O_{ij} = \langle \Phi_i | \Phi_j \rangle$ , and  $\mathbf{c}$  is a column vector with elements  $c_i$ . To illustrate the equivalence of these procedures, we begin by substituting (2.4) into (2.3) with  $\Psi = \Psi_{tr}$

$$\begin{aligned} E_{tr} &= \frac{\langle \Psi_{tr} | H | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle} \\ &= \frac{\sum_{ij} c_i^* c_j H_{ij}}{\sum_{ij} c_i^* c_j O_{ij}}. \end{aligned} \quad (2.6)$$

Next, we differentiate with respect to the coefficients

$$\begin{aligned} \frac{\partial E_{tr}}{\partial c_k} &= \frac{\sum_i c_i^* H_{ik}}{\sum_{ij} c_i^* c_j O_{ij}} - \left( \sum_i c_i^* c_j O_{ij} \right)^{-2} \sum_i O_{ik} c_i^* \sum_{ij} c_i^* c_j H_{ij} \\ &= \frac{\sum_i c_i^* H_{ik}}{\sum_{ij} c_i^* c_j O_{ij}} - \frac{E_{tr} \sum_i c_i^* O_{ik}}{\sum_{ij} c_i^* c_j O_{ij}}, \end{aligned} \quad (2.7)$$

Finally, setting (2.7) equal to zero we get the generalized eigenvalue equation (2.5).

We have thus shown that the variational principle leads us to solve Eq. (2.5) for the coefficients  $c_i$  and the corresponding eigenvalues  $\lambda_i$ ,  $i = 0, \dots, M$ . We shall now show that the lowest of these eigenvalues is necessarily greater than or equal to the true ground state eigenvalue. That is, we shall prove that

$$E_{tr} = \frac{\langle \Psi_{tr} | H | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle} \geq E_0, \quad (2.8)$$

where  $E_0$  is the smallest eigenvalue of  $H$ .



To this end, we begin by choosing an arbitrary eigenfunction  $\Psi_{tr}$  of the state space of space of the system. For convenience, we assume that  $\Psi_{tr}$  is normalized so that  $\langle \Psi_{tr} | \Psi_{tr} \rangle = \sum_i |c_i|^2 = 1$ . Now, if this function  $\Psi_{tr}$  is expanded in a complete set of eigenstates of  $H$ , denoted  $\Phi_i$ , with corresponding eigenvalues  $E_i$ , where  $i = 0, 1, 2, \dots, M$ , then we get

$$\begin{aligned}
E_{tr} &= \langle \Psi_{tr} | H | \Psi_{tr} \rangle = \sum_i^M \sum_j^M c_i^* \langle \Phi_i | H | \Phi_j \rangle c_j \\
&= \sum_i^M \sum_j^M c_i^* c_j E_j \langle \Phi_i | \Phi_j \rangle \\
&= \sum_i^M |c_i|^2 E_i \\
&\geq E_0 \sum_i^M |c_i|^2 = E_0,
\end{aligned} \tag{2.9}$$

which proves (2.8).

More generally, it can also be shown that for a spectrum which is bounded from below, the remaining exact energies  $E_1, E_2, \dots, E_M$ , will always lie below the corresponding higher trial energies  $\lambda_1, \lambda_2, \dots, \lambda_M$ . This is known as the Hylleraas-Undheim-MacDonald (HUM) Theorem. It follows from the matrix interleaving theorem which states that if an extra row and column is added to the matrices  $\mathbf{H}$  and  $\mathbf{O}$  then the  $M$  old eigenvalues interleave the  $M+1$  new ones. As a result, all but the highest of the  $M+1$  new eigenvalues will lie below the  $M$  old eigenvalues, and as the size of the matrices approaches infinity, the exact spectrum of the bound states will be approached from above.

In the case of the lithium calculation, the trial wavefunction was written as

$$\Psi = \mathcal{A} \left( c_0 \phi_0 + \sum_{\mu=1}^N \sum_{\nu=1}^{N_\mu} c_{\mu\nu} \phi_{\mu\nu} \right), \tag{2.10}$$

where  $\mathcal{A}$  is the three-particle antisymmetrizer given by

$$A = (1) - (12) - (13) - (23) + (123) + (132), \quad (2.11)$$

$N$  is the number of sets of exponential parameters  $\alpha_\mu$ ,  $\beta_\mu$ , and  $\gamma_\mu$  being used,  $N_\mu$  is the number of terms for a given set  $\mu$ ,  $c_0$  and the  $c_{\mu\nu}$  are the linear variational coefficients, and  $\phi_0$  and the  $\phi_{\mu\nu}$  are basis functions. The numbers in parentheses in Eq. (2.11) represent permutation operators which act to interchange the spacial and spin coordinates of the three particle wavefunction. For example, the operator (123) represents the permutation in which coordinate 1 takes the place of coordinate 3, coordinate 2 takes the place of coordinate 1, and coordinate 3 takes the place of coordinate 2.

The function  $\phi_0$  is of the form

$$\phi_0 = \phi(1s^2, Z)\phi(2l, Z - 2), \quad (2.12)$$

where  $\phi(1s^2, Z)$  is a variationally determined core wavefunction and  $\phi(2l, Z - 2)$  is the hydrogenic wavefunction with angular quantum number  $l$  and nuclear charge  $Z$ . The inclusion of  $\phi_0$  as a single term in the basis set is mainly for the purpose of improving upon the variational eigenvalue for a given basis set size for the higher states. To see how this works, consider the eigenvalues of (2.12), given by

$$E_0 = E(1s^2, Z) - \frac{(Z - 2)^2}{2n^2}. \quad (2.13)$$

Equation (2.13) gives the correct first several figures of the true energy for the higher states. For example, using a 135 term core wavefunction we obtain the following values for the  $1s^2 2p \ ^2P$  and  $1s^2 3d \ ^2D$  states of lithium

$$E_0(1s^2 2p \ ^2P) = -7.404\ 913\ 412 \text{ a.u.},$$

and

$$E_0(1s^2 3d \ ^2D) = -7.335\ 468\ 968 \text{ a.u.}$$

The actual values determined variationally without the core function [38] are given by  $-7.410\ 156\ 521\ 8(13)$  a.u. and  $-7.335\ 523\ 541\ 10(43)$  a.u. for the  $1s^2 2p^2 P$  and  $1s^2 3d^2 D$  states respectively. Thus, we see that there is agreement between  $E_0$  and the variational eigenvalues to two significant figures for the  $P$ -state and four significant figures for the  $D$ -state. For the  $S$ -state the agreement is only to one significant figure. This result shows that it is numerically advantageous to include  $\phi_0$  in the basis set for the higher states and rewrite the variational principle for  $\Delta E = E - E_0$ , so that

$$\Delta E(\Psi) = \frac{\langle \Psi | H - E_0 | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \min, \quad (2.14)$$

In this way, the variational principle is applied to  $H - E_0$ , which yields the correction to  $E_0$  directly, so that several significant figures in the evaluation of the matrix elements are saved.

From (2.10), the form of  $\phi_{\mu\nu}$  is given by

$$\phi_{\mu\nu}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_1^{j_{1\mu\nu}} r_2^{j_{2\mu\nu}} r_3^{j_{3\mu\nu}} r_{12}^{j_{12\mu\nu}} r_{23}^{j_{23\mu\nu}} r_{31}^{j_{31\mu\nu}} e^{-\alpha_\mu r_1 - \beta_\mu r_2 - \gamma_\mu r_3} \mathcal{Y}_{(l_1 l_2) l_{12}, l_3}^{LM}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi_1, \quad (2.15)$$

where

$$\begin{aligned} \mathcal{Y}_{(l_1 l_2) l_{12}, l_3}^{LM} &= r_1^{l_{1\mu\nu}} r_2^{l_{2\mu\nu}} r_3^{l_{3\mu\nu}} \sum_{m_i} (l_1 m_1; l_2 m_2 | l_{12} M_{12}) \langle l_{12} M_{12}; l_3 m_3 | l_{12} l_3; LM \rangle \\ &\times Y_{l_1 m_1}(\mathbf{r}_1) Y_{l_2 m_2}(\mathbf{r}_2) Y_{l_3 m_3}(\mathbf{r}_3), \end{aligned} \quad (2.16)$$

and

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \quad (2.17)$$

is the spin function with  $M_S = 1/2$ .

Now, from (2.15) we see that in addition to finding the optimum linear coefficients  $c_{\mu\nu}$ , we must also find the optimum nonlinear parameters  $\alpha_\mu$ ,  $\beta_\mu$ , and  $\gamma_\mu$ . To this end,  $N$  sets of exponential parameters are chosen and the generalized eigenvalue problem

(2.5) is first solved to find the linear coefficients  $c_{\mu\nu}$  and the corresponding variational eigenvalue  $\lambda$  for a given state. Next, the exponential parameters are separately optimized for each set, and the variational eigenvalue is recalculated with the new optimized values. However, optimization of these nonlinear parameters is not as straight forward as the optimization of the linear parameters. The reason for this is that the equation  $\partial E/\partial\rho = 0$ , where  $\rho$  represents any nonlinear parameter, is transcendental. This fact leads us to apply Newton's method to find the zeros of the first derivatives of the variational energy with respect to each of the nonlinear parameters. The implicit dependence of  $E$  on the nonlinear parameters through the linear coefficients vanishes as a result of the condition  $\partial E/\partial c_{\mu\nu} = 0$  used for the optimization of the linear coefficients. Thus, in order to optimize the nonlinear parameters, we only have to be concerned with the explicit dependence of  $E$  on these parameters. This explicit dependence is given by

$$\begin{aligned}
\partial E/\partial\rho &= \frac{\langle\partial\Psi_{tr}/\partial\rho|H|\Psi_{tr}\rangle + \langle\Psi_{tr}|H|\partial\Psi_{tr}/\partial\rho\rangle}{\langle\Psi_{tr}|\Psi_{tr}\rangle} \\
&\quad - \frac{[\langle\partial\Psi_{tr}/\partial\rho|\Psi_{tr}\rangle + \langle\Psi_{tr}|\partial\Psi_{tr}/\partial\rho\rangle]\langle\Psi_{tr}|H|\Psi_{tr}\rangle}{\langle\Psi_{tr}|\Psi_{tr}\rangle^2} \\
&= \frac{2\langle\Psi_{tr}|H|\partial\Psi_{tr}/\partial\rho\rangle}{\langle\Psi_{tr}|\Psi_{tr}\rangle} - \frac{2E\langle\Psi_{tr}|\partial\Psi_{tr}/\partial\rho\rangle}{\langle\Psi_{tr}|\Psi_{tr}\rangle} \\
&= \frac{2\langle\Psi_{tr}|H-E|\partial\Psi_{tr}/\partial\rho\rangle}{\langle\Psi_{tr}|\Psi_{tr}\rangle}. \tag{2.18}
\end{aligned}$$

Once the first derivatives are known, the second derivatives are estimated by taking the difference between two slightly differing pre-chosen exponential parameter sets. Newton's method is then employed to find the zeros of the first derivatives, and given that the initial exponential parameters are chosen close to a minimum, the procedure converges within several iterations.

To illustrate this procedure in more detail, consider one of the exponential parameters  $\rho$  and its first derivative  $D_k = \partial E/\partial\rho|_{\rho=\rho_k}$  to be given by  $(\rho_0, D_0)$ , and suppose another value for  $\rho$  is chosen close to  $\rho_0$  in the direction of decreasing energy. If we label this other value  $\rho_1$ , and calculate the first derivative  $D_1$ , we have a second point which may

be labeled  $(\rho_1, D_1)$ . Now, through any two points there is a unique line which may be extrapolated using the special case of Lagrange's classical formula for two points [32],

$$P(x) = \frac{(x - x_2)}{(x_1 - x_2)}y_1 + \frac{(x - x_1)}{(x_2 - x_1)}y_2, \quad (2.19)$$

where the two points are give by  $(x_1, y_1)$  and  $(x_2, y_2)$ . Since we want the value of  $\rho$  at  $\partial E/\partial \rho = 0$ , we set  $P(x) = 0$ , and rearrange (2.19), to obtain

$$x = \frac{(x_2 y_1 - x_1 y_2)}{(y_1 - y_2)}. \quad (2.20)$$

Substituting  $(x_1, y_1) = (\rho_0, D_0)$ , and  $(x_2, y_2) = (\rho_1, D_1)$  into (2.20), we get

$$\rho_2 = \frac{(\rho_1 D_0 - \rho_0 D_1)}{(D_0 - D_1)}. \quad (2.21)$$

This procedure is then repeated with the points  $(\rho_1, D_1)$ , and  $(\rho_2, D_2)$  to find  $(\rho_3, D_3)$ , and this point may then be used together with  $(\rho_2, D_2)$  to find the next point, and so on, until the changes in the derivatives and in the successive values of the energy are sufficiently small.

## 2.3 Construction of the Basis Sets

The basis set constructions used for the results obtained in this thesis are those of Yan and Drake [38]. In generating the finite basis sets, all terms from (2.15) are nominally included such that

$$j_{1\mu\nu} + j_{2\mu\nu} + j_{3\mu\nu} + j_{12\mu\nu} + j_{23\mu\nu} + j_{31\mu\nu} \leq \Omega, \quad (2.22)$$

where  $\Omega$  is a nonnegative integer. This systematic method for selecting terms for the basis sets allows a meaningful convergence study of the eigenvalues to be performed as  $\Omega$  is progressively increased. However, this method alone does not guarantee adequate

convergence. To be sure that the correct energy eigenvalues are obtained, a systematic search for possible classes of terms yielding a significant lowering of the eigenvalues must also be carried out. For example, the angular coupling for a given total angular momentum  $L$ , is given by

$$\begin{aligned} S \text{ states } (L = 0) : (l_1, l_2, l_3) &= (0, 0, 0)_A, \text{ and} \\ P \text{ states } (L = 1) : (l_1, l_2, l_3) &= (0, 0, 1)_A, (0, 1, 0)_B, \end{aligned}$$

where  $(l_1, l_2, l_3)$  denotes the angular momenta being used, and the subscripts  $A$  and  $B$  label the different nonlinear parameters for a given block of terms. Yan and Drake [38] found that the inclusion of at least a few  $(0, 1, 0)_B$  terms for the  $P$  states, which describe the core polarization, are necessary for adequate convergence. With the use of only the  $(0, 0, 1)_A$  terms, the energy eigenvalue for the  $1s^2 2p^2 P$  state of lithium converged to an incorrect value of  $-7.410\ 136\ 34$  a.u., even for basis set sizes as large as 1500 terms.

In order to increase the rate of convergence of the basis sets for a given total number of terms, the total basis set used is split up into different sectors with different scale factors  $\alpha$ ,  $\beta$ , and  $\gamma$ , which are optimized separately. This separation into different sectors increases the convergence of the basis sets by improving the representation of different correlations among the three electrons. The first block  $(0, 0, L)_A$  is partitioned into five sectors covering the different distance scales as follows:

$$\begin{aligned} \text{sector 1: } & \text{all } j_{12}, \quad j_{23} = 0, \quad j_{31} = 0; \\ \text{sector 2: } & \text{all } j_{12}, \quad j_{23} = 0, \quad j_{31} \neq 0; \\ \text{sector 3: } & \text{all } j_{12}, \quad j_{23} \neq 0, \quad j_{31} = 0; \\ \text{sector 4: } & j_{12} = 0, \quad j_{23} \neq 0, \quad j_{31} \neq 0; \\ \text{sector 5: } & j_{12} \neq 0, \quad j_{23} \neq 0, \quad j_{31} \neq 0. \end{aligned} \tag{2.23}$$

Thus, there are five sectors for the  $S$  states, and six sectors for the  $P$  states, since they contain the additional block  $(0, 1, 0)_B$ . The sizes of each of these sectors are controlled

by assigning an  $\Omega_i$  value to each of them according to

$$\begin{aligned}\{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5\} &= \{\Omega, \Omega, \Omega, (\Omega, 8)_{\min}, (\Omega, 8)_{\min}\}, \text{ for } L = 0, \text{ and} \\ \{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5, \Omega_6\} &= \{\Omega, \Omega, \Omega, (\Omega, 8)_{\min}, (\Omega, 8)_{\min}, \Omega - 2\}, \text{ for } L = 1, \end{aligned} \quad (2.24)$$

where  $(a, b)_{\min}$  denotes the minimum of  $a$  and  $b$ .

## 2.4 Calculation of the Integrals

In the above discussion of the variational method, it was shown that the variational eigenfunctions and eigenvalues may be found by solving the general eigenvalue problem (2.5). To solve this equation, the matrix elements of  $\mathbf{H}$  and  $\mathbf{O}$  must be evaluated. In this section, procedures for solving the general form of the integrals involved in the evaluation of these matrix elements is presented.

Let us define,  $\Phi(r_1, r_2, r_3, r_{12}, r_{23}, r_{31}) \equiv r_{12}^{v_{12}} r_{23}^{v_{23}} r_{31}^{v_{31}} \tilde{\Phi}(r_1, r_2, r_3)$ , where  $\tilde{\Phi}(r_1, r_2, r_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} e^{-\alpha r_1 - \beta r_2 - \gamma r_3}$ . Now, consider an integral of the form

$$\begin{aligned} I &= \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \Phi(r_1, r_2, r_3, r_{12}, r_{23}, r_{31}) Y_{l'_1 m'_1}^*(\hat{r}_1) Y_{l'_2 m'_2}^*(\hat{r}_2) Y_{l'_3 m'_3}^*(\hat{r}_3) \\ &\quad \times Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 m_2}(\hat{r}_2) Y_{l_3 m_3}(\hat{r}_3). \end{aligned} \quad (2.25)$$

All the matrix elements of  $\mathbf{H}$  and  $\mathbf{O}$  may be reduced to the evaluation of integrals of this form. To evaluate this integral, we begin by substituting the expansions derived by Perkins [30], for the interelectronic coordinates. For example, the expansion for  $r_{12}^{v_{12}}$  is

$$r_{12}^{v_{12}} = \sum_{q_{12}=0}^{L_{12}^{(1)}} P_{q_{12}}(\cos \theta_{12}) \sum_{k_{12}=0}^{L_{12}^{(2)}} C_{v_{12} q_{12} k_{12}} s_{12}^{q_{12} + 2k_{12}} g_{12}^{v_{12} - q_{12} - 2k_{12}} \quad (2.26)$$

where  $L_{12}^{(1)} = \frac{v_{12}}{2}$  and  $L_{12}^{(2)} = \frac{v_{12}}{2} - q_{12}$  for even values of  $v_{12}$ , and  $L_{12}^{(1)} = \infty$  and  $L_{12}^{(2)} = \frac{1}{2}(v_{12} + 1)$  for odd values of  $v_{12}$ . Also,  $s_{12} = \min(r_1, r_2)$  and  $g_{12} = \max(r_1, r_2)$ , and the

coefficients  $C_{\nu_{12}q_{12}k_{12}}$  are given by

$$C_{\nu_{12}q_{12}k_{12}} = \frac{2q_{12} + 1}{\nu_{12} + 2} \binom{\nu_{12} + 2}{2k_{12} + 1} \prod_{t=0}^{S_{q_{12}\nu_{12}}} \frac{2k_{12} + 2t - \nu_{12}}{2k_{12} + 2q_{12} - 2t + 1} \quad (2.27)$$

where  $S_{q_{12}\nu_{12}} = \min[q_{12} - 1, \frac{1}{2}(\nu_{12} + 1)]$ . Now, if we define,  $F(\nu q k)_{12} = C_{\nu_{12}q_{12}k_{12}} S_{12}^{q_{12} + 2k_{12}} g_{12}^{\nu_{12} - q_{12} - 2k_{12}}$ , and write similar expressions for  $r_{23}^{\nu_{23}}$  and  $r_{31}^{\nu_{31}}$ , Eq. (2.25) becomes

$$I = \sum_{q_{12}=0}^{L_{12}^{(1)}} \sum_{q_{23}=0}^{L_{23}^{(1)}} \sum_{q_{31}=0}^{L_{31}^{(1)}} \sum_{k_{12}=0}^{L_{12}^{(2)}} \sum_{k_{23}=0}^{L_{23}^{(2)}} \sum_{k_{31}=0}^{L_{31}^{(2)}} \int r_1^2 dr_1 r_2^2 dr_2 r_3^2 dr_3 \tilde{\Phi} F(\nu q k)_{12} F(\nu q k)_{23} F(\nu q k)_{31} \times \tilde{I}(q_{12}, q_{23}, q_{31}) \quad (2.28)$$

where

$$\tilde{I} = \int d\Omega_1 d\Omega_2 d\Omega_3 Y_{l'_1 m'_1}^*(\hat{r}_1) Y_{l'_2 m'_2}^*(\hat{r}_2) Y_{l'_3 m'_3}^*(\hat{r}_3) Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 m_2}(\hat{r}_2) Y_{l_3 m_3}(\hat{r}_3) \times P_{q_{12}}(\cos \theta_{12}) P_{q_{23}}(\cos \theta_{23}) P_{q_{31}}(\cos \theta_{31}). \quad (2.29)$$

is the angular part of the integral and  $d\Omega_i = \sin \theta_i d\theta_i d\phi_i$ .

From Eqs. (2.26) and (2.28), we have the terms  $s_{ij}$  and  $g_{ij}$  denoting the smaller and greater of  $r_i$  and  $r_j$  respectively. It would therefore be convenient to break up the radial part of (2.28) into different regions covering the various possibilities of the relative sizes of  $r_1$ ,  $r_2$ , and  $r_3$ . For example, an integral over a function,  $F(r_1, r_2, r_3) = f(r_1)f(r_2)f(r_3)$ , may be split up in the following way

$$\begin{aligned} \int_0^\infty f(r_1) dr_1 \int_0^\infty f(r_2) dr_2 \int_0^\infty f(r_3) dr_3 &= \int_0^\infty f(r_1) dr_1 \int_{r_1}^\infty f(r_2) dr_2 \int_{r_2}^\infty f(r_3) dr_3 \\ &+ \int_0^\infty f(r_1) dr_1 \int_{r_1}^\infty f(r_3) dr_3 \int_{r_3}^\infty f(r_2) dr_2 \\ &+ \int_0^\infty f(r_2) dr_2 \int_{r_2}^\infty f(r_1) dr_1 \int_{r_1}^\infty f(r_3) dr_3 \\ &+ \int_0^\infty f(r_2) dr_2 \int_{r_2}^\infty f(r_3) dr_3 \int_{r_3}^\infty f(r_1) dr_1 \end{aligned}$$



$$\begin{aligned}
& + \int_0^\infty f(r_3)dr_3 \int_{r_3}^\infty f(r_1)dr_1 \int_{r_1}^\infty f(r_2)dr_2 \\
& + \int_0^\infty f(r_3)dr_3 \int_{r_3}^\infty f(r_2)dr_2 \int_{r_2}^\infty f(r_1)dr_1.
\end{aligned} \tag{2.30}$$

The first term on the right of (2.30), represents the region where,  $r_1 < r_2 < r_3$ , and the following terms represent the regions,  $r_1 < r_3 < r_2$ ,  $r_2 < r_1 < r_3$ ,  $r_2 < r_3 < r_1$ ,  $r_3 < r_1 < r_2$ , and  $r_3 < r_2 < r_1$ , respectively.

Let us define

$$\begin{aligned}
W \equiv & r_1^2 r_2^2 r_3^2 r_1^{j_1} r_2^{j_2} r_3^{j_3} e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3} g_{12}^{q_{12}+2k_{12}} g_{12}^{v_{12}-q_{12}-2k_{12}} g_{23}^{q_{23}+2k_{23}} g_{23}^{v_{23}-q_{23}-2k_{23}} \\
& \times g_{31}^{q_{31}+2k_{31}} g_{31}^{v_{31}-q_{31}-2k_{31}}
\end{aligned} \tag{2.31}$$

so that for the first region, we have

$$\begin{aligned}
W(1) & = \iiint r_1^{j_1+2} r_2^{j_2+2} r_3^{j_3+2} e^{-\alpha r_1} e^{-\beta r_2} e^{-\gamma r_3} r_1^{q_{12}+2k_{12}} r_2^{v_{12}-q_{12}-2k_{12}} r_2^{q_{23}+2k_{23}} r_3^{v_{23}-q_{23}-2k_{23}} \\
& \times r_1^{q_{31}+2k_{31}} r_3^{v_{31}-q_{31}-2k_{31}} dr_1 dr_2 dr_3 \\
& = \int_0^\infty r_1^{j_1+2+q_{12}+q_{31}+2k_{12}+2k_{31}} e^{-\alpha r_1} dr_1 \int_{r_1}^\infty r_2^{j_2+2+v_{12}-q_{12}+q_{23}-2k_{12}+2k_{23}} e^{-\beta r_2} dr_2 \\
& \times \int_{r_2}^\infty r_3^{j_3+2+v_{23}+v_{31}-q_{23}-q_{31}-2k_{31}-2k_{23}} e^{-\gamma r_3} dr_3.
\end{aligned} \tag{2.32}$$

Now, we introduce the following definition

$$W(l, m, n; \alpha, \beta, \gamma) \equiv \int_0^\infty dx x^l e^{-\alpha x} \int_x^\infty dy y^m e^{-\beta y} \int_y^\infty dz z^n e^{-\gamma z}. \tag{2.33}$$

The general analytic expression for this integral, derived by Drake and Yan [11], is

$$\begin{aligned}
W(l, m, n; \alpha, \beta, \gamma) & = \frac{l!}{(\alpha + \beta + \gamma)^{l+m+n+3}} \sum_{p=0}^{\infty} \frac{(l+m+n+p+2)!}{(l+1+p)!(l+m+2+p)} \left( \frac{\alpha}{\alpha + \beta + \gamma} \right)^p \\
& \times {}_2F_1 \left( 1, l+m+n+p+3; l+m+p+3; \frac{\alpha + \beta}{\alpha + \beta + \gamma} \right),
\end{aligned} \tag{2.34}$$

where  ${}_2F_1$  is the hypergeometric function. Equation (2.34) is valid for  $l \geq 0, l+m+1 \geq 0$ , and  $l+m+n+2 \geq 0$ .

With definition (2.33), (2.32) may be rewritten more succinctly as

$$W(1) = W(j_1 + 2 + g_{12} + g_{31} + 2k_{12} + 2k_{31}, j_2 + 2 + v_{12} - q_{12} + q_{23} - 2k_{12} + 2k_{23}, \\ j_3 + 2 + v_{23} + v_{31} - q_{23} - q_{31} - 2k_{31} - 2k_{23}; \alpha, \beta, \gamma)$$

Integrals for the other five regions may be written in a similar way using (2.33). After writing the integrals in this way Eq. (2.28) may be rewritten as

$$\begin{aligned} I &= I(l'_1 m'_1, l'_2 m'_2, l'_3 m'_3; l_1 m_1, l_2 m_2, l_3 m_3; j_1, j_2, j_3, v_{12}, v_{23}, v_{31}, \alpha, \beta, \gamma) \\ &= \sum_{q_{12}=0}^{L_{12}^{(1)}} \sum_{q_{23}=0}^{L_{23}^{(1)}} \sum_{q_{31}=0}^{L_{31}^{(1)}} \sum_{k_{12}=0}^{L_{12}^{(2)}} \sum_{k_{23}=0}^{L_{23}^{(2)}} \sum_{k_{31}=0}^{L_{31}^{(2)}} C_{v_{12} q_{12} k_{12}} C_{v_{23} q_{23} k_{23}} C_{v_{31} q_{31} k_{31}} \tilde{I}(q_{12}, q_{23}, q_{31}) [W(j_1 + 2 \\ &\quad + q_{12} + 2k_{12} + q_{31} + 2k_{31}, j_2 + 2 + v_{12} - q_{12} + q_{23} - 2k_{12} + 2k_{23}, j_3 + 2 + v_{23} \\ &\quad - q_{23} - 2k_{23} + v_{31} - q_{31} - 2k_{31}; \alpha, \beta, \gamma) + W(j_1 + 2 + q_{12} + 2k_{12} + q_{31} + 2k_{31}, j_3 \\ &\quad + 2 + q_{23} + 2k_{23} + v_{31} - q_{31} - 2k_{31}, j_2 + 2 + v_{12} - q_{12} - 2k_{12} + v_{23} - q_{23} \\ &\quad - 2k_{23}; \alpha, \beta, \gamma) + W(j_2 + 2 + q_{12} + 2k_{12} + q_{23} + 2k_{23}, j_1 + 2 + v_{12} - q_{12} - 2k_{12} \\ &\quad + q_{31} + 2k_{31}, j_3 + 2 + v_{23} - q_{23} - 2k_{23} + v_{31} - q_{31} - 2k_{31}; \beta, \alpha, \gamma) + W(j_2 + 2 + q_{12} \\ &\quad + 2k_{12} + q_{23} + 2k_{23}, j_3 + 2 + v_{23} - q_{23} - 2k_{23} + q_{31} + 2k_{31}, j_1 + 2 + v_{12} - q_{12} \\ &\quad - 2k_{12} + v_{31} - q_{31} - 2k_{31}; \beta, \gamma, \alpha) + W(j_3 + 2 + q_{23} + 2k_{23} + q_{31} + 2k_{31}, j_1 + 2 + q_{12} \\ &\quad + 2k_{12} + v_{31} - q_{31} - 2k_{31}, j_2 + 2 + v_{12} - q_{12} - 2k_{12} + v_{23} - q_{23} - 2k_{23}; \gamma, \alpha, \beta) \\ &\quad + W(j_3 + 2 + q_{23} + 2k_{23} + q_{31} + 2k_{31}, j_2 + 2 + q_{12} + 2k_{12} + v_{23} - q_{23} - 2k_{23}, j_1 + 2 \\ &\quad + v_{12} - q_{12} - 2k_{12} + v_{31} - q_{31} - 2k_{31}; \gamma, \beta, \alpha)] \\ &\equiv \sum_{q_{12}=0}^{L_{12}^{(1)}} \sum_{q_{23}=0}^{L_{23}^{(1)}} \sum_{q_{31}=0}^{L_{31}^{(1)}} \sum_{k_{12}=0}^{L_{12}^{(2)}} \sum_{k_{23}=0}^{L_{23}^{(2)}} \sum_{k_{31}=0}^{L_{31}^{(2)}} \tilde{I}(q_{12}, q_{23}, q_{31}, l'_1 m'_1, l'_2 m'_2, l'_3 m'_3; l_1 m_1, l_2 m_2, l_3 m_3) \\ &\quad \times I_R(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, v_{12}, v_{23}, v_{31}, \alpha, \beta, \gamma) \end{aligned} \quad (2.35)$$

where  $I_R$  is the radial part.

Evaluating Eq. (2.29), see Appendix B, we obtain

$$\begin{aligned}
\tilde{I} &= (-1)^{m'_1+m'_2+m'_3} (-1)^{q_{12}+q_{23}+q_{31}} (l_1, l_2, l_3, l'_1, l'_2, l'_3)^{\frac{1}{2}} \sum_{n_1 n_2 n_3} (n_1, n_2, n_3) \begin{Bmatrix} n_1 & n_2 & n_3 \\ q_{23} & q_{31} & q_{12} \end{Bmatrix} \\
&\times \begin{pmatrix} n_1 & n_2 & n_3 \\ m'_1 - m_1 & m_2 - m'_2 & m'_3 - m_3 \end{pmatrix} \begin{pmatrix} l'_1 & l_1 & n_1 \\ -m'_1 & m_1 & m'_1 - m_1 \end{pmatrix} \\
&\times \begin{pmatrix} l'_2 & l_2 & n_2 \\ -m'_2 & m_2 & m'_2 - m_2 \end{pmatrix} \begin{pmatrix} l'_3 & l_3 & n_3 \\ -m'_3 & m_3 & m'_3 - m_3 \end{pmatrix} \begin{pmatrix} l'_1 & l_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & l_2 & n_2 \\ 0 & 0 & 0 \end{pmatrix} \\
&\times \begin{pmatrix} l'_3 & l_3 & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{23} & q_{12} & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{31} & q_{23} & n_3 \\ 0 & 0 & 0 \end{pmatrix} \\
&\equiv \tilde{I}(q_{12}, q_{23}, q_{31}, ; l'_1 m'_1, l'_2 m'_2, l'_3 m'_3; l_1 m_1, l_2 m_2, l_3 m_3) \tag{2.36}
\end{aligned}$$

for the angular part of the part of the integral. In the case of the  $S$  states the angular integral is particularly simple since,  $l_i = l'_i = m_i = m'_i = 0$ , so that (2.36) simply reduces to

$$\tilde{I} = \frac{1}{(2q_{12} + 1)^2} \delta_{q_{12}, q_{23}} \delta_{q_{23}, q_{31}}. \tag{2.37}$$

This result is easily arrived at by applying the triangle selection rule together with Eq. (2.36) and the relation

$$\begin{Bmatrix} a & b & 0 \\ A & B & C \end{Bmatrix} = (-1)^{a+A+C} [(2a+1)(2A+1)]^{-1/2} \delta_{a,b} \delta_{A,B}. \tag{2.38}$$

Thus, for the  $S$  states, Eq. (2.35) reduces to

$$I = \sum_{q_{12}=0}^{L_{12}^{(1)}} \sum_{k_{12}=0}^{L_{12}^{(2)}} \sum_{k_{23}=0}^{L_{23}^{(2)}} \sum_{k_{31}=0}^{L_{31}^{(2)}} \frac{1}{(2q_{12} + 1)^2} I_R(q_{12}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, v_{12}, v_{23}, v_{31}, \alpha, \beta, \gamma). \tag{2.39}$$

In general, it can be seen from the 3- $j$  symbols in Eq. (2.36), that all of the sums

$$\begin{aligned} l'_1 + l_1 + n_1, & \quad q_{12} + q_{31} + n_1 \\ l'_2 + l_2 + n_2, & \quad q_{23} + q_{12} + n_2 \\ l'_3 + l_3 + n_3, & \quad q_{31} + q_{23} + n_3 \end{aligned}$$

must be even in order for the integral  $I$  to be nonzero. Also, from (2.36) we see that the triangle selection rule requires that

$$\begin{aligned} |q_{12} - q_{31}| &\leq n_1 \leq |q_{12} + q_{31}|, \\ |q_{23} - q_{12}| &\leq n_2 \leq |q_{23} + q_{12}|, \text{ and} \\ |q_{31} - q_{23}| &\leq n_3 \leq |q_{31} + q_{23}|. \end{aligned} \tag{2.40}$$

Now, from (2.26), we see that the sum over the  $q_{ij}$ 's is infinite for odd values of  $v_{ij}$ , where  $i, j = 1, 2, 3$ . However, if at least one of the  $v_{ij}$ 's is even, the sums over the  $q_{ij}$ 's in (2.35) become finite due to the triangle inequalities (2.40). If all of the  $v_{ij}$ 's are odd numbers, then a numerical summation of an infinite series is required. In the past, these infinite summations have made calculations for the larger basis sets very time consuming. Recently, however, this problem has been overcome by Drake and Yan [11]. They used an asymptotic-expansion method which accelerated the rate of convergence of these infinite series. A concise description of this method is give in the following section.

### 2.4.1 The Asymptotic-Expansion Method

If  $v_{12}$ ,  $v_{23}$ , and  $v_{31}$  are all odd numbers, then it can be seen from (2.26) that the summations over  $q_{12}$ ,  $q_{23}$ , and  $q_{31}$  will be from zero to infinity. However, the  $q$ 's are related by the triangle inequalities (2.40) so that, in fact, only one of the summations over the  $q$ 's will be from zero to infinity. For example, if we choose the summation over  $q_{12}$  to be infinite, then the summations over  $q_{23}$  and  $q_{31}$  become finite. The upper limits are obtained from the relations (2.40). Thus, if all three powers  $v_{12}$ ,  $v_{23}$ , and  $v_{31}$  are odd,

(2.35) may be written as

$$I = \sum_{q=0}^{\infty} T(q), \quad (2.41)$$

where

$$\begin{aligned} T(q) = & \sum_{q_{23}=0}^{L_{23}^{(1)}} \sum_{q_{31}=0}^{L_{31}^{(1)}} \sum_{k_{12}=0}^{L_{12}^{(2)}} \sum_{k_{23}=0}^{L_{23}^{(2)}} \sum_{k_{31}=0}^{L_{31}^{(2)}} \tilde{I}(q_{12}, q_{23}, q_{31}, l'_1 m'_1, l'_2 m'_2, l'_3 m'_3; l_1 m_1, l_2 m_2, l_3 m_3) \\ & \times I_R(q_{12}, q_{23}, q_{31}, k_{12}, k_{23}, k_{31}; j_1, j_2, j_3, v_{12}, v_{23}, v_{31}, \alpha, \beta, \gamma), \end{aligned} \quad (2.42)$$

and  $q = q_{12}$ .

In calculating the integral  $I$ , we note that Eq. (2.41) is essentially composed of the  $W$  integral. The hypergeometric functions contained in this integral, Eq. (2.34), are calculated using the backward recursion relation

$${}_2F_1(1, s+t; s; z) = 1 + \left( \frac{s+t}{s} \right) z {}_2F_1(1, s+t+1; s+1; z). \quad (2.43)$$

A derivation of this result is given in Appendix C. To deal with the infinite sum over  $q$ , the asymptotic-expansion method is employed. This method follows from the asymptotic behaviour of  $T(q)$  as  $q \rightarrow \infty$ . From the  $W$  integral, Eq. (2.34), we see that  $W \sim 1/q^2$ , and from (2.27) we see that  $C_{\nu q k} \sim 1/q^{(\nu+1)/2}$ . Combining the asymptotic behaviour from  $W$  and the  $C_{\nu q k}$ 's in (2.35), we find that

$$T(q) \sim \frac{1}{q^\lambda}, \text{ as } q \rightarrow \infty, \quad (2.44)$$

where

$$\lambda = \frac{v_{12} + 1}{2} + \frac{v_{23} + 1}{2} + \frac{v_{31} + 1}{2} + 4. \quad (2.45)$$

To take advantage of the asymptotic behaviour of  $T(q)$ , Eq. (2.41) is split up into two parts

$$I = \sum_{q=0}^N T(q) + \sum_{q=N+1}^{\infty} T(q). \quad (2.46)$$

This way, the first  $N$  terms are calculated directly from (2.35), and the remaining  $T(q)$  terms may be estimated, for each  $q$ , from their asymptotic expansions

$$T(q) = \sum_{i=0}^{\infty} \frac{A_i}{q^{i+\lambda}}, \quad (2.47a)$$

provided that  $N$  is chosen sufficiently large. Substituting (2.47a) into (2.46), we obtain

$$\begin{aligned} I &= \sum_{q=0}^N T(q) + \sum_{q=N+1}^{\infty} \left( \sum_{i=0}^{\infty} \frac{A_i}{q^{i+\lambda}} \right) \\ &= \sum_{q=0}^N T(q) + \sum_{i=0}^{\infty} A_i \left( \sum_{q=N+1}^{\infty} \frac{1}{q^{i+\lambda}} \right) \\ &= \sum_{q=0}^N T(q) + \sum_{i=0}^{\infty} A_i \zeta_N(i + \lambda), \end{aligned} \quad (2.48)$$

where  $\zeta_N(i) = \sum_{k=N+1}^{\infty} 1/k^i$  is the Riemann zeta function with the first  $N$  terms subtracted. It can now be seen that the second sum in (2.48) converges as  $1/(N+1)^{i+\lambda}$ , and for  $N$  sufficiently large  $\zeta_N(i + \lambda) \sim 1/(N+1)^{i+\lambda}$  so that only the first few coefficients  $A_i$  need to be determined.

To determine these coefficients the infinite summation (2.47a) is truncated, and the new upper limit is taken to be some integer  $M$ . It is assumed that for a suitable choice of  $M$ , the directly calculated  $T(q)$  are given exactly by the truncated expansion, and for  $q$  large enough, this assumption is true to machine precision. Hence, for a large enough  $q$  and a suitable value of  $M$  we may use our calculated values of  $T(q)$  to obtain the following  $M + 1$  system of equations

$$\begin{aligned} T(N - M) &= \frac{A_0}{(N - M)^\lambda} + \frac{A_1}{(N - M)^{1+\lambda}} + \cdots + \frac{A_M}{(N - M)^{M+\lambda}} \\ T(N - M + 1) &= \frac{A_0}{(N - M + 1)^\lambda} + \frac{A_1}{(N - M + 1)^{1+\lambda}} + \cdots + \frac{A_M}{(N - M + 1)^{M+\lambda}} \\ &\vdots \end{aligned}$$

$$T(N) = \frac{A_0}{(N)^\lambda} + \frac{A_1}{(N)^{1+\lambda}} + \cdots + \frac{A_M}{(N)^{M+\lambda}}, \quad (2.49)$$

which may be solved for the  $M + 1$  unknowns,  $A_i$ , where  $i = 0, \dots, M$ . Therefore, the final estimate of the integral is obtained from

$$I = \sum_{q=0}^N T(q) + \sum_{i=0}^M A_i \zeta_N(i + \lambda). \quad (2.50)$$

The calculation is carried out by increasing  $N$  until  $I$  no longer changes to machine accuracy. The size of  $N$  required for convergence depends on the size of  $M$ , that is, the larger  $M$  is the smaller  $N$  needs to be to achieve the same convergence. However, as  $M$  gets larger, the time required to solve (2.49) becomes greater and calculation become less efficient. Therefore, the limits of  $M$  and  $N$  are adjusted so as to optimize the convergence and time required for the calculation.

# Chapter 3

## Calculation of the $Z$ -Expansions

A  $Z$ -expansion of a particular state is simply the energy of that state expressed as a power series in  $Z^{-1}$ . To see how the  $Z$ -expansion is found, we begin by breaking up our Hamiltonian for the three electron case, Eq. (2.2), so that we have

$$H = H_0 + H_1 \tag{3.1}$$

where

$$H_0 = -\frac{1}{2} \sum_{i=1}^3 \left( \nabla_i^2 - \frac{1}{r_i} \right) \tag{3.2}$$

and

$$H_1 = \frac{1}{Z} \sum_{i=1}^3 \sum_{j>i}^3 \frac{1}{r_{ij}} = \frac{1}{Z} \left( \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right). \tag{3.3}$$

We next define  $V \equiv \left( \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$ , and  $\lambda \equiv Z^{-1}$ , so that, (3.1) becomes

$$H = H_0 + \lambda V. \tag{3.4}$$

With the Hamiltonian written this way,  $\lambda = Z^{-1}$  appears explicitly as a perturbation parameter multiplying the electron-electron Coulomb interaction terms.

Now, if we were to ignore  $\lambda V$  in the total Hamiltonian (3.4), we would have a solution



to the eigenvalue problem for the noninteracting three-electron system. The eigenvalue equation for this system would be

$$H_0 \Psi_n^{(0)} = \varepsilon_n^{(0)} \Psi_n^{(0)} \quad (3.5)$$

where the eigenfunctions would be a simple product of one electron orbitals,

$$\Psi_n^{(0)} = \Psi_{n_1 l_1 m_{l_1} m_{s_1}}(\mathbf{r}_1) \Psi_{n_2 l_2 m_{l_2} m_{s_2}}(\mathbf{r}_2) \Psi_{n_3 l_3 m_{l_3} m_{s_3}}(\mathbf{r}_3) \quad (3.6)$$

(with the notation  $\Psi_{n_j l_j m_{l_j} m_{s_j}}(\mathbf{r}_j) = R_{n_j l_j}(r_j) Y_{l_j m_{l_j}}(\theta, \phi) |s m_s\rangle$ ) and the eigenvalues would be given by the sum of hydrogenic eigenvalues

$$\varepsilon_n^{(0)} = \varepsilon_{n_1} + \varepsilon_{n_2} + \varepsilon_{n_3} \quad (3.7)$$

where  $\varepsilon_{n_i} = -1/2n_i^2$ . Thus, we would have the eigenvalues and the complete set of eigenfunctions for the unperturbed Hamiltonian  $H_0$ . However, we seek the eigenvalues for the Hamiltonian (3.4). To this end, we use the fact that the  $\Psi_n^{(0)}$  form a complete set, so that the eigenfunctions of (3.4) may be expanded in a series involving all the  $\Psi_n^{(0)}$  as follows

$$\Phi_n = \Psi_n^{(0)} + \sum_{k \neq n} C_{nk}(\lambda) \Psi_k^{(0)}, \quad (3.8)$$

where

$$C_{nk}(\lambda) = \lambda C_{nk}^{(1)} + \lambda^2 C_{nk}^{(2)} + \dots, \quad (3.9)$$

and

$$\varepsilon_n = \sum_{i=0}^{\infty} \lambda^i \varepsilon_n^{(i)} = \varepsilon_n^{(0)} + \lambda \varepsilon_n^{(1)} + \lambda^2 \varepsilon_n^{(2)} + \dots, \quad (3.10)$$

The subscripts in these equations denote the particular eigenstate or eigenvalue, the superscripts in brackets denote the order of the correction, and  $\Phi_n$  and  $\varepsilon_n$  are the eigenfunctions and eigenvalues, respectively, corresponding to the Hamiltonian (3.4). To be

more compact, we rewrite (3.8) as

$$\Phi_n = \sum_{i=0}^{\infty} \lambda^i \Psi_n^{(i)} = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots, \quad (3.11)$$

where

$$\Psi_n^{(i)} = \sum_{k \neq n} C_{nk}^{(i)} \Psi_k^{(0)}. \quad (3.12)$$

Using this notation, we have

$$(H_0 + \lambda V) \Phi_n = \varepsilon_n \Phi_n \quad (3.13)$$

or

$$(H_0 + \lambda V) \sum_{i=0}^{\infty} \lambda^i \Psi_n^{(i)} = \varepsilon_n \sum_{i=0}^{\infty} \lambda^i \Psi_n^{(i)} \quad (3.14)$$

Expanding out the first few terms explicitly, we have

$$\begin{aligned} (H_0 + \lambda V) (\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots) &= (\varepsilon_n^{(0)} + \lambda \varepsilon_n^{(1)} + \lambda^2 \varepsilon_n^{(2)} + \dots) \\ &\times (\Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots) \end{aligned} \quad (3.15)$$

Now, collecting coefficients of equal powers of  $\lambda$  yields a series of equations. For example, the terms of the zeroth power in  $\lambda$  yield Eq. (3.5), and the terms of first power in  $\lambda$  gives us

$$V \Psi_n^{(0)} + H_0 \Psi_n^{(1)} = \varepsilon_n^{(0)} \Psi_n^{(1)} + \varepsilon_n^{(1)} \Psi_n^{(0)} \quad (3.16)$$

If we now take a scalar product of (3.16) with  $\Psi_n^{(0)}$ , and assume that the complete basis set is orthonormal, that is,  $\langle \Psi_k^{(0)} | \Psi_n^{(0)} \rangle = \delta_{kn}$ , we obtain

$$\varepsilon_n^{(1)} = \langle \Psi_n^{(0)} | V | \Psi_n^{(0)} \rangle \quad (3.17)$$

This is the second coefficient of our energy expansion (3.10), and it is just the expectation value of the potential with states  $\Psi_n^{(0)}$  which are known exactly (3.6). Since the states  $\Psi_n^{(0)}$  are known exactly, an exact analytic solution for the value of  $\varepsilon_n^{(1)}$  from (3.17) may

be found. However, in general we have

$$\varepsilon_n^{(k)} = \langle \Psi_n^{(0)} | V | \Psi_n^{(k-1)} \rangle \quad (3.18)$$

which contains the states  $\Psi_n^{(k-1)}$ , and for  $k > 1$ , these states are not known exactly. As a result, only the first two coefficients,  $\varepsilon_n^{(0)}$  and  $\varepsilon_n^{(1)}$ , of our energy expansion (3.10) may be determined exactly. An analytic calculation of these two terms as well as the least squares technique to determine some of the higher terms will be presented in the next two sections. These calculations will be done for the  $1s^2 2s^2 S$  and  $1s^2 2p^2 P$  states of the lithium isoelectronic sequence.

### 3.1 Analytic Calculation of $\varepsilon_n^{(0)}$ and $\varepsilon_n^{(1)}$

Before we proceed with the analytical calculation for the first two energy coefficients from (3.10), we multiply this expansion by  $Z^2 = \lambda^{-2}$  so that the energy is expressed back in atomic units. That is,

$$\begin{aligned} E_n &= Z^2 \varepsilon_n \\ &= Z^2 \varepsilon_n^{(0)} + Z \varepsilon_n^{(1)} + \varepsilon_n^{(2)} + Z^{-1} \varepsilon_n^{(3)} + \dots \end{aligned} \quad (3.19)$$

Equation (3.19) is the  $Z$ -expansion equation.

In order to calculate the first coefficient  $\varepsilon_n^{(0)}$  we refer to the separable eigenvalue equation (3.5) which has eigenvalues given by (3.7). Now the energy terms  $\varepsilon_{n_1}$ ,  $\varepsilon_{n_2}$ , and  $\varepsilon_{n_3}$  from (3.7) correspond to the hydrogen states  $\Psi_{n_1 l_1 m_{l_1} m_{s_1}}(\mathbf{r}_1)$ ,  $\Psi_{n_2 l_2 m_{l_2} m_{s_2}}(\mathbf{r}_2)$ , and  $\Psi_{n_3 l_3 m_{l_3} m_{s_3}}(\mathbf{r}_3)$  respectively, and are simply the hydrogen energies  $-1/2n_j^2$  (in  $Z$ -scaled atomic units), where  $j = 1, 2$ , or  $3$ . Thus, for the  $1s^2 2s^2 S$  and  $1s^2 2p^2 P$  states these

energies are given by

$$\begin{aligned}
\varepsilon_{2s}^{(0)} &= \varepsilon_{2p}^{(0)} = - \sum_{j=1}^3 \frac{1}{2r_j^2} \\
&= -\frac{1}{2} - \frac{1}{2} - \frac{1}{2(2)^2} \\
&= -\frac{9}{8}.
\end{aligned} \tag{3.20}$$

Next we present the less trivial analytical calculation for the second energy coefficient,  $\varepsilon_n^{(1)}$ .

In order to simplify the notation, we begin by writing out our product of hydrogen wave functions (3.6) as

$$\left| \Psi_{1s^2 2l}^{(0)} \right\rangle = |\Psi_{1s}(r_1)\alpha(1)\rangle |\Psi_{1s}(r_2)\beta(2)\rangle |\Psi_{2l}(r_3)\alpha(3)\rangle \tag{3.21}$$

where  $\alpha$  and  $\beta$  represent spin up and spin down respectively, and the subscript  $l$  in the third state represents the quantum label  $s$  or  $p$ . Now, due to the Pauli exclusion principle, the total wavefunction is the antisymmetrized product of the spin-orbitals. The antisymmetrizing of (3.21) may be expressed as

$$\left| \Psi_{1s^2 2l}^{(0)} \right\rangle = \mathcal{A} |\Psi_{1s}(r_1)\alpha(1)\rangle |\Psi_{1s}(r_2)\beta(2)\rangle |\Psi_{2l}(r_3)\alpha(3)\rangle \tag{3.22}$$

where  $\mathcal{A}$  is the three particle antisymmetrizer given by (2.11). Writing (3.22) out explicitly, we obtain

$$\begin{aligned}
\left| \Psi_{1s^2 2l}^{(0)} \right\rangle &= \frac{1}{\sqrt{6}} [ |\Psi_{1s}(r_1)\alpha(1)\rangle |\Psi_{1s}(r_2)\beta(2)\rangle |\Psi_{2l}(r_3)\alpha(3)\rangle - |\Psi_{1s}(r_2)\alpha(2)\rangle \\
&\quad \times |\Psi_{1s}(r_1)\beta(1)\rangle |\Psi_{2l}(r_3)\alpha(3)\rangle - |\Psi_{1s}(r_3)\alpha(3)\rangle |\Psi_{1s}(r_2)\beta(2)\rangle |\Psi_{2l}(r_1)\alpha(1)\rangle \\
&\quad - |\Psi_{1s}(r_1)\alpha(1)\rangle |\Psi_{1s}(r_3)\beta(3)\rangle |\Psi_{2l}(r_2)\alpha(2)\rangle + |\Psi_{1s}(r_2)\alpha(2)\rangle \\
&\quad \times |\Psi_{1s}(r_3)\beta(3)\rangle |\Psi_{2l}(r_1)\alpha(1)\rangle + |\Psi_{1s}(r_3)\alpha(3)\rangle |\Psi_{1s}(r_1)\beta(1)\rangle |\Psi_{2l}(r_2)\alpha(2)\rangle ]
\end{aligned}$$

Rewriting the orbital and spin part separately, this becomes

$$\begin{aligned}
\left| \Psi_{1s^2 2l}^{(0)} \right\rangle &= \frac{1}{\sqrt{6}} [ |\Psi_{1s}(r_1)\Psi_{1s}(r_2)\Psi_{2l}(r_1)\rangle |\alpha(1)\beta(2)\alpha(3)\rangle - |\Psi_{1s}(r_2)\Psi_{1s}(r_1)\Psi_{2l}(r_3)\rangle \\
&\quad \times |\beta(1)\alpha(2)\alpha(3)\rangle - |\Psi_{1s}(r_3)\Psi_{1s}(r_2)\Psi_{2l}(r_1)\rangle |\alpha(1)\beta(2)\alpha(3)\rangle \\
&\quad - |\Psi_{1s}(r_1)\Psi_{1s}(r_3)\Psi_{2l}(r_2)\rangle |\alpha(1)\alpha(2)\beta(3)\rangle + |\Psi_{1s}(r_2)\Psi_{1s}(r_3)\Psi_{2l}(r_1)\rangle \\
&\quad \times |\alpha(1)\alpha(2)\beta(3)\rangle + |\Psi_{1s}(r_3)\Psi_{1s}(r_3)\Psi_{2l}(r_2)\rangle |\beta(1)\alpha(2)\alpha(3)\rangle ] \\
&= \frac{1}{\sqrt{6}} [ |\Psi_{1s}(r_1)\Psi_{1s}(r_2)\Psi_{2l}(r_3)\rangle (|\alpha(1)\beta(2)\alpha(3)\rangle - |\beta(1)\alpha(2)\alpha(3)\rangle) \\
&\quad + |\Psi_{1s}(r_3)\Psi_{1s}(r_1)\Psi_{2l}(r_2)\rangle (|\beta(1)\alpha(2)\alpha(3)\rangle - |\alpha(1)\alpha(2)\beta(3)\rangle) \\
&\quad + |\Psi_{1s}(r_2)\Psi_{1s}(r_3)\Psi_{2l}(r_1)\rangle (|\alpha(1)\alpha(2)\beta(3)\rangle - |\alpha(1)\beta(2)\alpha(3)\rangle) ]
\end{aligned}$$

To be more compact, let us set

$$|u\rangle = |\Psi_{1s}(r_1)\Psi_{1s}(r_2)\Psi_{2l}(r_3)\rangle, \quad (3.23)$$

$$|v\rangle = |\Psi_{1s}(r_3)\Psi_{1s}(r_1)\Psi_{2l}(r_2)\rangle, \quad (3.24)$$

and

$$|w\rangle = |\Psi_{1s}(r_2)\Psi_{1s}(r_3)\Psi_{2l}(r_1)\rangle. \quad (3.25)$$

Using this more compact notation, and suppressing the spin coordinates, the second energy coefficient of the  $Z$ -expansion can be written as

$$\begin{aligned}
\varepsilon_n^{(1)} &= \left\langle \Psi_{1s^2 2l}^{(0)} \left| V \right| \Psi_{1s^2 2l}^{(0)} \right\rangle \\
&= [\langle u | (\langle \alpha\beta\alpha | - \langle \beta\alpha\alpha |) + \langle v | (\langle \beta\alpha\alpha | - \langle \alpha\alpha\beta |) + \langle w | (\langle \alpha\alpha\beta | - \langle \alpha\beta\alpha |)] \\
&\quad V [|u\rangle (|\alpha\beta\alpha\rangle - |\beta\alpha\alpha\rangle) + |v\rangle (|\beta\alpha\alpha\rangle - |\alpha\alpha\beta\rangle) + |w\rangle (|\alpha\alpha\beta\rangle - |\alpha\beta\alpha\rangle)] \\
&= \langle u | V |u\rangle (\langle \alpha\beta\alpha | \alpha\beta\alpha\rangle + \langle \beta\alpha\alpha | \beta\alpha\alpha\rangle) + \langle v | V |v\rangle (\langle \beta\alpha\alpha | \beta\alpha\alpha\rangle + \langle \alpha\alpha\beta | \alpha\alpha\beta\rangle) \\
&\quad + \langle w | V |w\rangle (\langle \alpha\alpha\beta | \alpha\alpha\beta\rangle + \langle \alpha\beta\alpha | \alpha\beta\alpha\rangle) - \langle u | V |v\rangle \langle \beta\alpha\alpha | \beta\alpha\alpha\rangle \\
&\quad - \langle u | V |w\rangle \langle \alpha\beta\alpha | \alpha\beta\alpha\rangle - \langle v | V |u\rangle \langle \beta\alpha\alpha | \beta\alpha\alpha\rangle - \langle v | V |w\rangle \langle \alpha\alpha\beta | \alpha\alpha\beta\rangle \\
&\quad - \langle w | V |u\rangle \langle \alpha\beta\alpha | \alpha\beta\alpha\rangle - \langle w | V |v\rangle \langle \alpha\alpha\beta | \alpha\alpha\beta\rangle
\end{aligned}$$

$$= \frac{1}{6} \iiint V(2u^*u + 2v^*v + 2w^*w - u^*v - v^*u - u^*w - w^*u - v^*w - w^*v) d^3r_1 d^3r_2 d^3r_3. \quad (3.26)$$

Now, without loss of generality, let us choose the magnetic quantum number  $m$  equal to zero for the  $\Psi_{2l}$  state. With this choice for  $m$ , the states  $u$ ,  $v$ , and  $w$  will be real and the above integral simplifies to

$$\epsilon_n^{(1)} = \frac{1}{3} \iiint \left( \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right) (u^2 + v^2 + w^2 - uv - uw - vw) d^3r_1 d^3r_2 d^3r_3, \quad (3.27)$$

where we have written out  $V$  explicitly.

Evaluation of the above integral (3.27) may be further simplified by grouping integrals that are the same and eliminating cases that vanish due to the orthogonality of  $\Psi_{1s}(r)$  and  $\Psi_{2l}(r)$ . For example, integrals such as

$$\iiint u \frac{1}{r_{13}} v d^3r_1 d^3r_2 d^3r_3 = \iiint \Psi_{1s}(r_1) \Psi_{1s}(r_2) \Psi_{2l}(r_3) \frac{1}{r_{13}} \Psi_{1s}(r_1) \Psi_{1s}(r_2) \Psi_{2l}(r_3) d^3r_1 d^3r_2 d^3r_3, \quad (3.28)$$

and

$$\iiint v \frac{1}{r_{12}} u d^3r_1 d^3r_2 d^3r_3 = \iiint \Psi_{1s}(r_1) \Psi_{2l}(r_2) \Psi_{1s}(r_3) \frac{1}{r_{12}} \Psi_{1s}(r_1) \Psi_{2l}(r_2) \Psi_{1s}(r_3) d^3r_1 d^3r_2 d^3r_3 \quad (3.29)$$

are clearly identical, and integrals of the type

$$\begin{aligned} \iiint u \frac{1}{r_{13}} v d^3r_1 d^3r_2 d^3r_3 &= \iiint \Psi_{1s}(r_1) \Psi_{1s}(r_2) \Psi_{2l}(r_3) \frac{1}{r_{13}} \Psi_{1s}(r_1) \Psi_{2l}(r_2) \Psi_{1s}(r_3) d^3r_1 d^3r_2 d^3r_3 \\ &= \int \frac{1}{r_{13}} \Psi_{1s}^2(r_1) \left[ \int \Psi_{2l}(r_3) \Psi_{1s}(r_3) d^3r_3 \right] d^3r_1 \int \Psi_{1s}^2(r_2) d^3r_2 \end{aligned} \quad (3.30)$$

are equal to zero. A summary of all such possible integrals is shown in Table 3.1.

From Table 3.1 we see that there are three distinct types of integrals which have nonzero values. There are six integrals of type (A), three integrals of type (B), and three

Table 3.1: The different types of integrals involved in the calculation of  $\varepsilon_n^{(1)}$ .

INTEGRALS OF TYPE (A)	INTEGRALS OF TYPE (B)
$\iiint u \frac{1}{r_{13}} u d^3 r_1 d^3 r_2 d^3 r_3 = \iiint u \frac{1}{r_{23}} u d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$	$\iiint u \frac{1}{r_{12}} u d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$
$\iiint v \frac{1}{r_{12}} v d^3 r_1 d^3 r_2 d^3 r_3 = \iiint v \frac{1}{r_{23}} v d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$	$\iiint v \frac{1}{r_{13}} v d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$
$\iiint w \frac{1}{r_{12}} w d^3 r_1 d^3 r_2 d^3 r_3 = \iiint w \frac{1}{r_{13}} w d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$	$\iiint w \frac{1}{r_{23}} w d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$
INTEGRALS OF TYPE (D)	INTEGRALS OF TYPE (C)
$\iiint u \frac{1}{r_{12}} v d^3 r_1 d^3 r_2 d^3 r_3 = \iiint u \frac{1}{r_{13}} v d^3 r_1 d^3 r_2 d^3 r_3 = 0$	$\iiint u \frac{1}{r_{23}} v d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$
$\iiint u \frac{1}{r_{12}} w d^3 r_1 d^3 r_2 d^3 r_3 = \iiint u \frac{1}{r_{23}} w d^3 r_1 d^3 r_2 d^3 r_3 = 0$	$\iiint u \frac{1}{r_{13}} w d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$
$\iiint v \frac{1}{r_{13}} w d^3 r_1 d^3 r_2 d^3 r_3 = \iiint v \frac{1}{r_{23}} w d^3 r_1 d^3 r_2 d^3 r_3 = 0$	$\iiint v \frac{1}{r_{12}} w d^3 r_1 d^3 r_2 d^3 r_3 \neq 0$

integrals of type (C). Let us choose to evaluate the integrals

$$\iiint u \frac{1}{r_{13}} u d^3 r_1 d^3 r_2 d^3 r_3 = A, \quad (3.31)$$

$$\iiint v \frac{1}{r_{13}} v d^3 r_1 d^3 r_2 d^3 r_3 = B, \quad (3.32)$$

and

$$\iiint u \frac{1}{r_{13}} w d^3 r_1 d^3 r_2 d^3 r_3 = C \quad (3.33)$$

from each of the three distinct types. Thus, the integral for the second coefficient (3.27) reduces to

$$\varepsilon_n^{(1)} = \frac{1}{3} (6A + 3B - 3C). \quad (3.34)$$

Techniques for the evaluation of the general form of the integrals (3.31), (3.32), and (3.33) are given in Appendix D. In the following two sections, we make use of the results derived in Appendix D to calculate the first order energy corrections  $\varepsilon_{2s}^{(1)}$  and  $\varepsilon_{2p}^{(1)}$ , for the  $1s^2 2s^2 S$  and  $1s^2 2p^2 P$  states, respectively.

In Table 3.2 the principal and angular quantum numbers for the two states for which the integrals to be evaluated are shown. For the particular state being evaluated, the

Table 3.2: The principal and angular quantum numbers for the  $1s^2 2s^2 S$  and  $1s^2 2p^2 P$  states.

Integrals	State	$n_1$	$n_2$	$n_3$	$n'_1$	$n'_2$	$n'_3$	$l_1$	$l_2$	$l_3$	$l'_1$	$l'_2$	$l'_3$
$A = \iiint u \frac{1}{r_{13}} v d^3 r_1 d^3 r_2 d^3 r_3$	$1s^2 2s^2 S$	1	1	2	1	1	2	0	0	0	0	0	0
	$1s^2 2p^2 P$	1	1	2	1	1	2	0	0	1	0	0	1
$B = \iiint v \frac{1}{r_{13}} v d^3 r_1 d^3 r_2 d^3 r_3$	$1s^2 2s^2 S$	1	2	1	1	2	1	0	0	0	0	0	0
	$1s^2 2p^2 P$	1	2	1	1	2	1	0	1	0	0	1	0
$C = \iiint u \frac{1}{r_{13}} w d^3 r_1 d^3 r_2 d^3 r_3$	$1s^2 2s^2 S$	1	1	2	2	1	1	0	0	0	0	0	0
	$1s^2 2p^2 P$	1	1	2	2	1	1	0	0	1	1	0	0

corresponding quantum numbers are substituted into into (D.17) in order to determine the value of the angular part of the integral.

### Calculation of $\varepsilon_n^{(1)}$ for the $1s^2 2s^2 S$ States

From Table 3.2 we see that the angular momentum quantum numbers for the  $1s^2 2s^2 S$  state are all zero. Thus, Eq. (D.18) becomes

$$\begin{aligned}
 I &= \sum_{k=0}^{\infty} R_{13}^{(k)} \sum_{q=-k}^k \frac{(2k+1)}{4\pi} \begin{pmatrix} k & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & 0 & 0 \\ q & 0 & 0 \end{pmatrix} \begin{pmatrix} k & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & 0 & 0 \\ q & 0 & 0 \end{pmatrix} \\
 &= \sum_{k=0}^{\infty} R_{13}^{(k)} \delta_{k,0} = R_{13}^{(0)}, \tag{3.35}
 \end{aligned}$$

since by the triangular rule, the 3- $j$  symbols vanish for  $k \neq 0$ . Thus, we have

$$\begin{aligned}
 I &= R_{13}^{(0)} \\
 &= \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \int_0^{\infty} r_3^2 dr_3 R_{n_1 0}(r_1) R_{n_2 0}(r_2) R_{n_3 0}(r_3) \\
 &\quad \times \frac{1}{r_{>}} R_{n'_1 0}(r_1) R_{n'_2 0}(r_2) R_{n'_3 0}(r_3), \tag{3.36}
 \end{aligned}$$

where  $r_{>}$  is the greater of  $r_i$  and  $r_j$ , where  $i$  and  $j$  are the subscripts of the radial integrals represented by  $R_{ij}^{(k)}$ , see Eq. (D.5). Now using relation (D.20), and Eqs. (D.21), (D.22),



and (D.23) we calculate the integrals  $A$ ,  $B$ , and  $C$ . Calculating integral  $A$ , we get

$$\begin{aligned}
A &= \iiint u \frac{1}{r_{13}} u d^3 r_1 d^3 r_2 d^3 r_3 = R_{13}^{(0)}(10, 10, 20, 10, 10, 20) \\
&= \int_0^\infty \frac{1}{r_>} r_1^2 R_{10}^2(r_1) dr_1 \int_0^\infty r_2^2 R_{10}^2(r_2) dr_2 \int_0^\infty r_3^2 R_{20}^2(r_3) dr_3 \\
&= 4 \int_0^\infty \frac{1}{r_>} r_1^2 e^{-2r_1} dr_1 4 \int_0^\infty r_2^2 e^{-2r_2} dr_2 \frac{1}{8} \int_0^\infty r_3^2 (2 - r_3) e^{-r_3} dr_3 \\
&= 2 \left[ \frac{1}{r_3} \int_0^{r_3} r_1^2 e^{-2r_1} dr_1 + \int_{r_3}^\infty r_1 e^{-2r_1} dr_1 \right] \left[ \frac{2!}{2^3} \right] \int_0^\infty (4r_3^2 - 4r_3^3 - r_3^4) e^{-r_3} dr_3 \\
&= \frac{17}{81}, \tag{3.37}
\end{aligned}$$

and calculating integrals  $B$ , and  $C$ , we have

$$\begin{aligned}
B &= \iiint v \frac{1}{r_{13}} v d^3 r_1 d^3 r_2 d^3 r_3 = R_{13}^{(0)}(10, 20, 10, 10, 20, 10) \\
&= 2 \int_0^\infty \frac{1}{r_>} r_1^2 e^{-2r_1} dr_1 \int_0^\infty r_2^2 (2 - r_2) e^{-r_2} dr_2 \int_0^\infty r_3^2 e^{-2r_3} dr_3 \\
&= \frac{5}{8}, \tag{3.38}
\end{aligned}$$

and

$$\begin{aligned}
C &= \iiint u \frac{1}{r_{13}} w d^3 r_1 d^3 r_2 d^3 r_3 = R_{13}^{(0)}(10, 10, 20, 20, 10, 10) \\
&= 2 \int_0^\infty r_1^2 (2 - r_1) e^{-3r_1/2} dr_1 \int_0^\infty r_2^2 e^{-2r_2} dr_2 \int_0^\infty \frac{1}{r_>} r_3^2 (2 - r_3) e^{-3r_3/2} dr_3 \\
&= \frac{16}{729}. \tag{3.39}
\end{aligned}$$

Thus, substituting (3.37), (3.38), and (3.39) into Eq. (3.34), we find that for the  $1s^2 2s$   $^2S$  states the second coefficient of the  $Z$ -expansion is

$$\epsilon_{2s}^{(1)} = \frac{5965}{5832}. \tag{3.40}$$

### Calculation of $\epsilon_n^{(1)}$ for the $1s^22p \ ^2P$ States

The integrals for the  $1s^22p \ ^2P$  states are calculated in a similar way. For each of the distinct integral cases  $A$ ,  $B$ , and  $C$ , the angular momentum quantum numbers from Table 3.2 are substituted into the angular part of the integral Eq. (D.17), and with the use of the triangular rule and Eq. (B.4),  $\tilde{I}_0$  may be determined for each case. This angular part of the integral is then substituted into Eq. (D.18), and the resultant integral is evaluated with the use of relation (D.20), and Eqs. (D.21), (D.22), and (D.23). Following this procedure, we find that  $\tilde{I}_0 = 1$  for the integrals  $A$  and  $B$ . Therefore, for these two integrals, we have

$$\begin{aligned}
 A &= R_{13}^{(0)}(10, 10, 21, 10, 10, 21) \\
 &= \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int_0^\infty r_3^2 dr_3 \frac{1}{r_>} R_{10}^2(r_1) R_{10}^2(r_2) R_{21}^2(r_3) \\
 &= \frac{2}{3} \int_0^\infty \frac{1}{r_>} r_1^2 e^{-2r_1} dr_1 \int_0^\infty r_2^2 e^{-2r_2} dr_2 \int_0^\infty r_3^4 e^{-r_3} dr_3 \\
 &= \frac{59}{243}
 \end{aligned} \tag{3.41}$$

and

$$\begin{aligned}
 B &= R_{13}^{(0)}(10, 21, 10, 10, 21, 10) \\
 &= \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int_0^\infty r_3^2 dr_3 \frac{1}{r_>} R_{10}^2(r_1) R_{21}^2(r_2) R_{10}^2(r_3) \\
 &= \frac{2}{3} \int_0^\infty r_1^2 e^{-2r_1} dr_1 \int_0^\infty r_2^4 e^{-r_2} dr_2 \int_0^\infty \frac{1}{r_>} r_3^2 e^{-2r_3} dr_3 \\
 &= \frac{5}{8}.
 \end{aligned} \tag{3.42}$$

However, for integral  $C$ , we find that  $\tilde{I}_0 = 1/3$ . Thus, in this case, we have that

$$\begin{aligned}
 C &= \frac{1}{3} R_{13}^{(1)}(10, 21, 10, 10, 21, 10) \\
 &= \frac{1}{3} \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int_0^\infty r_3^2 dr_3 \frac{r_<}{r_>} R_{10}(r_1) R_{21}(r_1) R_{10}^2(r_2) R_{21}(r_3) R_{10}(r_3)
 \end{aligned}$$

$$\begin{aligned}
&= \frac{2}{9} \int_0^\infty \frac{r_{<}}{r_{>}^2} r_1^3 e^{-3r_1/2} dr_1 \int_0^\infty r_2^2 e^{-2r_2} dr_2 \int_0^\infty r_3^3 e^{-3r_3/2} dr_3 \\
&= \frac{112}{6561}.
\end{aligned} \tag{3.43}$$

Thus, substituting (3.41), (3.42), and (3.43) into Eq. (3.34), we find that for the  $1s^2 2s$   $^2P$  states the second coefficient of the  $Z$ -expansion is

$$\varepsilon_{2p}^{(1)} = \frac{57\,397}{52\,488}. \tag{3.44}$$

## 3.2 Linear Least Squares Method For Obtaining the Remaining Coefficients

In the previous sections, the first two coefficients of the  $Z$ -expansion, Eq. (3.19), were calculated for the  $1s^2 2s$   $^2S$  and  $1s^2 2p$   $^2P$  states. We now wish to find the next several coefficients of this expansion. In this thesis, improved electron-pair energies are obtained by performing a least squares fit of helium variational eigenvalue data provided by G. W. F. Drake. Using these improved electron-pair energies and the exact single-electron energy solutions given by Chisholm and Dalgarno [7], and Chisholm *et al.* [5], values for the second order coefficient  $\varepsilon_n^{(2)}$  for the  $^2S$  and  $^2P$ -states may be determined to 12 significant figures (see the Results and Discussion chapter). Next, we will turn to the linear least squares method [32] for obtaining approximate values for the next several coefficients  $\varepsilon_n^{(3)}, \varepsilon_n^{(4)}, \dots$  for these states.

The general principle of the least squares method is to find a “smooth” functional approximation to a given set of  $N$  data points  $(x_i, y_i)$ . This is done by minimizing

$$\chi^2 = \sum_{i=1}^N \left[ \frac{y_i - y(x_i)}{\sigma_i} \right]^2, \tag{3.45}$$

where

$$y(x_i) = \sum_{k=1}^m a_k(m) \phi_k(x_i) \quad (3.46)$$

is the function modeling the data and  $\sigma_i$  is the measurement error of the  $i^{\text{th}}$  data point. In Eq. (3.46), the  $\{\phi_k\}$ ,  $k = 1, \dots, m$  are arbitrary fixed functions of  $x_i$ , and the  $a_k(m)$  are the parameters with respect to which  $\chi^2$  is minimized. The  $m$  in the parentheses denotes the dependence of these parameters on the set  $\{\phi_k\}$ . To carry out the minimization, we take the derivative of  $\chi^2$  with respect to all the parameters  $a_k(m)$ , and set the result equal to zero, so that (3.45) becomes

$$0 = \sum_{i=1}^N \frac{1}{\sigma_i^2} \left[ y_i - \sum_{j=1}^m a_j(m) \phi_j(x_i) \right] \phi_k(x_i), \quad (3.47)$$

where  $k = 1, \dots, m$ . In doing this we obtain  $m$  equations which are solved for the  $m$  unknown parameters  $a_j(m)$ .

Before applying this method to find some of the other coefficients of our  $Z$ -expansion, we subtract the first three terms from both sides of (3.19), to obtain

$$E_n - Z^2 \varepsilon_n^{(0)} - Z \varepsilon_n^{(1)} - \varepsilon_n^{(2)} = Z^{-1} \varepsilon_n^{(3)} + Z^{-2} \varepsilon_n^{(4)} + \dots \quad (3.48)$$

This is done because we have already determined the first two coefficients  $\varepsilon_n^{(0)}$  and  $\varepsilon_n^{(1)}$  analytically, and the third coefficient  $\varepsilon_n^{(2)}$  will be determined by the above method. Hence, subtracting these three terms from both sides allows us to fit the remaining coefficients with a higher accuracy. From Eq. (3.48), we make the associations  $y_i = E_{n_i} - Z_i^2 \varepsilon_n^{(0)} - Z_i \varepsilon_n^{(1)} - \varepsilon_n^{(2)}$ ,  $a_k(m) = \varepsilon_n^{(k)}(m)$ , and  $\{\phi_j(Z_i)\} = \{Z_i^{-(j-1)}\}$ . After calculating the  $\varepsilon_n^{(k)}(m)$ , it remains to determine the uncertainties for each of these estimated parameters. To find these uncertainties we make use of the *bootstrap method* [18] described below.

### 3.2.1 The Bootstrap Method

The basic idea of the bootstrap method is to generate a number of synthetic data sets from the actual data set, and to calculate the standard deviation of corresponding parameters obtained by finding the least squares fit for each data set. For example, the first parameters  $a_1^{(1)}(m), a_1^{(2)}(m), \dots, a_1^{(N)}(m)$  found from taking the least squares fit of  $N$  synthetic data sets will yield a distribution around the first parameter  $a_1(m)$  calculated from the actual data set. This distribution may then be used to determine the standard deviation for the first parameter. The method used for generating the synthetic data sets and calculating the standard deviation of each parameter is the following:

1. For actual input data  $(Z_1, E_1), (Z_2, E_2), \dots, (Z_N, E_N)$ , the least squares fit to Eq. (3.48) is determined, and the deviations  $\Delta_i = E_n(Z_i) - E_i$  are calculated.
2. Next,  $N$  random integers  $R_i$ , uniformly distributed in the range 1 to  $N$ , are generated, and the deviations  $\Delta_{R_i}$  are added to the original  $E_i$  to obtain new energies  $E'_i = E_i + \Delta_{R_i} \omega_{R_i} / \omega_i$ , where  $\omega_i = 1/\sigma_i^2$  is the weight of the  $i^{\text{th}}$  energy.
3. The new energies  $E'_i$  constitute the first synthetic data set for which a least squares fit is then found, and new parameters  $\varepsilon_n^{(2)}, \varepsilon_n^{(3)}, \dots, \varepsilon_n^{(N)}$  are obtained.
4. This Procedure is repeated many times until the desired number of synthetic data sets is generated.
5. Finally, the average value and standard deviation for each of the parameters  $\varepsilon_n^{(2)}, \varepsilon_n^{(3)}, \dots, \varepsilon_n^{(N)}$  is calculated.

# Chapter 4

## Results And Discussion

The Tables 4.1 and 4.2 illustrate the convergence of the nonrelativistic energies with increasing  $\Omega$ . If  $E(\Omega)$  represents the explicit dependence of the energy on  $\Omega$ , then the fourth and fifth columns of the tables are defined as

$$\textit{difference} \equiv E(\Omega) - E(\Omega - 1), \quad (4.1)$$

and

$$\textit{ratio} = R(\Omega) \equiv \frac{E(\Omega - 1) - E(\Omega - 2)}{E(\Omega) - E(\Omega - 1)}, \quad (4.2)$$

respectively. For a constant ratio  $R(\Omega)$ , each series of eigenvalues in Tables 4.1 and 4.2 would converge as a geometric series to the value

$$E_{\textit{extrap.}} = E(\Omega_{\textit{max}}) + \frac{E(\Omega_{\textit{max}}) - E(\Omega_{\textit{max}} - 1)}{R - 1}, \quad (4.3)$$

but it turns out that the values of  $R$  are not constant. The values of  $R$  vary slightly with  $\Omega$ , however this variation with  $\Omega$  is smooth enough for a useful extrapolation of the energies to the limit  $\Omega \rightarrow \infty$ . To take the variation of  $R$  with  $\Omega$  into account, the extrapolations are done by assuming the functional form [10]

$$R(\Omega) = 1 + \frac{a}{\Omega^b} \quad (4.4)$$

and determining the values of  $a$  and  $b$  by performing a least squares fit of the points  $(\Omega, R(\Omega))$ . The extrapolation converges for  $b < 1$ . Since there is no absolute guarantee that the total amount of the extrapolation is correct, this amount is taken as a conservative estimate of the uncertainty in the extrapolated values.

For the  $^2S$ -states, all the numerical calculations from the smallest basis set to the one containing 919 terms were done in double precision (approximately 16 decimal places). In order to achieve convergence to the energy values listed in Tables 4.1 and 4.2 for a given basis set size, the calculations ran from about 30 iterations, for the smallest basis set to about 8 iterations for the 919-term basis set, with each iteration providing a step toward optimization of the nonlinear parameters. The last four of the 8 iterations for the 919-term basis set were performed using quadruple precision (approximately 32 decimal digits). Quadruple precision calculations were also performed for the 1590 and 2210-term basis sets, however an optimization of the nonlinear parameters was not carried out in these cases. This was due to the large computational time required for the optimization of these largest basis sets ( $\Omega > 7$ ). For example, approximately 330 hours of CPU time are required for just two iterations of the 1590-term basis set using an IBM RISC/6000 350 workstation. It is also generally true (as long as the nonlinear parameters remain close to the optimum values) that an improvement in the energy due to an optimization of the nonlinear parameters is small in comparison with the improvement possible by increasing the basis set size to the next  $\Omega$ . Thus, as long as there is no evidence of numerical instability, which may be detected by erratic behaviour of the ratios  $R(\Omega)$ , optimization of these largest basis sets is not necessary.

The nonlinear parameters for the largest basis sets can be extrapolated from graphs showing the variation of these parameters with increasing basis size  $\Omega$ . In this thesis, however, the nonlinear parameters used for the largest basis sizes ( $\Omega > 7$ ) were simply those obtained from the near by optimized  $\Omega = 7$  basis set parameters.

Results for the  ${}^2P$ -states with nuclear charge  $3 \leq Z \leq 10$  were obtained from Zong-Chao Yan at the *Harvard-Smithsonian Center for Astrophysics*, and an extension up to  $Z = 15$  was carried out in this thesis. These results were calculated in a similar fashion as those above for the  ${}^2S$ -states. However, computer memory limitations prevented the extension up to  $Z = 15$  from being carried out beyond  $\Omega \geq 10$ .

Figures 4.1 to 4.6 show the variation of the nonlinear parameters as a function of  $1/Z$ . From these figures we see that some of the nonlinear parameters exhibit “irregular behaviour” for  $Z > 5$ , or 6. This irregular behaviour (characterized by sharp jumps in the nonlinear parameters) may be the result of incomplete optimization for the  $\Omega > 7$  basis set sizes, or it may be due to the existence of multiple minima on the energy surface. To determine which of these is the case, a closer study exploring the multiple root structure of the energy surface is needed.



Table 4.1: Nonrelativistic energies for the  $1s^2 2s \ ^2S$  states of the lithium isoelectronic sequence, in atomic units.

$Z = 3$				
$\Omega$	No. of terms	Energy	Difference	Ratio
2	19	-7.477 555 720 32		
3	51	-7.477 995 835 14	-0.000 440 114 82	
4	121	-7.478 053 567 30	-0.000 057 732 16	7.623
5	257	-7.478 059 464 46	-0.000 005 897 16	9.790
6	503	-7.478 060 228 08	-0.000 000 763 62	7.723
7	919	-7.478 060 310 78	-0.000 000 082 70	9.234
8	1590	-7.478 060 321 03	-0.000 000 010 26	8.061
9	2210	-7.478 060 322 54	-0.000 000 001 50	6.828
	Extrapolation	-7.478 060 322 74(20)		
$Z = 4$				
$\Omega$	No. of terms	Energy	Difference	Ratio
2	19	-14.324 365 883 92		
3	51	-14.324 715 319 21	-0.000 349 435 28	
4	121	-14.324 758 497 16	-0.000 043 177 95	8.093
5	257	-14.324 762 509 32	-0.000 004 012 16	10.762
6	503	-14.324 763 099 39	-0.000 000 590 07	6.800
7	919	-14.324 763 165 56	-0.000 000 066 17	8.917
8	1590	-14.324 763 174 52	-0.000 000 008 96	7.388
9	2210	-14.324 763 175 61	-0.000 000 001 09	8.195
	Extrapolation	-14.324 763 175 78(17)		

Table 4.1 (*Continued*).

$Z = 5$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-23.424 566 701 01		
4	121	-23.424 601 544 40	-0.000 034 843 39	
5	257	-23.424 605 116 47	-0.000 003 572 07	9.754
6	503	-23.424 605 654 16	-0.000 000 537 69	6.643
7	919	-23.424 605 710 24	-0.000 000 056 08	9.588
8	1590	-23.424 605 719 36	-0.000 000 009 12	6.149
9	2210	-23.424 605 720 32	-0.000 000 000 96	9.500
	Extrapolation	-23.424 605 720 50(18)		
$Z = 6$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-34.775 475 415 28		
4	121	-34.775 506 714 18	-0.000 031 298 90	
5	257	-34.775 510 611 47	-0.000 003 897 29	8.031
6	503	-34.775 511 199 23	-0.000 000 587 76	6.631
7	919	-34.775 511 266 59	-0.000 000 067 37	8.725
8	1590	-34.775 511 273 93	-0.000 000 007 33	9.186
9	2210	-34.775 511 274 95	-0.000 000 001 02	7.165
	Extrapolation	-34.775 511 275 11(16)		

Table 4.1 (*Continued*).

$Z = 7$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-48.376 863 363 39		
4	121	-48.376 894 128 34	-0.000 030 764 95	
5	257	-48.376 897 718 71	-0.000 003 590 37	8.569
6	503	-48.376 898 260 95	-0.000 000 542 24	6.621
7	919	-48.376 898 310 50	-0.000 000 049 55	10.943
8	1590	-48.376 898 317 47	-0.000 000 006 97	7.109
9	2210	-48.376 898 318 30	-0.000 000 000 83	8.398
	Extrapolation	-48.376 898 318 43(13)		
$Z = 8$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-64.228 507 126 82		
4	121	-64.228 538 145 79	-0.000 031 018 97	
5	257	-64.228 541 520 49	-0.000 003 374 70	9.192
6	503	-64.228 542 027 78	-0.000 000 507 29	6.652
7	919	-64.228 542 074 85	-0.000 000 047 07	10.777
8	1590	-64.228 542 081 04	-0.000 000 006 19	7.604
9	2210	-64.228 542 081 87	-0.000 000 000 83	7.457
	Extrapolation	-64.228 542 082 00(13)		

Table 4.1 (Continued).

$Z = 9$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-82.330 302 805 99		
4	121	-82.330 334 349 54	-0.000 031 543 55	
5	257	-82.330 337 576 74	-0.000 003 227 20	9.774
6	503	-82.330 338 039 07	-0.000 000 462 33	6.980
7	919	-82.330 338 089 14	-0.000 000 050 07	9.234
8	1590	-82.330 338 095 52	-0.000 000 006 38	7.848
9	2210	-82.330 338 096 49	-0.000 000 000 97	6.577
	Extrapolation	-82.330 338 096 65(16)		

$Z = 10$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-102.682 195 705 64		
4	121	-102.682 227 858 93	-0.000 032 153 29	
5	257	-102.682 230 992 82	-0.000 003 133 89	10.260
6	503	-102.682 231 427 96	-0.000 000 435 14	7.202
7	919	-102.682 231 474 96	-0.000 000 047 00	9.258
8	1590	-102.682 231 480 65	-0.000 000 005 69	8.260
9	2210	-102.682 231 481 62	-0.000 000 000 97	5.896
	Extrapolation	-102.682 231 481 79(17)		

Table 4.1 (*Continued*).

$Z = 11$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-125.284 159 109 78		
4	121	-125.284 186 776 09	-0.000 027 666 31	
5	257	-125.284 190 320 77	-0.000 003 544 68	7.805
6	503	-125.284 190 701 36	-0.000 000 380 59	9.314
7	919	-125.284 190 746 48	-0.000 000 045 12	8.435
8	1590	-125.284 190 752 02	-0.000 000 005 54	8.144
9	2210	-125.284 190 753 06	-0.000 000 001 04	5.357
	Extrapolation	-125.284 190 753 24(18)		
$Z = 12$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-150.136 165 037 27		
4	121	-150.136 192 994 58	-0.000 027 957 31	
5	257	-150.136 196 184 18	-0.000 003 189 60	8.765
6	503	-150.136 196 553 34	-0.000 000 369 16	8.640
7	919	-150.136 196 597 48	-0.000 000 044 14	8.363
8	1590	-150.136 196 602 81	-0.000 000 005 33	8.281
9	2210	-150.136 196 603 69	-0.000 000 000 88	6.057
	Extrapolation	-150.136 196 603 84(15)		

Table 4.1 (*Continued*).

$Z = 13$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-177.238 205 001 86		
4	121	-177.238 232 822 28	-0.000 027 820 42	
5	257	-177.238 236 160 79	-0.000 003 338 51	8.333
6	503	-177.238 236 512 46	-0.000 000 351 67	9.493
7	919	-177.238 236 552 30	-0.000 000 039 84	8.827
8	1590	-177.238 236 557 87	-0.000 000 005 57	7.153
9	2210	-177.238 236 558 89	-0.000 000 001 02	5.461
	Extrapolation	-177.238 236 559 11(22)		
$Z = 14$				
$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-206.590 270 865 35		
4	121	-206.590 298 667 99	-0.000 027 802 64	
5	257	-206.590 301 824 55	-0.000 003 156 56	8.808
6	503	-206.590 302 166 14	-0.000 000 341 59	9.241
7	919	-206.590 302 205 34	-0.000 000 039 20	8.714
8	1590	-206.590 302 210 55	-0.000 000 005 21	7.524
9	2210	-206.590 302 211 43	-0.000 000 000 88	5.920
	Extrapolation	-206.590 302 211 61(18)		

Table 4.1 (*Continued*). $Z = 15$ 

$\Omega$	No. of terms	Energy	Difference	Ratio
3	51	-238.192 354 015 19		
4	121	-238.192 384 131 35	-0.000 030 116 16	
5	257	-238.192 387 291 90	-0.000 003 160 55	9.529
6	503	-238.192 387 645 79	-0.000 000 353 89	8.931
7	919	-238.192 387 687 65	-0.000 000 041 86	8.454
8	1590	-238.192 387 692 48	-0.000 000 004 83	8.667
9	2210	-238.192 387 693 38	-0.000 000 000 90	5.367
	Extrapolation	-238.192 387 693 56(18)		

Table 4.2: Nonrelativistic energies for the  $1s^2 2p \ ^2P$  states of the lithium isoelectronic sequence, in atomic units.

$Z = 3$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-7.410 146 240 952		
5	139	-7.410 155 057 909	-0.000 008 816 956	
6	307	-7.410 156 274 821	-0.000 001 216 912	7.245
7	623	-7.410 156 490 483	-0.000 000 215 662	5.643
8	1175	-7.410 156 524 272	-0.000 000 033 789	6.383
9	1846	-7.410 156 530 070	-0.000 000 005 798	5.828
10	2466	-7.410 156 530 955	-0.000 000 000 885	6.550
11	3047	-7.410 156 531 185	-0.000 000 000 230	3.843
	Extrapolation	-7.410 156 531 252(67)		
$Z = 4$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-14.179 313 470 581		
5	139	-14.179 330 528 846	-0.000 017 058 265	
6	307	-14.179 332 918 492	-0.000 002 389 646	7.138
7	623	-14.179 333 238 248	-0.000 000 319 756	7.473
8	1175	-14.179 333 282 444	-0.000 000 044 195	7.235
9	1846	-14.179 333 290 202	-0.000 000 007 758	5.697
10	2466	-14.179 333 291 213	-0.000 000 001 011	7.673
11	3047	-14.179 333 291 472	-0.000 000 000 259	3.905
	Extrapolation	-14.179 333 291 542(70)		



Table 4.2 (Continued).

$Z = 5$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-23.204 416 706 02		
5	139	-23.204 437 896 83	-0.000 021 190 81	
6	307	-23.204 440 728 17	-0.000 002 831 34	7.484
7	623	-23.204 441 127 99	-0.000 000 399 82	7.082
8	1175	-23.204 441 180 80	-0.000 000 052 81	7.571
9	1846	-23.204 441 189 86	-0.000 000 009 06	5.829
10	2466	-23.204 441 190 98	-0.000 000 001 12	8.089
11	3047	-23.204 441 191 31	-0.000 000 000 33	3.394
	Extrapolation	-23.204 441 191 42(11)		
$Z = 6$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-34.482 076 048 46		
5	139	-34.482 099 271 11	-0.000 023 222 65	
6	307	-34.482 102 715 58	-0.000 003 444 47	6.742
7	623	-34.482 103 111 19	-0.000 000 395 61	8.707
8	1175	-34.482 103 167 48	-0.000 000 056 29	7.028
9	1846	-34.482 103 176 67	-0.000 000 009 19	6.122
10	2466	-34.482 103 177 78	-0.000 000 001 11	8.286
11	3047	-34.482 103 178 19	-0.000 000 000 41	2.684
	Extrapolation	-34.482 103 178 34(15)		

Table 4.2 (Continued).

$Z = 7$				
$\Omega$	No. of terms	Energy	Difference	Ratio
	56	-48.011 024 850 90		
	139	-48.011 050 050 88	-0.000 025 199 98	
	307	-48.011 053 805 56	-0.000 003 754 68	6.712
	623	-48.011 054 210 24	-0.000 000 404 68	9.278
	1175	-48.011 054 268 21	-0.000 000 057 97	6.981
	1846	-48.011 054 279 07	-0.000 000 010 86	5.338
	2466	-48.011 054 280 17	-0.000 000 001 10	9.906
	3047	-48.011 054 280 54	-0.000 000 000 38	2.922
	Extrapolation	-48.011 054 280 66(12)		
$Z = 8$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-63.790 714 553 94		
5	139	-63.790 736 011 83	-0.000 021 457 89	
6	307	-63.790 739 072 10	-0.000 003 060 27	7.012
7	623	-63.790 739 503 42	-0.000 000 431 32	7.095
8	1175	-63.790 739 566 00	-0.000 000 062 58	6.892
9	1846	-63.790 739 576 54	-0.000 000 010 54	5.937
10	2466	-63.790 739 577 72	-0.000 000 001 18	8.932
11	3047	-63.790 739 578 09	-0.000 000 000 37	3.189
	Extrapolation	-63.790 739 578 21(12)		

Table 4.2 (Continued).

$Z = 9$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-81.820 856 247 55		
5	139	-81.820 877 306 35	-0.000 021 058 80	
6	307	-81.820 880 414 73	-0.000 003 108 38	6.775
7	623	-81.820 880 836 63	-0.000 000 421 91	7.368
8	1175	-81.820 880 900 23	-0.000 000 063 59	6.634
9	1846	-81.820 880 910 44	-0.000 000 010 21	6.229
10	2466	-81.820 880 911 50	-0.000 000 001 06	9.654
11	3047	-81.820 880 911 89	-0.000 000 000 40	2.656
	Extrapolation	-81.820 880 912 03(14)		
$Z = 10$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-102.101 299 252 851		
5	139	-102.101 320 579 421	-0.000 021 326 569	
6	307	-102.101 323 786 036	-0.000 003 206 616	6.651
7	623	-102.101 324 217 958	-0.000 000 431 922	7.424
8	1175	-102.101 324 281 583	-0.000 000 063 625	6.789
9	1846	-102.101 324 292 317	-0.000 000 010 734	5.928
10	2466	-102.101 324 293 431	-0.000 000 001 114	9.638
11	3047	-102.101 324 293 685	-0.000 000 000 254	4.388
	Extrapolation	-102.101 324 293 732(47)		

Table 4.2 (*Continued*).

$Z = 11$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-124.631 952 538 7		
5	139	-124.631 974 018 5	-0.000 021 479 8	
6	307	-124.631 977 293 0	-0.000 003 274 5	6.560
7	623	-124.631 977 738 9	-0.000 000 445 9	7.344
8	1175	-124.631 977 805 4	-0.000 000 066 5	6.705
9	1846	-124.631 977 815 9	-0.000 000 010 5	6.333
	Extrapolation	-124.631 977 817 7(18)		
$Z = 12$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-149.412 757 501 3		
5	139	-149.412 779 532 5	-0.000 022 031 2	
6	307	-149.412 782 807 6	-0.000 003 275 1	6.727
7	623	-149.412 783 251 5	-0.000 000 443 9	7.378
8	1175	-149.412 783 319 6	-0.000 000 068 1	6.518
9	1846	-149.412 783 329 6	-0.000 000 010 0	6.810
	Extrapolation	-149.412 783 331 3(17)		

Table 4.2 (*Continued*).

$Z = 13$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-176.443 676 192 6		
5	139	-176.443 698 446 9	-0.000 022 254 3	
6	307	-176.443 701 737 6	-0.000 003 290 7	6.763
7	623	-176.443 702 193 2	-0.000 000 455 6	7.223
8	1175	-176.443 702 262 2	-0.000 000 069 0	6.603
9	1846	-176.443 702 272 9	-0.000 000 010 7	6.449
	Extrapolation	-176.443 702 274 8(19)		
$Z = 14$				
$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-205.724 681 924 1		
5	139	-205.724 704 192 7	-0.000 022 268 6	
6	307	-205.724 707 546 6	-0.000 003 353 9	6.640
7	623	-205.724 708 005 9	-0.000 000 459 3	7.302
8	1175	-205.724 708 076 6	-0.000 000 070 7	6.496
9	1846	-205.724 708 087 6	-0.000 000 011 0	6.427
	Extrapolation	-205.724 708 089 6(20)		

Table 4.2 (*Continued*). $Z = 15$ 

$\Omega$	No. of terms	Energy	Difference	Ratio
4	56	-237.255 755 093 3		
5	139	-237.255 777 962 9	-0.000 022 869 6	
6	307	-237.255 781 344 7	-0.000 003 381 8	6.763
7	623	-237.255 781 808 0	-0.000 000 463 3	7.299
8	1175	-237.255 781 879 7	-0.000 000 071 7	6.462
9	1846	-237.255 781 890 7	-0.000 000 011 0	6.518
	Extrapolation	-237.255 781 892 6(19)		

Alpha Vs. 1/Z

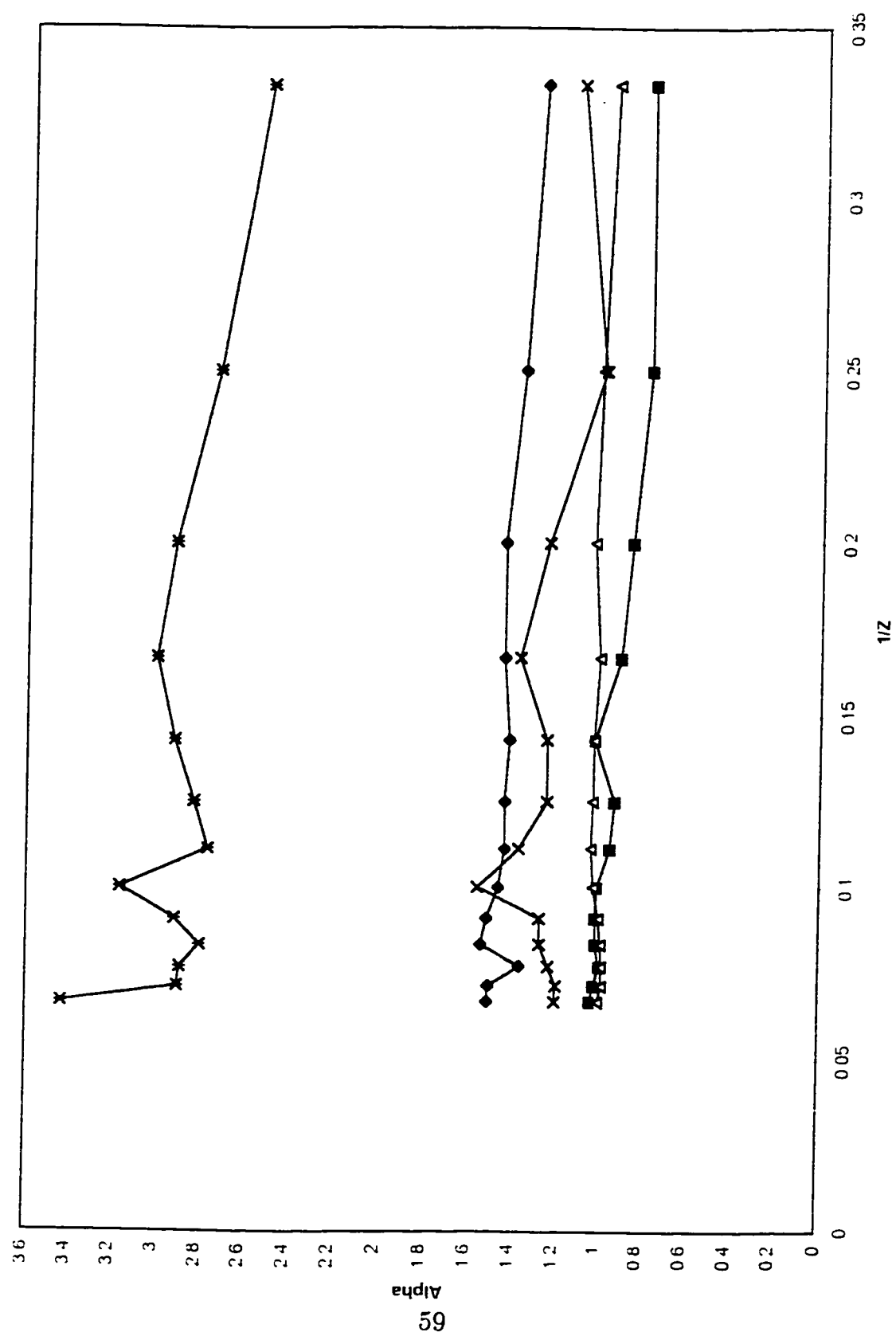


Figure 4.1: Nonlinear parameters  $\alpha_i$ ,  $i = 1, \dots, 5$  plotted as a function of inverse  $Z$  for the  $1s^2 2s^2 S$  states ( $\Omega = 7$ ).

Beta Vs. 1/Z

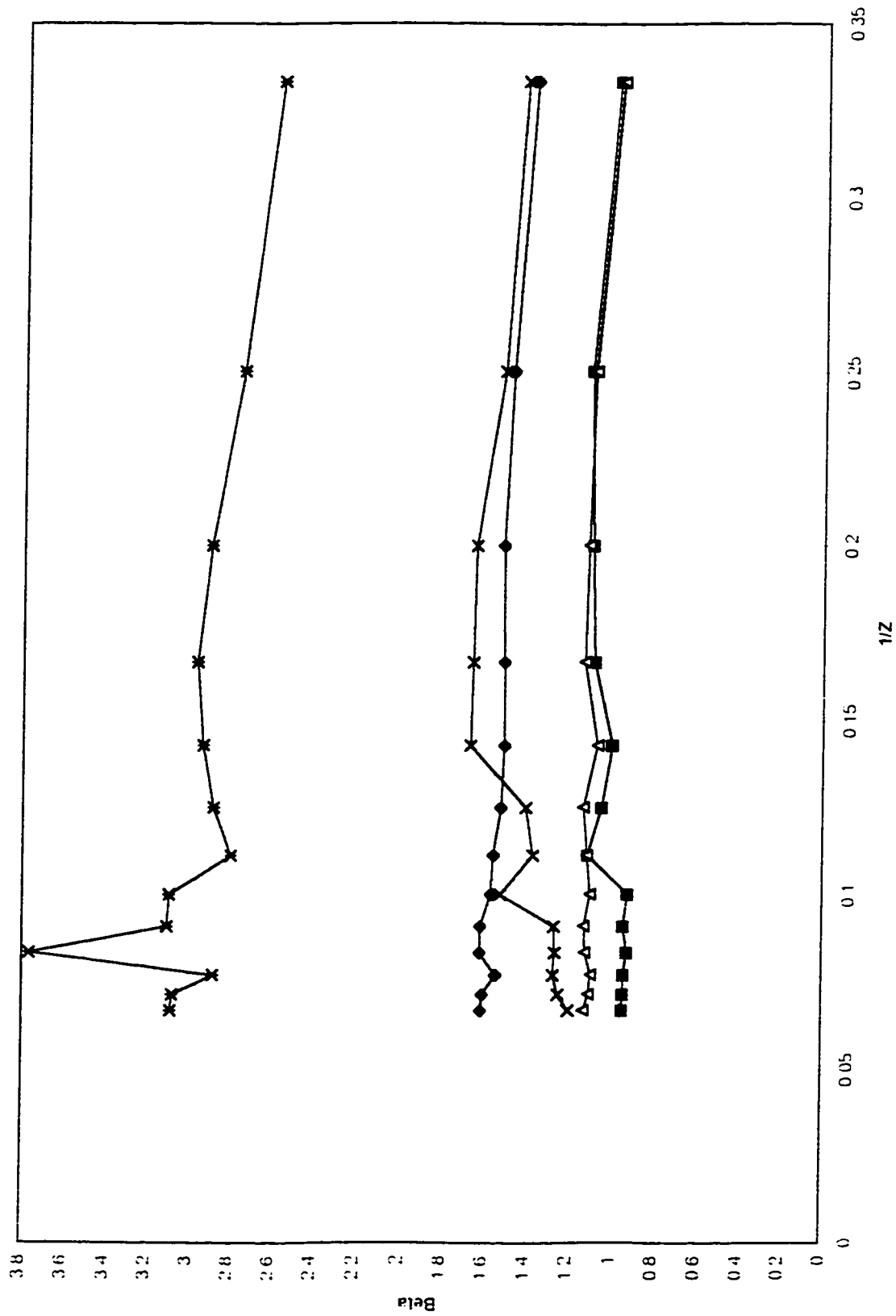


Figure 4.2: Nonlinear parameters  $\beta_i$ ,  $i = 1, \dots, 5$  plotted as a function of inverse  $Z$  for the  $1s^2 2s^2 S$  states ( $\Omega = 7$ ).



Gamma Vs. 1/Z

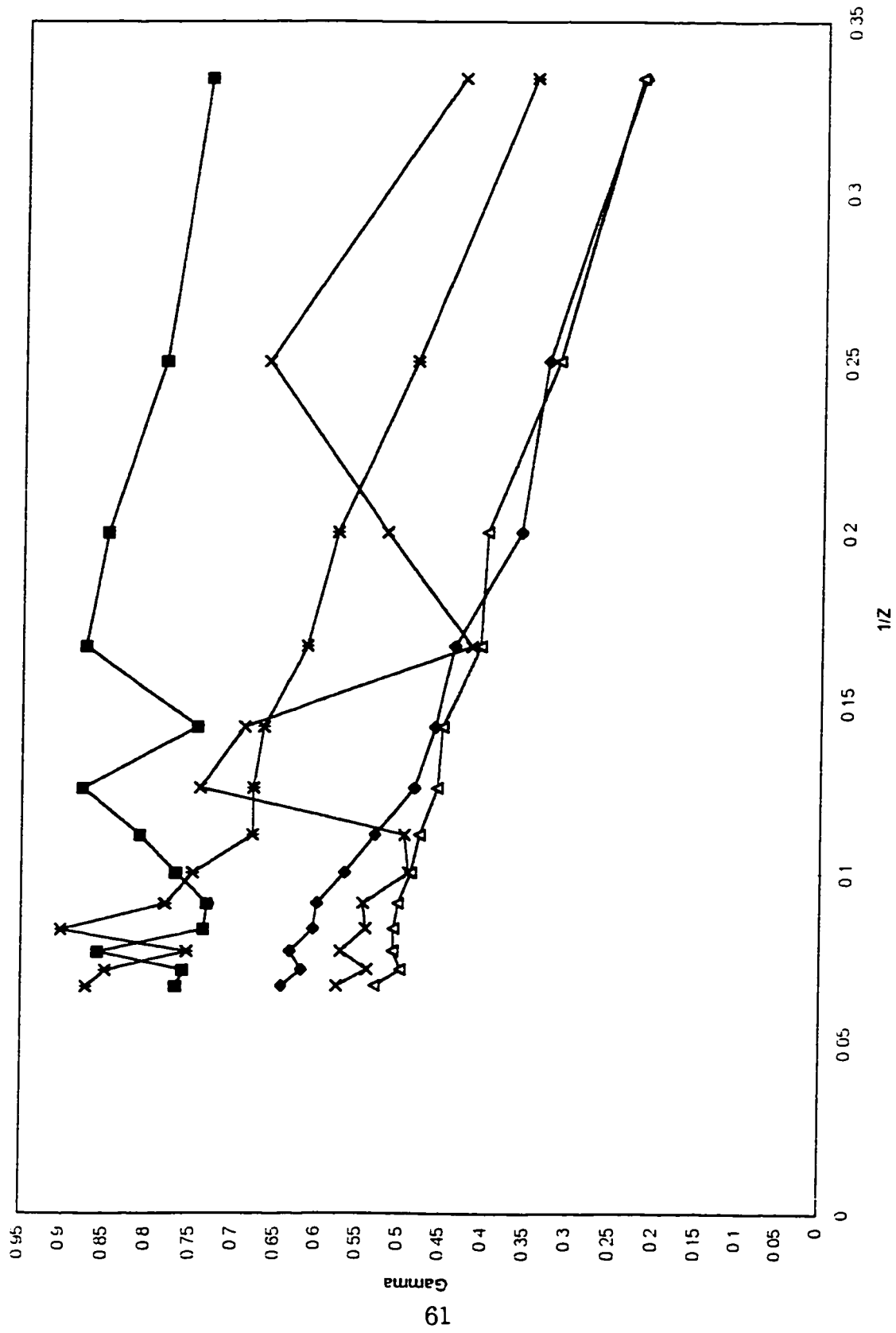


Figure 4.3: Nonlinear parameters  $\gamma_i$ ,  $i = 1, \dots, 5$  plotted as a function of inverse  $Z$  for the  $1s^2 2s^2 S$  states ( $\Omega = 7$ ).

Alpha Vs. 1/Z

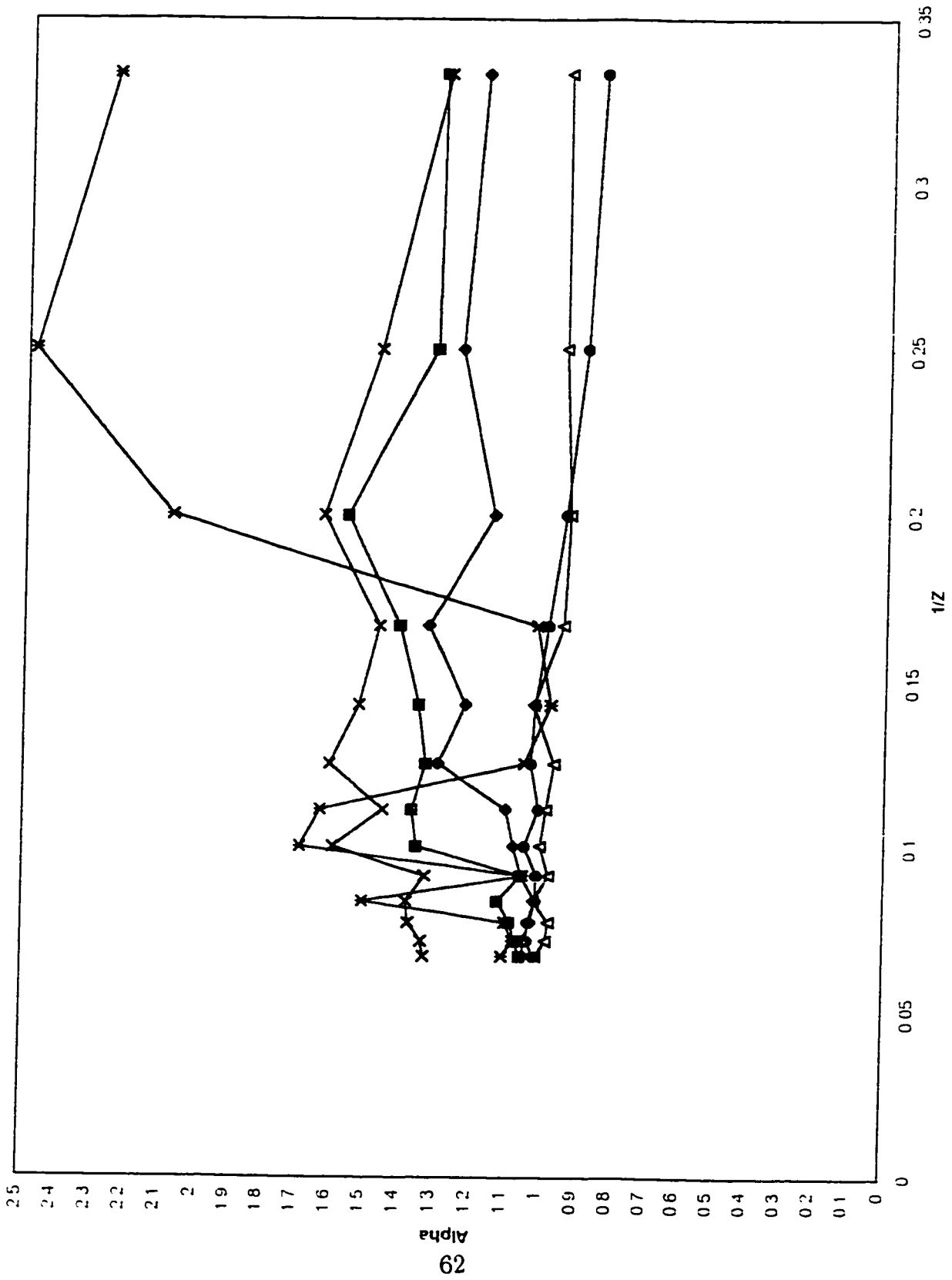


Figure 4.4: Nonlinear parameters  $\alpha_i$ ,  $i = 1, \dots, 6$  plotted as a function of inverse  $Z$  for the  $1s^2 2p^2 P$  states ( $\Omega = 8$ ).

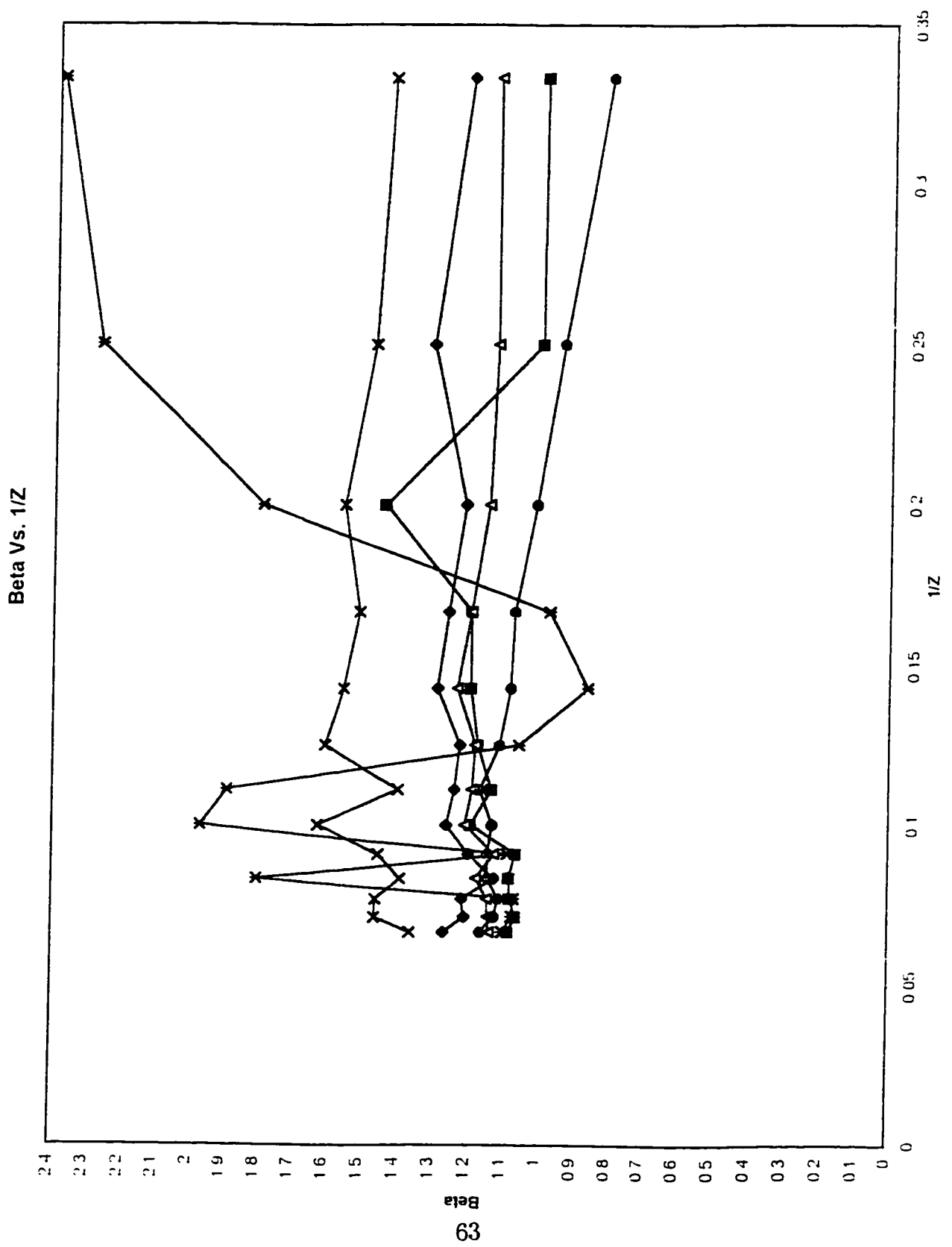


Figure 4.5: Nonlinear parameters  $\beta_i$ ,  $i = 1, \dots, 6$  plotted as a function of inverse  $Z$  for the  $1s^2 2p^2 P$  states ( $\Omega = 8$ ).

Gamma Vs. 1/Z

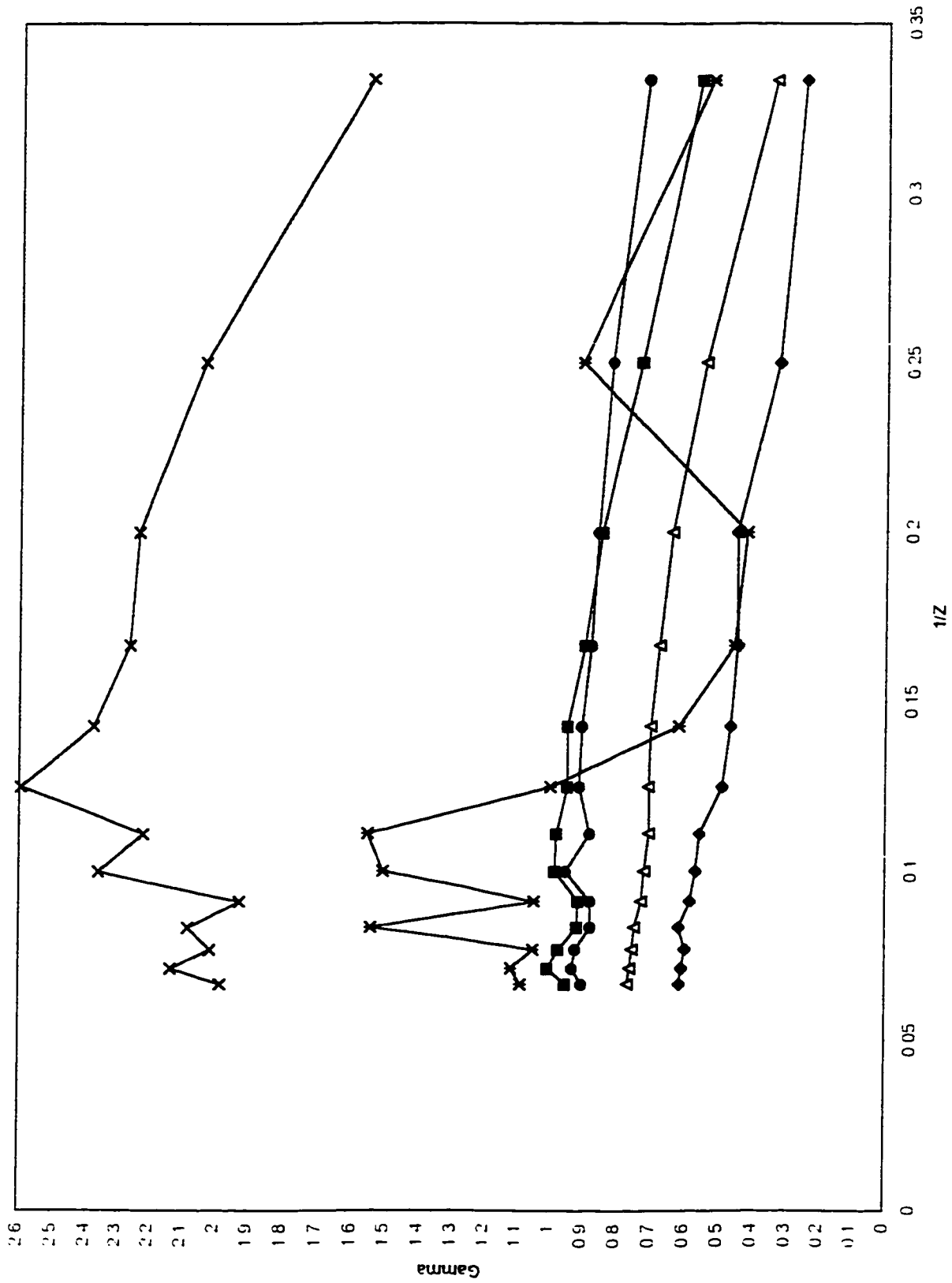


Figure 4.6: Nonlinear parameters  $\gamma_i$ ,  $i = 1, \dots, 6$  plotted as a function of inverse  $Z$  for the  $1s^2 2p^2 P$  states ( $\Omega = 8$ ).

## 4.1 Z-Expansions From the Least Squares Fit

In Tables 4.1 and 4.2, we have listed the extrapolated energies obtained from the variational eigenvalues. The computation time required to obtain the variational eigenvalues for the construction of each of these tables is about 280 hours using an IBM RISC/6000 350 workstation and about 150 hours if the IBM RISC System/6000 3CT is used for the final largest basis set. Since a large amount of computation time is required to obtain these results, it is advantageous at some point to simply determine the nonrelativistic energies of the  $1s^22s\ ^2S$  and  $1s^22p\ ^2P$  states from their  $Z$ -expansions. The first two coefficients  $\varepsilon_n^{(0)}$  and  $\varepsilon_n^{(1)}$  for these expansions were determined analytically in the previous chapter. In this section, electron-pair energies are found and used to determine more accurate values for the third coefficient  $\varepsilon_n^{(2)}$  of these expansions. Achieving higher accuracy for  $\varepsilon^{(2)}$  is important since it is the accuracy in this coefficient which ultimately limits the accuracy to which the energies from Eq. (1.1) may be calculated. Finally, the least squares method is used to determine the next several coefficients of expansion (3.48) for the  $^2S$  and  $^2P$ -states, and from the expansions for these states, the nonrelativistic energies for  $3 \leq Z \leq 92$  are calculated.

### 4.1.1 The Electron-Pair Energies

For Tables 4.3 to 4.13, the average values of  $\varepsilon^{(2)}$  for each of the states were obtained by applying the bootstrap method, described in the previous chapter, to the eigenvalues for the corresponding states which were provided by G. W. F. Drake. The form of the function used for the fit is given by

$$E_n - Z^2\varepsilon_n^{(0)} - Z\varepsilon_n^{(1)} = \varepsilon_n^{(2)} + Z^{-1}\varepsilon_n^{(3)} + Z^{-2}\varepsilon_n^{(4)} + \dots, \quad (4.5)$$

where the  $\varepsilon^{(0)}$  values are given by  $\varepsilon^{(0)} = -\sum_{i=1}^2 1/2n_i^2$ , where  $n$  is the principal quantum number, and the  $\varepsilon^{(1)}$  values were obtained from Sanders and Scherr [35]. In Tables 4.3 to 4.13, the numbers in parentheses in the average values of  $\varepsilon^{(2)}$  denote the uncertainties

in the final figures quoted, which in this case are the standard deviations obtained from the bootstrap method.

Table 4.3 was used to determine the number of data sets (original+synthetic) that are needed to produce an average value which converges to the last figure for which the uncertainty is quoted. For example, it may be seen from Table 4.3 that about 10 data sets are needed for the average value of  $\varepsilon^{(2)}(1s^2 \ 1S)$  to converge to the last figure containing the uncertainty. To ensure that statistically meaningful standard deviations were obtained for the average values, the number of data sets used to obtain the results listed in Tables 4.4 to 4.13 was chosen to be 100. As seen from Table 4.3, the standard deviations do not change with the use of data sets larger than 100.

One important point that arises in applying the least squares method is which number of parameters  $m$  yields the best fit to a data set of size  $N$ . If we choose  $m = N$ , we can make  $\chi^2$  given by Eq. (3.45) equal to zero. However in doing so, we lose all the smoothing properties of the least squares method. It turns out that the best fit is achieved as soon as a value of  $m$  is reached after which no significant decrease occurs in  $\chi^2$  [33]. This is the general rule used to determine the number of parameters needed to yield the best values in Tables 4.5, 4.7, 4.9, 4.11, and 4.13.

Another point that must be considered is whether the standard deviation obtained from the bootstrap method accurately represents the uncertainty in the average values of the coefficients. This point is addressed in Tables 4.4 to 4.13. In these tables, the change in the average values for  $\varepsilon^{(2)}$  may be seen for various parameter sizes and ranges of data sets used, and this change may be used as a guideline in determining where the uncertainty lies. In Tables 4.4 to 4.13 the change generally occurs in the 13<sup>th</sup> significant figure. For example, from Tables 4.4, 4.6, 4.8, 4.10, and 4.12, it may be seen that the average values for  $\varepsilon^{(2)}$  for the various parameter sizes having the same order of magnitude for  $\chi^2$ , agree to the first 12 significant figures. Also, from Tables 4.5, 4.7, 4.9, 4.11, and 4.13, it may be seen that there is no change in the first 12 figures of the average value for  $\varepsilon^{(2)}$  when the first or last several data values are omitted. From these results, we

conclude that the uncertainty obtained from the bootstrap method is a factor of 10 too small in some cases, for example, see Table 4.9. In such cases, the uncertainty was estimated by comparing neighbouring values and taking the largest difference between neighbouring values as the uncertainty. In doing so, the following values were obtained for the electron-pair energies

$$\begin{aligned}\varepsilon^{(2)}(1s^2\ ^1S) &= -0.157\ 666\ 429\ 469\ 3(4), \\ \varepsilon^{(2)}(1s2s\ ^2S) &= -0.114\ 510\ 136\ 167\ 2(4), \\ \varepsilon^{(2)}(1s2s\ ^3S) &= -0.047\ 409\ 304\ 175\ 4(6), \\ \varepsilon^{(2)}(1s2p\ ^1P) &= -0.157\ 028\ 662\ 934\ 7(2),\end{aligned}$$

and

$$\varepsilon^{(2)}(1s2p\ ^3P) = -0.072\ 998\ 983\ 472\ 6(8).$$

Comparing the first value  $\varepsilon^{(2)}(1s^2\ ^1S)$  with Morgan's value [27] of  $-0.157\ 666\ 429\ 469\ 14$ , we see that they agree within the uncertainty quoted in the result obtained here. The above results for the electron-pair energies are much more accurate than the ones used by Horak *et al.* [39], which were accurate to only 6 or 7 significant figures.

### 4.1.2 The $S$ and $P$ -state Lithium $Z$ -Expansions

With the improved electron-pair energies, better values for the second order coefficients  $\varepsilon^{(2)}(1s^2 2s^2 S)$  and  $\varepsilon^{(2)}(1s^2 2p^2 P)$  may be obtained using [39]

$$\varepsilon^{(2)}(1s^2 2l^2 L) = \varepsilon^{(2)}(1s^2 {}^1S) + \frac{1}{2}\varepsilon^{(2)}(1s 2l {}^1L) + \frac{3}{2}\varepsilon^{(2)}(1s 2l {}^3L) + \zeta(2l), \quad (4.6)$$

where  $l = s$ , or  $p$  depending on the state being evaluated, and  $\zeta(2l)$  is a sum of single-electron integrals which are evaluated exactly by Chisholm and Dalgarno [7] for the  $S$ -state and by Chisholm *et al.* [5] for the  $P$ -state. Expression (4.6) may be derived by noting that the solution  $\Psi^{(1)}$  of (3.16) can be written in terms of first order independent two-electron systems. For example,  $\Psi^{(1)}$  for the ground state of lithium is given by Eq. (1.5).

Substituting the above electron-pair energies into Eq. (4.6), we get

$$\varepsilon^{(2)}(1s^2 2s^2 S) = -0.408\ 166\ 165\ 261\ 15(8), \quad (4.7)$$

and

$$\varepsilon^{(2)}(1s^2 2p^2 P) = -0.528\ 578\ 868\ 140\ 59(11). \quad (4.8)$$

Now using values of  $\varepsilon^{(0)}$ ,  $\varepsilon^{(1)}$ , and  $\varepsilon^{(2)}$  from Eqs. (3.20), (3.40), (3.44), (4.7), and (4.8), and the function being fitted given by (3.48), the bootstrap method may be applied to obtain the next several coefficients of the  $Z$ -expansions for the  $S$  and  $P$ -states. Tables 4.14 to 4.21 show the results obtained for the third order coefficient of these expansions. The first two tables 4.14 and 4.15 were obtained to determine the number of data sets needed to achieve convergence in the third order coefficients  $\varepsilon^{(3)}$ , and the remaining tables were constructed to determine the uncertainty in the coefficients. This was all done using a similar procedure to the one presented above for obtaining the electron-pair energies. In this case however, it is seen from Tables 4.14 to 4.21 that the third order coefficients of the  $Z$ -expansion are determined to only 5 or 6 significant figures. Also, it



Table 4.3: Convergence with the number of data sets used. (11 parameters).

Number of data sets	Average value for $\varepsilon^{(2)}(1s^2 \ ^1S)$
2	-0.157 666 429 469 37(4)
6	-0.157 666 429 469 34(3)
10	-0.157 666 429 469 33(4)
20	-0.157 666 429 469 33(4)
50	-0.157 666 429 469 33(5)
100	-0.157 666 429 469 33(4)
200	-0.157 666 429 469 33(4)
1000	-0.157 666 429 469 33(4)

Table 4.4:  $\varepsilon^{(2)}(1s^2 \ ^1S)$  for various parameter sizes. (100 data sets).

Number of parameters	Average value for $\varepsilon^{(2)}(1s^2 \ ^1S)$	$\chi^2$
6	-0.157 666 401 1(44)	$4.3 \times 10^{14}$
7	-0.157 666 432 23(31)	$5.1 \times 10^{11}$
8	-0.157 666 429 214(26)	$4.8 \times 10^8$
9	-0.157 666 429 493 4(21)	$2.9 \times 10^5$
10	-0.157 666 429 467 20(17)	$1.3 \times 10^2$
11	-0.157 666 429 469 33(4)	$3.4 \times 10^{-1}$
12	-0.157 666 429 468 95(10)	$1.6 \times 10^{-1}$
13	-0.157 666 429 468 30(50)	$1.7 \times 10^{-1}$
14	-0.157 666 429 460 75(15)	$4.8 \times 10^{-2}$
15	-0.157 666 429 493 54(52)	$2.0 \times 10^0$

Table 4.5:  $\varepsilon^{(2)}(1s^2 \ ^1S)$  for data sets consisting of various ranges for  $Z$ . (100 data sets).

Range for $Z$	Average value for $\varepsilon^{(2)}(1s^2 \ ^1S)$	Number of parameters
2 – 18	-0.157 666 429 469 33(4)	11
3 – 18	-0.157 666 429 469 94(1)	10
4 – 18	-0.157 666 429 469 00(8)	10
5 – 18	-0.157 666 429 469 34(6)	9
6 – 18	-0.157 666 429 469 1(2)	9
7 – 18	-0.157 666 429 469 4(6)	8
8 – 18	-0.157 666 429 469 2(2)	8
9 – 18	-0.157 666 429 469 7(4)	8
2 – 14	-0.157 666 429 469 7(2)	11
2 – 15	-0.157 666 429 469 50(6)	11
2 – 16	-0.157 666 429 469 47(3)	11
2 – 17	-0.157 666 429 469 45(1)	11

Table 4.6:  $\varepsilon^{(2)}(1s2s \ ^1S)$  for various parameter sizes. (100 data sets).

Number of parameters	Average value for $\varepsilon^{(2)}(1s2s \ ^1S)$	$\chi^2$
8	-0.114 510 136 135 95(10)	$1.1 \times 10^5$
9	-0.114 510 136 316 37(13)	$6.8 \times 10^3$
10	-0.114 510 136 154 24(10)	$3.4 \times 10^0$
11	-0.114 510 136 167 24(85)	$3.0 \times 10^{-3}$
12	-0.114 510 136 167 25(39)	$3.7 \times 10^{-3}$
13	-0.114 510 136 163 16(15)	$3.6 \times 10^{-3}$

Table 4.7: Average  $\varepsilon^{(2)}(1s2s\ ^1S)$  for data sets consisting of various ranges for  $Z$ . (100 data sets).

Range for $Z$	Average value for $\varepsilon^{(2)}(1s2s\ ^1S)$	Number of parameters
2 – 18	-0.114 510 136 167 24(10)	11
3 – 18	-0.114 510 136 167 26(37)	10
4 – 18	-0.114 510 136 166 50(28)	10
5 – 18	-0.114 510 136 168 48(22)	9
6 – 18	-0.114 510 136 166 85(49)	9
7 – 18	-0.114 510 136 163 85(13)	8
2 – 15	-0.114 510 136 167 17(30)	11
2 – 16	-0.114 510 136 167 40(28)	11
2 – 17	-0.114 510 136 167 32(15)	11

Table 4.8:  $\varepsilon^{(2)}(1s2s\ ^3S)$  for various parameter sizes. (100 data sets).

Number of parameters	Average value for $\varepsilon^{(2)}(1s2s\ ^3S)$	$\chi^2$
8	-0.047 409 303 400(79)	$6.4 \times 10^9$
9	-0.047 409 304 253 8(60)	$5.7 \times 10^6$
10	-0.047 409 304 168 40(54)	$3.8 \times 10^3$
11	-0.047 409 304 176 111(50)	$2.1 \times 10^0$
12	-0.047 409 304 175 398(25)	$5.3 \times 10^{-1}$
13	-0.047 409 304 175 120(10)	$4.8 \times 10^{-1}$

Table 4.9: Average  $\epsilon^{(2)}(1s2s\ ^3S)$  for data sets consisting of various ranges for  $Z$ . (100 data sets).

Range for $Z$	Average value for $\epsilon^{(2)}(1s2s\ ^3S)$	Number of parameters
2 – 18	-0.047 409 304 175 398(25)	12
3 – 18	-0.047 409 304 175 537(25)	11
4 – 18	-0.047 409 304 175 245(15)	10
5 – 18	-0.047 409 304 175 266(53)	10
6 – 18	-0.047 409 304 175 739(40)	9
7 – 18	-0.047 409 304 175 376(89)	9
2 – 15	-0.047 409 304 175 666(56)	12
2 – 16	-0.047 409 304 175 553(81)	12
2 – 17	-0.047 409 304 176 440(56)	11

Table 4.10:  $\epsilon^{(2)}(1s2p\ ^1P)$  for various parameter sizes. (100 data sets).

Number of parameters	Average value for $\epsilon^{(2)}(1s2p\ ^1P)$	$\chi^2$
8	-0.157 028 661 887(70)	$1.9 \times 10^9$
9	-0.157 028 662 811 1(90)	$3.4 \times 10^6$
10	-0.157 028 662 952 1(11)	$3.8 \times 10^3$
11	-0.157 028 662 934 679 4(95)	$1.8 \times 10^{-1}$
12	-0.157 028 662 934 546 (22)	$7.2 \times 10^{-2}$
13	-0.157 028 662 934 540 (12)	$9.6 \times 10^{-2}$

Table 4.11: Average  $\varepsilon^{(2)}(1s2p\ ^1P)$  for data sets consisting of various ranges for  $Z$ . (100 data sets).

Range for $Z$	Average value for $\varepsilon^{(2)}(1s2p\ ^1P)$	Number of parameters
2 – 18	-0.157 028 662 934 679 4(95)	12
3 – 18	-0.157 028 662 934 570(19)	11
4 – 18	-0.157 028 662 934 560(84)	11
5 – 18	-0.157 028 662 934 939(12)	9
6 – 18	-0.157 028 662 934 934(43)	9
7 – 18	-0.157 028 662 934 62(13)	9
2 – 15	-0.157 028 662 934 723(25)	12
2 – 16	-0.157 028 662 934 740(13)	11
2 – 17	-0.157 028 662 934 582(36)	11

Table 4.12:  $\varepsilon^{(2)}(1s2p\ ^3P)$  for various parameter sizes. (100 data sets).

Number of parameters	Average value for $\varepsilon^{(2)}(1s2p\ ^3P)$	$\chi^2$
8	-0.072 998 988 18(39)	$7.9 \times 10^{10}$
9	-0.072 998 983 282(11)	$7.6 \times 10^6$
10	-0.072 998 983 455 2(15)	$1.0 \times 10^4$
11	-0.072 998 988 478 41(37)	$2.6 \times 10^{-2}$
12	-0.072 998 988 472 618(34)	$9.5 \times 10^{-5}$
13	-0.072 998 988 473 334 7(85)	$1.1 \times 10^{-4}$
14	-0.072 998 988 473 129(11)	$2.9 \times 10^{-2}$

was found that omitting the first data point ( $Z = 3, E_{n_1}$ ), see Tables 4.20, 4.21, 4.22, and 4.23, yielded more stability in the values for  $\varepsilon^{(3)}$  and the higher coefficients, and resulted in more accurate values in the energies obtained from these expansions. This result makes sense physically since the higher order terms of the  $Z$ -expansion Eq. (1.1) are of the form  $1/Z^n$ , where  $n = 1, 2, 3, \dots$ , so that the accuracy of our finite expansion determined from the fit increases with increasing  $Z$ . Hence, omitting the first data point ( $Z = 3, E_{n_1}$ ) tends to yield a better fit to our finite expansion. Another important point to note, which is partially illustrated by Tables 4.22, and 4.23 is that the  $Z$ -expansions became “unphysical” when the number of parameters used was equal to or larger than eight. That is, the higher order coefficients obtained in the expansions using a number of parameters greater or equal to eight became unusually large (of the order  $10^0$  for eight parameters, and up to  $10^3$  for nine or ten parameters). Also, the uncertainties (determined by the bootstrap method) in these higher order coefficients are in some cases larger than the values of the coefficients themselves, which is another indication that these values are not physically meaningful. Thus, the higher order coefficients  $\varepsilon^{(3)}, \varepsilon^{(4)}, \dots$  the  $Z$ -expansions are taken from the third columns of Tables 4.22, and 4.23. These higher order coefficients together with the lower order coefficients  $\varepsilon^{(0)}, \varepsilon^{(1)}$ , and  $\varepsilon^{(2)}$  from Eqs. (3.20), (3.40), (3.44), (4.7), and (4.8) form the  $Z$ -expansions used to obtain the nonrelativistic values in the third column of Tables 4.24 and 4.26.

From Tables 4.24, 4.26, 4.27 and 4.28 it is seen that the nonrelativistic values obtained from the  $Z$ -expansions are accurate to 8 and 7 figures after the decimal for the  $^2S$  and  $^2P$ -states, respectively, for  $Z = 15$ . The accuracy increases for increasing nuclear charge  $Z$ . Also, from Tables 4.24, 4.25, and 4.26 a comparison is made between the nonrelativistic energies obtained in this thesis and those obtained by K. T. Chung [8], [40] using the multiconfiguration interaction method and those of F. W. King [22] using the variational method with Hylleraas type wavefunctions. It is seen from these tables that King’s results are more accurate than those of Chung, and the results obtained in this thesis have improved these best previous results by about three orders of magnitude. Also, from

from Table 4.25, we see that King's results are higher than the ones obtained in this thesis by  $1 \times 10^{-6}$  a.u. ( $0.22\text{cm}^{-1}$ ) for  $Z = 3$  to  $2 \times 10^{-6}$  a.u. ( $0.44\text{cm}^{-1}$ ) for  $Z = 10$ . These differences do not vary much with  $Z$ , and the  $Z$ -expansions formed from a least squares fit of King's results would be less accurate for a given  $Z$ . For  $Z = 3$  the difference between King's result, and the one obtained in this thesis is of the same order of magnitude as the QED correction shown in Table 4.32. This shows that King's results would not be accurate enough to extract good QED corrections for the lower  $Z$  values, and it also demonstrates the importance of having very accurate nonrelativistic values.

### 4.1.3 Comparison With Experiment

To make a meaningful comparison with experiment, one must include the relativistic and mass polarization effects with the nonrelativistic values. These effects were calculated using first order perturbation theory, by K. T. Chung [8], [9] for the  $1s^2 2s^2 S$  states, and by Wang *et al.* [40] for the  $1s^2 2p^2 P$  states. The perturbations are given by the expectation values  $\langle H_1 + H_2 \rangle$ ,  $\langle H_3 \rangle$ ,  $\langle H_4 \rangle$ , and  $\langle H_5 \rangle$ , where

$$H_1 = -\frac{\alpha^2}{8} \sum_{i=1}^3 \mathbf{P}_i^4 \quad (4.9)$$

(correction to the kinetic energy arising from the variation of the masses with velocity),

$$H_2 = \frac{Z\pi\alpha^2}{2} \sum_{i=1}^3 \delta(\mathbf{r}_i) \quad (4.10)$$

(Darwin term which gives the electromagnetic correction to the static coulomb interaction due to the motion of the particles) ,

$$H_3 = -\pi\alpha^2 \sum_{\substack{i,j=1 \\ i < j}}^3 \left( 1 + \frac{8}{3} \mathbf{s}_i \cdot \mathbf{s}_j \right) \delta(\mathbf{r}_{ij}) \quad (4.11)$$

Table 4.13: Average  $\varepsilon^{(2)}(1s2p\ ^3P)$  for data sets consisting of various ranges for  $Z$ . (100 data sets).

Range for $Z$	Average value for $\varepsilon^{(2)}(1s2p\ ^3P)$	Number of parameters
2 – 18	-0.072 998 983 472 618(34)	12
3 – 18	-0.072 998 983 473 2 116(44)	12
4 – 18	-0.072 998 983 473 187(19)	12
5 – 18	-0.072 998 983 473 233(15)	11
6 – 18	-0.072 998 983 473 337(12)	10
7 – 18	-0.072 998 983 473 196(30)	10
2 – 15	-0.072 998 983 472 040(51)	13
2 – 16	-0.072 998 983 473 393 9(98)	13
2 – 17	-0.072 998 983 473 390 5(40)	12

Table 4.14: Convergence with the number of data sets used. (Eight parameters).

Number of data sets	Average value for $\varepsilon^{(3)}(1s^22s\ ^2S)$
2	-0.0165 483(6)
10	-0.0165 484(7)
50	-0.0165 483(6)
100	-0.0165 482(6)
200	-0.0165 481(6)
300	-0.0165 481(6)
1000	-0.0165 481(6)



Table 4.15: Average  $\varepsilon^{(3)}(1s^22p^2P)$  for data sets consisting of various ranges for  $Z$ . (300 data sets).

Number of data sets	Average value for $\varepsilon^{(3)}(1s^22p^2P)$
2	-0.069 831(4)
10	-0.069 827(7)
50	-0.069 826(6)
100	-0.069 827(7)
200	-0.069 827(6)
300	-0.069 827(7)
1000	-0.069 827(7)

Table 4.16:  $\varepsilon^{(3)}(1s^22s^2S)$  for various parameter sizes. (300 data sets, and  $Z = 3, 4, \dots, 15$ ).

Number of parameters	Average value for $\varepsilon^{(3)}(1s^22s^2S)$	$\chi^2$
6	-0.016 528(4)	$2.5 \times 10^3$
7	-0.016 556(2)	$1.7 \times 10^2$
8	-0.016 548 1(6)	$9.6 \times 10^{-1}$
9	-0.016 535(2)	$7.4 \times 10^{-1}$
10	-0.016 570(9)	$8.5 \times 10^{-1}$

Table 4.17: Average  $\varepsilon^{(3)}(1s^22s^2S)$  for data sets consisting of various ranges for  $Z$ . (300 data sets).

Range for $Z$	Average value for $\varepsilon_2(1s^22s^2S)$	Number of parameters
3 - 15	-0.016 548 1(6)	8
3 - 14	-0.016 547(1)	8
3 - 13	-0.016 545 1(5)	8
4 - 15	-0.016 551 1(2)	7
5 - 15	-0.016 551 2(7)	7

Table 4.18:  $\varepsilon^{(3)}(1s^22p^2P)$  for various parameter sizes. (300 data sets, and  $Z = 3, 4, \dots, 15$ ).

Number of parameters	Average value for $\varepsilon^{(3)}(1s^22p^2P)$	$\chi^2$
6	-0.069 927(45)	$6.4 \times 10^3$
7	-0.069 816(11)	$7.1 \times 10^0$
8	-0.069 827(7)	$4.4 \times 10^{-1}$
9	-0.069 818(35)	$4.1 \times 10^{-1}$
10	-0.069 886(37)	$2.0 \times 10^{-1}$

Table 4.19: Average  $\varepsilon^{(3)}(1s^22p^2P)$  for data sets consisting of various ranges for  $Z$ . (300 data sets).

Range for $Z$	Average value for $\varepsilon_2(1s^22p^2P)$	Number of parameters
3 - 15	-0.069 827(7)	8
3 - 14	-0.069 829(12)	8
3 - 13	-0.069 827(18)	8
4 - 15	-0.069 822(4)	7
5 - 15	-0.069 819(9)	7

Table 4.20:  $\varepsilon^{(3)}(1s^22s^2S)$  for various parameter sizes. (300 data sets, and  $Z = 4, 5, \dots, 15$ ).

Number of parameters	Average value for $\varepsilon^{(3)}(1s^22s^2S)$	$\chi^2$
6	-0.016 433(1)	$3.6 \times 10^1$
7	-0.016 551 1(2)	$6.3 \times 10^{-1}$
8	-0.016 551(1)	$7.8 \times 10^{-1}$
9	-0.016 565(7)	$8.3 \times 10^{-1}$
10	-0.016 49(6)	$1.1 \times 10^0$

Table 4.21:  $\epsilon^{(3)}(1s^2 2p \ ^2P)$  for various parameter sizes. (300 data sets, and  $Z = 4, 5, \dots, 15$ ).

Number of parameters	Average value for $\epsilon^{(3)}(1s^2 2p \ ^2P)$	$\chi^2$
6	-0.069 85(3)	$8.4 \times 10^1$
7	-0.069 822(4)	$3.3 \times 10^{-1}$
8	-0.069 82(2)	$3.8 \times 10^{-1}$
9	-0.069 87(3)	$1.8 \times 10^{-1}$
10	-0.069 46(6)	$3.5 \times 10^{-2}$

Table 4.22: Comparison of the coefficients obtained for the  $1s^2 2s \ ^2S$  state  $Z$ -expansion for various parameter sizes and ranges. (300 data sets).

Coefficient	$Z = 3, 4, \dots, 15$	$Z = 4, 5, \dots, 15$	$Z = 4, 5, \dots, 15$
	8 Parameters	7 Parameters	8 Parameters
$\epsilon^{(3)}$	-0.016 548 1(5)	-0.016 551 1(2)	-0.016 552(1)
$\epsilon^{(4)}$	-0.040 70(3)	-0.040 53(1)	-0.040 49(6)
$\epsilon^{(5)}$	-0.047 0(7)	-0.051 1(2)	-0.052(2)
$\epsilon^{(6)}$	-0.092(8)	-0.038(2)	-0.03(2)
$\epsilon^{(7)}$	+0.15(5)	-0.25(1)	-0.3(1)
$\epsilon^{(8)}$	-1.3(2)	+0.49(3)	+0.8(7)
$\epsilon^{(9)}$	+3±4	-1.23(3)	-2±2
$\epsilon^{(10)}$	-4±4		+0.9±2

Table 4.23: Comparison of the coefficients obtained for the  $1s^2 2p \ ^2P$  state  $Z$ -expansion for various parameter sizes and ranges. (300 data sets).

Coefficient	$Z = 3, 4, \dots, 15$	$Z = 4, 5, \dots, 15$	$Z = 4, 5, \dots, 15$
	8 Parameters	7 Parameters	8 Parameters
$\epsilon^{(3)}$	-0.069 827(7)	-0.069 822(4)	-0.069 82(2)
$\epsilon^{(4)}$	-0.092 6(3)	-0.092 9(1)	-0.093(1)
$\epsilon^{(5)}$	-0.092(6)	-0.086(2)	-0.08(2)
$\epsilon^{(6)}$	-0.06(6)	-0.14(2)	-0.2 $\pm$ 0.3
$\epsilon^{(7)}$	-0.07 $\pm$ 0.3	+0.4(1)	-0.9 $\pm$ 2
$\epsilon^{(8)}$	-0.6 $\pm$ 1	-1.5(3)	-4 $\pm$ 9
$\epsilon^{(9)}$	-1.4 $\pm$ 2	+3.3(3)	-8 $\pm$ 20
$\epsilon^{(10)}$	-4 $\pm$ 2		-5 $\pm$ 19

Table 4.24: Comparison of the nonrelativistic energies of the  $1s^2 2s \ ^2S$  states of the lithium isoelectronic sequence with those of K. T. Chung.

$Z$	Nonrelativistic Energy (a.u.)		
	This Work (Variational method)	Chung <sup>a</sup> (Full core plus correlation)	$Z$ -expansion
3	-7.478 060 322 74(20)	-7.478 059 7(9)	-7.478 052(65)
4	-14.324 763 175 78(17)	-14.324 761 0(11)	-14.324 763(15)
5	-23.424 605 720 78(48)	-23.424 603 1(13)	-23.424 605 5(51)
6	-34.775 511 275 11(16)	-34.775 508 2(15)	-34.775 511 2(23)
7	-48.376 898 318 43(13)	-48.376 849 9(18)	-48.376 898 3(12)
8	-64.228 542 082 00(13)	-64.228 538 5(19)	-64.228 542 06(72)
9	-82.330 338 096 65(16)	-82.330 334 8(21)	-82.330 338 09(46)
10	-102.682 231 481 79(17)	-102.682 227 8(22)	-102.682 231 48(31)
11	-125.284 190 753 24(18)	-125.248 189 4(22)	-125.284 190 76(23)
12	-150.136 196 603 84(15)	-150.136 195 8(23)	-150.136 196 61(17)
13	-177.238 236 559 11(22)	-177.238 235 7(23)	-177.238 236 57(13)
14	-206.590 302 212 14(47)	-206.590 301 7(24)	-206.590 302 22(10)
15	-238.192 387 693 56(18)	-238.192 387 3(24)	-238.192 387 70(9)

<sup>a</sup>Reference [9].

Table 4.25: Comparison of the nonrelativistic energies of the  $1s^2 2s^2 S$  states of the lithium isoelectronic sequence with those of F. W. King.

$Z$	Nonrelativistic Energy (a.u.)		
	This Work (Variational method)	King <sup>a</sup> (Variational method)	$Z$ -expansion
3	-7.478 060 322 74(20)	-7.478 059	-7.478 052(65)
4	-14.324 763 175 78(17)		-14.324 763(15)
5	-23.424 605 720 78(48)	-23.424 604	-23.424 605 5(51)
6	-34.775 511 275 11(16)	-34.775 509	-34.775 511 2(23)
7	-48.376 898 318 43(13)	-48.376 896	-48.376 898 3(12)
8	-64.228 542 082 00(13)	-64.228 540	-64.228 542 06(72)
9	-82.330 338 096 65(16)	-82.330 336	-82.330 338 09(46)
10	-102.682 231 481 79(17)	-102.682 229	-102.682 231 48(31)

<sup>a</sup>Reference [22].

Table 4.26: Comparison of the nonrelativistic energies of the  $1s^2 2p^2 P$  states of the lithium isoelectronic sequence with those of Wang *et al.* [39].

$Z$	Nonrelativistic Energy (a.u.)		
	This Work (Variational method)	Wang <i>et al.</i> <sup>a</sup> (Restricted variation method)	$Z$ -expansion
3	-7.410 156 531 252(67)	-7.410 154 1 (9)	-7.410 4(7)
4	-14.179 333 291 542(70)	-14.179 323 2	-14.179 4(1)
5	-23.204 441 191 42(11)	-23.204 423 2	-23.204 47(5)
6	-34.482 103 178 34(16)	-34.482 081 1	-34.482 11(2)
7	-48.011 054 280 66(12)	-48.011 030 8	-48.011 06(1)
8	-63.790 739 578 21(12)	-63.790 703 6	-63.790 743(7)
9	-81.820 880 912 03(14)	-81.820 852 1	-81.820 883(5)
10	-102.101 324 293 732(47)	-102.101 288 1	-102.101 326(3)
11	-124.631 977 817 7(18)		-124.631 979(2)
12	-149.412 783 331 3(17)		-149.412 784(2)
13	-176.443 702 274 8(19)		-176.443 703(1)
14	-205.724 708 089 6(20)		-205.724 709(1)
15	-237.255 781 892 6(19)		-237.255 782 3(9)

<sup>a</sup>Reference [40].

Table 4.27: The nonrelativistic energies (a.u.) from the  $Z$ -expansions ( $16 \leq Z \leq 54$ ).

$Z$	$1s2s \ ^2S$ States	$1s2p \ ^2P$ States
16	-272.044 488 80(7)	-271.036 910 2(7)
17	-308.146 602 40(6)	-307.068 082 1(6)
18	-346.498 726 18(5)	-345.349 290 0(5)
19	-387.100 858 34(4)	-385.880 527 9(4)
20	-429.952 997 49(4)	-428.661 791 0(4)
21	-475.055 142 52(3)	-473.693 075 4(3)
22	-522.407 292 56(3)	-520.974 378 1(3)
23	-572.009 446 88(3)	-570.505 696 5(3)
24	-623.861 604 90(2)	-622.287 028 7(2)
25	-677.963 766 13(2)	-676.318 372 7(2)
26	-734.315 930 18(2)	-732.599 727 3(2)
27	-792.918 096 709(18)	-791.131 091 15(19)
28	-853.770 265 422(18)	-851.912 463 23(18)
29	-916.872 436 080(16)	-914.943 842 65(16)
30	-982.224 608 473(15)	-980.225 228 65(15)
31	-1049.826 782 420(14)	-1047.756 620 57(14)
32	-1119.678 957 766(13)	-1117.538 017 82(13)
33	-1191.781 134 375(12)	-1189.569 419 90(12)
34	-1266.133 312 128(12)	-1263.850 826 37(12)
35	-1342.735 490 920(11)	-1340.382 236 84(11)
36	-1421.587 670 659(10)	-1419.163 650 96(10)
37	-1502.689 851 263(10)	-1500.195 068 422(95)
38	-1586.042 032 661 3(95)	-1583.476 488 961(95)
39	-1671.644 214 787 7(90)	-1669.007 912 327(90)
40	-1759.496 397 584 8(86)	-1756.789 338 303(86)
41	-1849.598 581 000 8(82)	-1846.820 766 691(83)
42	-1941.950 764 989 0(79)	-1939.102 197 313(79)
43	-2036.552 949 507 3(76)	-2033.633 630 009(76)
44	-2133.405 134 517 7(73)	-2130.415 064 632(73)
45	-2232.507 319 985 7(70)	-2229.446 501 052(70)
46	-2333.859 505 880 0(68)	-2330.727 939 146(68)
47	-2437.461 692 171 9(65)	-2434.259 378 806(65)
48	-2543.313 878 835 4(63)	-2540.040 819 930(63)
49	-2651.416 065 846 7(61)	-2648.072 262 427(61)
50	-2761.768 253 183 9(59)	-2758.353 706 212(59)
51	-2874.370 440 827 0(57)	-2870.885 151 207(57)
52	-2989.222 628 757 6(55)	-2985.666 597 341(55)
53	-3106.324 816 958 6(54)	-3102.698 044 548(54)
54	-3225.677 005 414 3(52)	-3221.979 492 766(52)

Table 4.28: The nonrelativistic energies (a.u.) from the  $Z$ -expansions ( $55 \leq Z \leq 92$ ).

$Z$	$1s2s$ $^2S$ States	$1s2p$ $^2P$ States
55	-3347.279 194 110 4(51)	-3343.510 941 939(51)
56	-3471.131 383 033 3(49)	-3467.292 392 015(49)
57	-3597.233 572 170 6(48)	-3593.323 842 945(48)
58	-3725.585 761 510 9(47)	-3721.605 294 684(47)
59	-3856.187 951 043 3(46)	-3852.136 747 190(46)
60	-3989.040 140 757 9(44)	-3984.918 200 424(44)
61	-4124.142 330 645 3(43)	-4119.949 654 348(43)
62	-4261.494 520 697 0(42)	-4257.231 108 930(42)
63	-4401.096 710 904 7(41)	-4396.762 564 136(41)
64	-4542.948 901 261 0(40)	-4538.544 019 938(40)
65	-4687.051 091 758 6(40)	-4682.575 476 307(39)
66	-4833.403 282 390 9(39)	-4828.856 933 216(39)
67	-4982.005 473 151 8(38)	-4977.388 390 642(38)
68	-5132.857 664 035 2(37)	-5128.169 848 560(37)
69	-5285.959 855 035 8(36)	-5281.201 306 949(36)
70	-5441.312 046 148 3(36)	-5436.482 765 789(36)
71	-5598.914 237 367 8(35)	-5594.014 225 060(35)
72	-5758.766 428 689 7(34)	-5753.795 684 744(34)
73	-5920.868 620 109 6(34)	-5915.827 144 823(34)
74	-6085.220 811 623 8(33)	-6080.108 605 282(33)
75	-6251.823 003 227 9(32)	-6246.640 066 104(32)
76	-6420.675 194 918 4(32)	-6415.421 527 275(32)
77	-6591.777 386 691 9(31)	-6586.452 988 782(31)
78	-6765.129 578 545 0(31)	-6759.734 450 610(31)
79	-6940.731 770 474 7(30)	-6935.265 912 749(30)
80	-7118.583 962 478 0(30)	-7113.047 375 185(30)
81	-7298.686 154 552 1(29)	-7293.078 837 908(29)
82	-7481.038 346 694 3(29)	-7475.360 300 908(29)
83	-7665.640 538 902 2(28)	-7659.891 764 173(28)
84	-7852.492 731 173 2(28)	-7846.673 227 694(28)
85	-8041.594 923 505 1(27)	-8035.704 691 463(27)
86	-8232.947 115 895 7(27)	-8226.986 155 470(27)
87	-8426.549 308 342 9(27)	-8420.517 619 707(27)
88	-8622.401 500 844 8(26)	-8616.299 084 166(26)
89	-8820.503 693 399 4(26)	-8814.330 548 839(26)
90	-9020.855 886 005 0(26)	-9014.612 013 720(26)
91	-9223.458 078 659 8(25)	-9217.143 478 800(25)
92	-9428.310 271 362 2(25)	-9421.924 944 075(25)

(electron-electron contact term which represents the interaction between the spin magnetic dipole moments of the electrons),

$$H_4 = -\frac{1}{M} \sum_{\substack{i,j=1 \\ i < j}} \nabla_i \cdot \nabla_j \quad (4.12)$$

(mass polarization effect which takes the finite mass of the nucleus into account),

$$H_5 = -\frac{\alpha^2}{2} \sum_{\substack{i,j=1 \\ i < j}} \frac{1}{r_{ij}} \left[ \mathbf{P}_i \cdot \mathbf{P}_j + \frac{\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{P}_i) \cdot \mathbf{P}_j}{r_{ij}^2} \right] \quad (4.13)$$

(orbit-orbit interaction which represents the correction due to the retardation of the electromagnetic field produced by one of the electrons at the site of the other), where  $M$  is the nuclear mass in a.u., and  $\alpha = 1/137.035\,989\,5(61)$  is the fine structure constant.

In Tables 4.29, and 4.30 the above relativistic and mass polarization corrections calculated by Chung *et al.* [8], [9], and [40] are added to the nonrelativistic values obtained in this thesis. Since Chung *et al.* do not quote uncertainties for these corrections, the uncertainties shown in Tables 4.29, and 4.30 had to be estimated. Chung *et al.* compare their restricted configuration-interaction calculations for the relativistic corrections of the  $1s^2$  core states to the more accurate high precision variational calculations of Pekeris [29]. The deviation between these results was used to determine the percentage error for the relativistic corrections of the  $1s^2$  core states. To estimate the uncertainties for the corrections shown in Tables 4.29, and 4.30 this percentage error was applied to the differences between the corrections of the  $1s^2 2s$  (or  $1s^2 2p$ ) states and those of the  $1s^2$  core states. Estimating the uncertainties in this way is reasonable since the percentage error in the energy difference that comes from adding an electron to the  $1s^2$  core should be about the same as the percentage error in the core energies.

Using the above method for estimating the uncertainties, it was found that for the  $^2P$ -states with  $Z = 3, 4,$  and  $5$  the error is in the eighth or ninth figure after the decimal, however Wang *et al.* [40] round off their values to seven significant figures. Thus, the error



in the total value for these energies (nonrelativistic + relativistic and mass polarizations corrections) in Table 4.30 was calculated by assuming a round off error of  $\pm 0.4$  in the final figures of the correction terms.

In Table 4.31, the total energies from Tables 4.29, and 4.30 are collected together and compared with experiment to obtain the “experimental” QED corrections shown in the second column of Table 4.32. This column was constructed using

$$E_{\text{QED}} = E_{\text{exp}} - (E_{\text{NR}} + E_{\text{rel}}), \quad (4.14)$$

where the  $E_{\text{exp}}$  are the experimental values from the fourth column of Table 4.31, the  $E_{\text{NR}}$  are the nonrelativistic values obtained in this thesis, and the  $E_{\text{rel}}$  are the first order relativistic and mass polarization corrections obtained from Chung *et al.* [8], [40]. The conversion from a.u. to  $\text{cm}^{-1}$  in Table 4.31 was done by multiplying the  $i^{\text{th}}$  energy value in the second column by two times the corresponding reduced Rydberg constant  $R_{M_i}$  calculated by Chung [8]. In Table 4.32, the experimental values for the QED energies are compared to theoretical estimates of these terms made by McKenzie and Drake [25], and by Chung *et al.* [9], [40] shown in the third and fourth columns, respectively. From this table, it may be seen that all the theoretical QED values, except for  $Z = 3$ , of McKenzie and Drake are consistently larger than the experimental values obtained in this thesis. The discrepancy ranges from about 13.8% larger for  $Z = 9$  to about 21.3% larger for  $Z = 8$ . It may also be observed from Table 4.32 that Chung *et al.*'s theoretical QED corrections are consistently smaller than the experimental values with a discrepancy between them which decreases steadily from 69.2% for  $Z = 3$  to 25% for  $Z = 10$ .

A possible explanation for Chung *et al.*'s exceptionally small value for  $Z = 3$  is given by McKenzie and Drake [25]. To determine the  $1s^2 2s \ ^2S - 1s^2 2p \ ^2P$  transition energies Chung *et al.* subtract the ionization potential of the  $^2S$ -state from that of the  $^2P$ -state. For each of these states, the QED effects of the core is assumed to cancel out in the ionization potential. Thus, the QED corrections are evaluated by them only for

the valence electron using the hydrogenic formulas [3]

$$\Delta E_{\text{QED}}(n, 0) = \frac{8Z_{\text{eff}}^4 \alpha^3 R}{3\pi n^3} \left\{ \frac{19}{30} - 2 \ln(\alpha Z_{\text{eff}}) - \ln[K_0(n, 0)] \right\} \quad (4.15)$$

for the valence 2s electron, and

$$\Delta E_{\text{QED}}(n, 1) = \frac{4Z_{\text{eff}}^4 \alpha^3 R}{3\pi n^3} \left\{ \frac{1}{8} C_{1J} - \ln[K_0(n, 1)] \right\}, \quad (4.16)$$

for the valence 2p electron, where

$$C_{1J} = \begin{cases} \frac{1}{2} & \text{for } J = \frac{3}{2} \\ -1 & \text{for } J = \frac{1}{2} \end{cases}.$$

In these equations,  $R$  is the Rydberg constant,  $n$  is the principal quantum number which equals 2 in this case,  $K_0(n, l)$  are the Bethe logarithms, and  $Z_{\text{eff}}$  is the effective nuclear charge which Chung et al. estimate from the equation

$$E_{\text{nonrel}}(1s^2 2l) - E_{\text{nonrel}}(1s^2) = -\frac{Z_{\text{eff}}^2}{2n^2}. \quad (4.17)$$

McKenzie and Drake [25] point out that the effective nuclear charge obtained from Eq. (4.17) overestimates the screening of the electron density at the nucleus leading to a value for  $Z = 3$  in Table 4.32 which is much too small.

The theoretical calculations for the QED corrections carried out by McKenzie and Drake [25] were an extension of a method developed previously for two-electron ions, and although it yields better results than the calculations of Chung *et al.* [9], [40] the discrepancy with the experimental values obtained in this thesis is still quite large.

#### 4.1.4 Conclusion, and Suggestions for Future Work

It is evident that the variational method using multiple basis sets in Hylleraas coordinates yields very accurate eigenvalues for the  $^2S$  and  $^2P$ -states of the lithium isoelectronic

sequence. The nonrelativistic energies presented in this thesis are the most accurate theoretical energies to date. However, the convergence characteristics and the extrapolated energies obtained in Tables 4.1 and 4.2 may be improved upon further by investigating the possibility of multiple roots in the energy surfaces (plots of the energies as a function of the nonlinear parameters), and by extrapolating the optimum nonlinear parameters for the larger basis sets from plots of the variational nonlinear parameters versus the basis set size  $\Omega$ .

Using the nonrelativistic energies obtained in this thesis, it has been possible to calculate some of the higher coefficients  $\varepsilon^{(3)}, \varepsilon^{(4)}, \dots$  of  $Z$ -expansions for the  $^2S$  and  $^2P$ -states. With these expansions, the nonrelativistic energies of the higher members of the lithium isoelectronic sequence ( $15 < Z < 92$ ) may be calculated to 9 or 10 significant figures after the decimal. The ultimate accuracy of the  $Z$ -expansions for higher  $Z$  is limited only by the accuracy of the second order coefficients  $\varepsilon^{(2)}$  which have been determined to about 12 significant figures.

With the first order relativistic and mass polarization effects calculated by Chung *et al.* [8], [40], Eq. (4.14) has been used to extract the QED corrections from experimental data, and a comparison with theoretical estimates has been made. From this comparison, it is seen that a substantial discrepancy exists between theory and experiment. The source of this discrepancy probably lies in the theoretical methods used to obtain the QED corrections. To be sure, more work is needed in this area.

In order to improve the accuracy of the experimental QED correction more accurate relativistic corrections are needed. However, there are difficulties in calculating the matrix elements of the Breit interaction using the more accurate wavefunctions containing Hylleraas coordinates. These difficulties arise from the fact that the integrals associated with these matrix elements contain inverse powers of the interelectron coordinates (from the Breit operator) which make these integrals very singular. Work on resolving these difficulties is currently being carried out by Zong-Chao Yan. These corrections could also be carried out for the higher  $Z$  members of the lithium isoelectronic sequence, however,

the leading higher-order relativistic contributions which are proportional to  $Z^6\alpha^4$  start to become more important for the higher nuclear charge ions. Thus, these higher-order corrections may also have to be calculated in order to obtain more accurate QED corrections for higher members of the lithium isoelectronic sequence. Finally, higher precision experimental values for  $Z > 3$  will be needed as the theoretical work continues to increase in accuracy.

Table 4.29: First order relativistic and mass polarization corrections added to the non-relativistic  $1s^2 2s \ ^2S$  state energies.

$Z$	3	4	5
Nonrel.	-7.478 060 322 74(20)	-14.324 763 175 78(17)	-23.424 605 720 96(66)
$\langle H_1 + H_2 \rangle$	-0.000 707 48(4)	-0.002 537 37(19)	-0.006 722 88(43)
$\langle H_3 \rangle$	0.000 095 340(89)	0.000 273 55(35)	0.000 597 386(76)
$\langle H_5 \rangle$	-0.000 023 331(2)	-0.000 048 626(6)	-0.000 083 357(8)
$\langle H_4 \rangle$	0.000 023 635(1)	0.000 027 603(2)	0.000 030 235(3)
Total	-7.478 672 158(97)	-14.327 048 02(40)	-23.430 784 33(88)
$Z$	6	7	8
Nonrel.	-34.775 511 275 11(16)	-48.376 898 318 43(13)	-64.228 542 082 00(12)
$\langle H_1 + H_2 \rangle$	-0.014 754 45(85)	-0.028 489 0(13)	-0.050 155 7(19)
$\langle H_3 \rangle$	0.001 111 3(14)	0.001 858 2(21)	0.002 882 8(31)
$\langle H_5 \rangle$	-0.000 127 541(8)	-0.000 181 166(5)	-0.000 244 241(3)
$\langle H_4 \rangle$	0.000 034 788(3)	0.000 035 872(3)	0.000 036 721(3)
Total	-34.789 247 2(16)	-48.403 674 4(25)	-64.276 022 4(36)
$Z$	9	10	
Nonrel.	-82.330 338 096 65(16)	-102.682 231 481 79(17)	
$\langle H_1 + H_2 \rangle$	-0.082 350 9(27)	-0.128 041 4(39)	
$\langle H_3 \rangle$	0.004 228 8(42)	0.005 939 9(55)	
$\langle H_5 \rangle$	-0.000 316 769(9)	-0.000 398 744(19)	
$\langle H_4 \rangle$	0.000 035 397(3)	0.000 037 900(3)	
Total	-82.408 741 6(50)	-102.804 693 8(68)	

Table 4.30: First order relativistic and mass polarization corrections added to the non-relativistic  $1s^2 2p \ ^2P$  state energies.

$Z$	3	4	5
Nonrel.	-7.410 156 531 252(67)	-14.179 333 291 542(70)	-23.204 441 191 42(10)
$\langle H_1 + H_2 \rangle$	-0.000 693 3(0)	-0.002 440 5(0)	-0.006 397 4(0)
$\langle H_3 \rangle$	0.000 093 6(0)	0.000 263 8(0)	0.000 571 3(0)
$\langle H_5 \rangle$	-0.000 021 3(0)	-0.000 032 9(0)	-0.000 033 9(0)
$\langle H_4 \rangle$	0.000 019 4(0)	0.000 010 2(0)	-0.000 004 1(0)
Total	-7.410 758 1(1)	-14.181 532 7(1)	-23.210 305 3(1)

$Z$	6	7	8
Nonrel.	-34.482 103 178 34(15)	-48.011 054 280 66(12)	-63.790 739 578 21(12)
$\langle H_1 + H_2 \rangle$	-0.013 951 4(2)	-0.026 831 6(4)	-0.047 103 7(6)
$\langle H_3 \rangle$	0.001 057 1(1)	0.001 762 7(2)	0.002 729 5(4)
$\langle H_5 \rangle$	-0.000 016 7(1)	0.000 026 4(1)	0.000 103 4(0)
$\langle H_4 \rangle$	-0.000 022 6(0)	-0.000 041 8(1)	-0.000 061 5(1)
Total	-34.495 036 8(2)	-48.036 138 6(5)	-63.835 071 9(7)

$Z$	9	10
Nonrel.	-81.820 880 912 03(14)	-102.101 324 293 732(47)
$\langle H_1 + H_2 \rangle$	-0.077 206 3(9)	-0.119 878 2(13)
$\langle H_3 \rangle$	0.003 998 6(7)	0.005 611 8(10)
$\langle H_5 \rangle$	0.000 221 8(22)	0.000 389 6(6)
$\langle H_4 \rangle$	-0.000 077 4(1)	-0.000 102 1(1)
Total	-81.893 944 2(25)	-102.215 303 2(18)

Table 4.31: Comparison between theory and experiment for the  $1s^22s\ ^2S - 1s^22p\ ^2P$  transition energies of the lithium isoelectronic sequence.

$Z$	Theory		Experiment
	(a.u.)	( $\text{cm}^{-1}$ )	( $\text{cm}^{-1}$ )
3	0.067 914 0(1)	14 904.13(2)	14 903.871 689(10) <sup>a</sup>
4	0.145 515 3(4)	31 934.69(10)	31 933.14(2) <sup>b</sup>
5	0.220 479 0(9)	48 386.3(2)	48 380.8(7) <sup>c</sup>
6	0.294 210 4(16)	64 567.8(4)	64 555.5(7) <sup>c</sup>
7	0.367 535 8(26)	80 660.3(6)	80 635.7(1.0) <sup>c</sup>
8	0.440 950 5(37)	96 771.2(8)	96 730.0(1.0) <sup>c</sup>
9	0.514 973 6(56)	112 981.3(1.2)	112 910.7(9) <sup>d</sup>
10	0.589 390 7(70)	129 352.7(1.5)	129 250.3(1.3) <sup>c</sup>

<sup>a</sup>Reference [6].

<sup>b</sup>Reference [14].

<sup>c</sup>Reference [15].

<sup>d</sup>Reference [16].

Table 4.32: Comparison of Theory minus Experiment with directly calculated QED corrections.

$Z$	Theory–Expt. ( $\text{cm}^{-1}$ )	QED Corr. <sup>e</sup> ( $\text{cm}^{-1}$ )	QED Corr. <sup>f</sup> ( $\text{cm}^{-1}$ )
3	0.26(2)	0.23(2)	0.08(1)
4	1.55(10)		0.78(5)
5	5.1(5)		2.96(18)
6	12.3(8)		7.69(54)
7	25(1)	29.2	16.2(1.1)
8	41(1)	50.0	29.6(2.4)
9	71(2)	80.1	49.3(3.4)
10	102(2)	120.7	76.5(5.3)

<sup>e</sup>Reference [25].

<sup>f</sup>Reference [9], and [40].

# Appendix A

## Determination the Del Operators

To determine the effect of  $\nabla_i^2$ , operating on a member of the basis set, we begin by writing the variable dependence of our trial wave function:

$$\Psi = R(r_1, r_2, r_3, r_{12}, r_{13}, r_{23})\Omega,$$

where  $\Omega = Y_{l_1 m_1}(\hat{r}_1)Y_{l_2 m_2}(\hat{r}_2)Y_{l_3 m_3}(\hat{r}_3)$ . Next, we apply  $\nabla_i^2$  to  $\Psi$  so that we may find the form of the  $\nabla_i^2$  operators. For example,

$$\begin{aligned} \nabla_1 \Psi &= \left[ \left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1} \right) R \right] \Omega + R \nabla_1^y \Omega \\ &= \left[ \left( \frac{\partial R}{\partial r_1} \frac{\partial r_1}{\partial x_1} + \frac{\partial R}{\partial r_{12}} \frac{\partial r_{12}}{\partial x_1} + \frac{\partial R}{\partial r_{13}} \frac{\partial r_{13}}{\partial x_1} \right), \left( \frac{\partial R}{\partial r_1} \frac{\partial r_1}{\partial y_1} + \frac{\partial R}{\partial r_{12}} \frac{\partial r_{12}}{\partial y_1} + \frac{\partial R}{\partial r_{13}} \frac{\partial r_{13}}{\partial y_1} \right), \right. \\ &\quad \left. \left( \frac{\partial R}{\partial r_1} \frac{\partial r_1}{\partial z_1} + \frac{\partial R}{\partial r_{12}} \frac{\partial r_{12}}{\partial z_1} + \frac{\partial R}{\partial r_{13}} \frac{\partial r_{13}}{\partial z_1} \right) \right] \Omega + R \nabla_1^y \Omega \\ &= \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \Omega + R \nabla_1^y \Omega, \end{aligned} \tag{A.1}$$

where  $\nabla_1^y$  acts only on the spherical part. Then,

$$\begin{aligned} \nabla_1^2 \Psi &= \nabla_1 \cdot \left[ \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \Omega \right] + \nabla_1 \cdot (R \nabla_1^y \Omega) \\ &= \text{I} + \text{II} \end{aligned} \tag{A.2}$$



where,

$$\begin{aligned} \text{I} &= \left[ \nabla_1 \cdot \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \right] \Omega, \\ \text{II} &= \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \cdot \nabla_1^y \Omega + (\nabla_1 R) (\nabla_1^y \Omega) + R \nabla_1^2 \Omega. \end{aligned}$$

Now,

$$\begin{aligned} \text{I} &= \left[ \nabla_1 \cdot \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \right] \Omega \\ &= \left[ \nabla_1 \cdot \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} \right) + \nabla_1 \cdot \left( \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} \right) + \nabla_1 \cdot \left( \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \right] \Omega, \end{aligned}$$

where

$$\begin{aligned} \nabla_1 \cdot \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} \right) &= \frac{2}{r_1} \frac{\partial R}{\partial r_1} + \frac{\partial^2 R}{\partial r_1^2} + \frac{\mathbf{r}_1 \cdot \mathbf{r}_{12}}{r_1 r_{12}} \frac{\partial^2 R}{\partial r_{12} \partial r_1} + \frac{\mathbf{r}_1 \cdot \mathbf{r}_{13}}{r_1 r_{13}} \frac{\partial^2 R}{\partial r_{13} \partial r_1}, \\ \nabla_1 \cdot \left( \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} \right) &= \frac{2}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\partial^2 R}{\partial r_{12}^2} + \frac{\mathbf{r}_1 \cdot \mathbf{r}_{12}}{r_1 r_{12}} \frac{\partial^2 R}{\partial r_1 \partial r_{12}} + \frac{\mathbf{r}_{12} \cdot \mathbf{r}_{13}}{r_{12} r_{13}} \frac{\partial^2 R}{\partial r_{12} \partial r_{13}}, \end{aligned}$$

and

$$\nabla_1 \cdot \left( \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) = \frac{2}{r_{13}} \frac{\partial R}{\partial r_{13}} + \frac{\partial^2 R}{\partial r_{13}^2} + \frac{\mathbf{r}_1 \cdot \mathbf{r}_{13}}{r_1 r_{13}} \frac{\partial^2 R}{\partial r_1 \partial r_{13}} + \frac{\mathbf{r}_{12} \cdot \mathbf{r}_{13}}{r_{12} r_{13}} \frac{\partial^2 R}{\partial r_{12} \partial r_{13}}.$$

Using the fact that  $\mathbf{r}_1 \cdot \mathbf{r}_{12} = \frac{1}{2}(r_1^2 - r_2^2 + r_{12}^2)$ , and  $\mathbf{r}_{12} \cdot \mathbf{r}_{13} = \frac{1}{2}(r_{12}^2 - r_{13}^2 + r_{23}^2)$ , we get

$$\begin{aligned} \text{I} &= \left[ \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{\partial^2}{\partial r_{13}^2} + 2 \left( \frac{1}{r_1} \frac{\partial}{\partial r_1} + \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} + \frac{1}{r_{13}} \frac{\partial}{\partial r_{13}} \right) + \left( \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_{12} \partial r_1} \right. \right. \\ &\quad \left. \left. + \frac{r_1^2 - r_{13}^2 + r_{12}^2}{r_1 r_{13}} \frac{\partial^2}{\partial r_1 \partial r_{13}} + \frac{r_{12}^2 - r_{13}^2 + r_{23}^2}{r_{12} r_{13}} \frac{\partial^2}{\partial r_{12} \partial r_{13}} \right) \right] \Psi \end{aligned}$$

Also,

$$\text{II} = \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \cdot \nabla_1^y \Omega + (\nabla_1 R) (\nabla_1^y \Omega) + R \nabla_1^2 \Omega$$

$$\begin{aligned}
&= \frac{1}{r_1} \frac{\partial R}{\partial r_1} (\mathbf{r}_1 \cdot \nabla_1^y \Omega) + \frac{1}{r_{12}} \frac{\partial R}{\partial r_{12}} (\mathbf{r}_{12} \cdot \nabla_1^y \Omega) + \frac{1}{r_{13}} \frac{\partial R}{\partial r_{13}} (\mathbf{r}_{13} \cdot \nabla_1^y \Omega) \\
&\quad + (\nabla_1 R) (\nabla_1^y \Omega) - R \frac{l_1(l_1+1)}{r_1^2} \Omega,
\end{aligned}$$

but,  $\mathbf{r}_1 \perp \nabla_1^y Y_{l_1 m_1}(\hat{\mathbf{r}}_1)$ , so that,

$$\begin{aligned}
\mathbf{r}_1 \cdot \nabla_1^y \Omega &= [\mathbf{r}_1 \cdot \nabla_1^y Y_{l_1 m_1}(\hat{\mathbf{r}}_1)] Y_{l_2 m_2}(\hat{\mathbf{r}}_2) Y_{l_3 m_3}(\hat{\mathbf{r}}_3) \\
&= 0.
\end{aligned}$$

Similarly,

$$\begin{aligned}
\mathbf{r}_{12} \cdot \nabla_1^y \Omega &= (\mathbf{r}_1 - \mathbf{r}_2) \cdot \nabla_1^y \Omega \\
&= \mathbf{r}_1 \cdot \nabla_1^y \Omega - \mathbf{r}_2 \cdot \nabla_1^y \Omega \\
&= -\mathbf{r}_2 \cdot \nabla_1^y \Omega,
\end{aligned}$$

and,  $\mathbf{r}_{13} \cdot \nabla_1^y \Omega = -\mathbf{r}_3 \cdot \nabla_1^y \Omega$ . Thus,

$$\begin{aligned}
\text{II} &= -\frac{1}{r_{12}} \frac{\partial R}{\partial r_{12}} (\mathbf{r}_2 \cdot \nabla_1^y \Omega) - \frac{1}{r_{13}} \frac{\partial R}{\partial r_{13}} (\mathbf{r}_3 \cdot \nabla_1^y \Omega) + (\nabla_1 R) (\nabla_1^y \Omega) - R \frac{l_1(l_1+1)}{r_1^2} \Omega \\
&= -\frac{1}{r_{12}} \frac{\partial R}{\partial r_{12}} (\mathbf{r}_2 \cdot \nabla_1^y \Omega) - \frac{1}{r_{13}} \frac{\partial R}{\partial r_{13}} (\mathbf{r}_3 \cdot \nabla_1^y \Omega) + \left( \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial R}{\partial r_{12}} + \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial R}{\partial r_{13}} \right) \\
&\quad \times (\nabla_1^y \Omega) - R \frac{l_1(l_1+1)}{r_1^2} \Omega \\
&= -\frac{1}{r_{12}} \frac{\partial R}{\partial r_{12}} (\mathbf{r}_2 \cdot \nabla_1^y \Omega) - \frac{1}{r_{13}} \frac{\partial R}{\partial r_{13}} (\mathbf{r}_3 \cdot \nabla_1^y \Omega) - \frac{1}{r_{12}} \frac{\partial R}{\partial r_{12}} (\mathbf{r}_2 \cdot \nabla_1^y \Omega) \\
&\quad - \frac{1}{r_{13}} \frac{\partial R}{\partial r_{13}} (\mathbf{r}_3 \cdot \nabla_1^y \Omega) - R \frac{l_1(l_1+1)}{r_1^2} \Omega \\
&= \left[ -2(\mathbf{r}_2 \cdot \nabla_1^y) \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} - 2(\mathbf{r}_3 \cdot \nabla_1^y) \frac{1}{r_{13}} \frac{\partial}{\partial r_{13}} - \frac{l_1(l_1+1)}{r_1^2} \right] R \Omega.
\end{aligned}$$

Now adding I and II, we get

$$\nabla_1^2 \Psi = \text{I} + \text{II}$$

$$\begin{aligned}
&= \left[ \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{\partial^2}{\partial r_{13}^2} + 2 \left( \frac{1}{r_1} \frac{\partial}{\partial r_1} + \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} + \frac{1}{r_{13}} \frac{\partial}{\partial r_{13}} \right) \right. \\
&\quad + \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_{12} \partial r_1} + \frac{r_1^2 - r_3^2 + r_{13}^2}{r_1 r_{13}} \frac{\partial^2}{\partial r_1 \partial r_{13}} \\
&\quad + \frac{r_{12}^2 - r_3^2 + r_{23}^2}{r_{12} r_{13}} \frac{\partial^2}{\partial r_{12} \partial r_{13}} - 2(\mathbf{r}_2 \cdot \nabla_1^y) \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} - 2(\mathbf{r}_3 \cdot \nabla_1^y) \frac{1}{r_{13}} \frac{\partial}{\partial r_{13}} \\
&\quad \left. - \frac{l_1(l_1 + 1)}{r_1^2} \right] \Psi.
\end{aligned}$$

Therefore,

$$\begin{aligned}
\nabla_1^2 &= \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{\partial^2}{\partial r_{13}^2} + 2 \left( \frac{1}{r_1} \frac{\partial}{\partial r_1} + \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} + \frac{1}{r_{13}} \frac{\partial}{\partial r_{13}} \right) \\
&\quad + \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_{12} \partial r_1} + \frac{r_1^2 - r_3^2 + r_{13}^2}{r_1 r_{13}} \frac{\partial^2}{\partial r_1 \partial r_{13}} \\
&\quad + \frac{r_{12}^2 - r_3^2 + r_{23}^2}{r_{12} r_{13}} \frac{\partial^2}{\partial r_{12} \partial r_{13}} - 2(\mathbf{r}_2 \cdot \nabla_1^y) \frac{1}{r_{12}} - 2(\mathbf{r}_3 \cdot \nabla_1^y) \frac{1}{r_{13}} \frac{\partial}{\partial r_{13}} \\
&\quad - \frac{l_1(l_1 + 1)}{r_1^2}. \tag{A.3}
\end{aligned}$$

A similar result is obtained for  $\nabla_2^2$  but with the indices 1 and 2 interchanged, and also for  $\nabla_3^2$  but with the indices 1 and 3 interchanged.

## Appendix B

### Evaluation of the Angular Integral $\tilde{I}$

With the use of the spherical harmonic addition theorem,

$$P_{q_{ab}}(\cos \theta_{ab}) = \frac{4\pi}{2q_{ab} + 1} \sum_{m_{ab}} Y_{q_{ab}m_{ab}}^*(\hat{r}_1) Y_{q_{ab}m_{ab}}(\hat{r}_2) \quad (\text{B.1})$$

the angular integral (2.29), becomes

$$\tilde{I} = \int d\Omega_1 d\Omega_2 d\Omega_3 \frac{64\pi^3}{(2q_{12} + 1)(2q_{23} + 1)(2q_{31} + 1)} \sum_{m_{12}} \sum_{m_{23}} \sum_{m_{31}} A_1 A_2 A_3 \quad (\text{B.2})$$

where

$$A_1 = Y_{l'_1 m'_1}^*(\hat{r}_1) Y_{l_1 m_1}(\hat{r}_1) Y_{q_{12} m_{12}}^*(\hat{r}_1) Y_{q_{31} m_{31}}(\hat{r}_1)$$

$$A_2 = Y_{l'_2 m'_2}^*(\hat{r}_2) Y_{l_2 m_2}(\hat{r}_2) Y_{q_{12} m_{12}}^*(\hat{r}_2) Y_{q_{23} m_{23}}(\hat{r}_2),$$

and

$$A_3 = Y_{l'_3 m'_3}^*(\hat{r}_3) Y_{l_3 m_3}(\hat{r}_3) Y_{q_{31} m_{31}}^*(\hat{r}_3) Y_{q_{23} m_{23}}(\hat{r}_3).$$

Then using,  $Y_{LM}^* = (-1)^M Y_{L-M}$ , we obtain

$$A_1 = (-1)^{m'_1} Y_{l'_1 -m'_1}(\hat{r}_1) Y_{l_1 m_1}(\hat{r}_1) (-1)^{m_{12}} Y_{q_{12} -m_{12}}(\hat{r}_1) Y_{q_{31} m_{31}}(\hat{r}_1),$$

and with the relation,

$$Y_{LM}(\hat{r})Y_{L'M'}(\hat{r}) = \sum_{L''M''} Y_{L''M''}^*(\hat{r}) \frac{(L, L', L'')^{\frac{1}{2}}}{\sqrt{4\pi}} (-1)^{M''} \begin{pmatrix} L & L' & L'' \\ M & M' & -M'' \end{pmatrix} \begin{pmatrix} L & L' & L'' \\ 0 & 0 & 0 \end{pmatrix}, \quad (\text{B.3})$$

where,  $M'' = M + M'$  and  $(L, L', L'')^{\frac{1}{2}} = (2L + 1)^{\frac{1}{2}}(2L' + 1)^{\frac{1}{2}}(2L'' + 1)^{\frac{1}{2}}$ , we get

$$A_1 = (-1)^{m'_1+m_{12}} \left\{ \sum_{n_1 s_1} \frac{(L, L', n_1)^{\frac{1}{2}}}{\sqrt{4\pi}} \begin{pmatrix} l'_1 & l_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & l_1 & n_1 \\ -m'_1 & m_1 & s_1 \end{pmatrix} (-1)^{s_1} Y_{n_1 s_1}^*(\hat{r}_1) \right. \\ \left. \times \sum_{n_{23} s_{23}} \frac{(q_{12}, q_{31}, q_{23})^{\frac{1}{2}}}{\sqrt{4\pi}} \begin{pmatrix} q_{12} & q_{31} & q_{23} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_{23} \\ -m_{12} & m_{31} & s_{23} \end{pmatrix} (-1)^{s_{23}} Y_{n_{23} s_{23}}^*(\hat{r}_1) \right\}$$

where,  $s_1 = m'_1 - m_1$ , and  $s_{23} = m_{12} - m_{31}$ . Now, evaluating this further using again relation (B.3), we get

$$A_1 = (-1)^{m'_1+m_{12}} \frac{1}{(4\pi)^{\frac{3}{2}}} \sum_{n_1 n_{23} n_0} \sum_{s_1 s_{23} s_0} (n_1, n_{23}) (l'_1, l_1, q_{12}, q_{31}, n_0)^{\frac{1}{2}} \begin{pmatrix} l'_1 & l_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} q_{12} & q_{31} & n_{23} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n_1 & n_{23} & n_0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & l_1 & n_1 \\ -m'_1 & m_1 & s_1 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_{23} \\ -m_{12} & m_{31} & s_{23} \end{pmatrix} \\ \times \begin{pmatrix} n_1 & n_{23} & n_0 \\ s_1 & s_{23} & s_0 \end{pmatrix} Y_{n_0 s_0}(\hat{r}_1) (-1)^{s_1+s_{23}+s_0}$$

where,  $s_0 = s_{23} - s_1$ . Similarly,

$$A_2 = (-1)^{m'_2+m_{23}} \frac{1}{(4\pi)^{\frac{3}{2}}} \sum_{n_2 n_{13} n'_0} \sum_{s_2 s_{13} s'_0} (n_{21}, n_{13}) (l'_2, l_2, q_{12}, q_{23}, n'_0)^{\frac{1}{2}} \begin{pmatrix} l'_2 & l_2 & n_2 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} q_{23} & q_{12} & n_{13} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n_2 & n_{13} & n'_0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & l_2 & n_2 \\ -m'_2 & m_2 & s_2 \end{pmatrix} \begin{pmatrix} q_{23} & q_{12} & n_{13} \\ -m_{23} & m_{12} & s_{13} \end{pmatrix}$$

$$\times \begin{pmatrix} n_2 & n_{13} & n'_0 \\ s_2 & s_{13} & s'_0 \end{pmatrix} Y_{n'_0 s'_0}(\widehat{r}_2) (-1)^{s_1 + s_{23} + s'_0},$$

and

$$\begin{aligned} A_3 &= (-1)^{m'_3 + m_{31}} \frac{1}{(4\pi)^{\frac{3}{2}}} \sum_{n_3 n_{12} n''_0} \sum_{s_3 s_{12} s''_0} (n_3, n_{12}) (l'_3, l_3, q_{31}, q_{23}, n''_0)^{\frac{1}{2}} \begin{pmatrix} l'_3 & l_3 & n_3 \\ 0 & 0 & 0 \end{pmatrix} \\ &\times \begin{pmatrix} q_{31} & q_{23} & n_{12} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n_3 & n_{12} & n''_0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_3 & l_3 & n_3 \\ -m'_3 & m_3 & s_3 \end{pmatrix} \begin{pmatrix} q_{31} & q_{23} & n_{12} \\ -m_{31} & m_{23} & s_{12} \end{pmatrix} \\ &\times \begin{pmatrix} n_3 & n_{12} & n''_0 \\ s_3 & s_{12} & s''_0 \end{pmatrix} Y_{n''_0 s''_0}(\widehat{r}_3) (-1)^{s_3 + s_{12} + s''_0}. \end{aligned}$$

Now using,  $\sqrt{4\pi} \int d\Omega_1 Y_{n_0 s_0}(\widehat{r}_1) Y_{00}(\widehat{r}_1) = \sqrt{4\pi} \delta_{n_0,0} \delta_{s_0,0}$ , we have

$$\int d\Omega_1 d\Omega_2 d\Omega_3 Y_{n_0 s_0}(\widehat{r}_1) Y_{n'_0 s'_0}(\widehat{r}_2) Y_{n''_0 s''_0}(\widehat{r}_3) = (4\pi)^{\frac{3}{2}} \delta_{n_0,0} \delta_{n'_0,0} \delta_{n''_0,0} \delta_{s_0,0} \delta_{s'_0,0} \delta_{s''_0,0},$$

so that,

$$\begin{aligned} \int A_1 d\Omega_1 &= (-1)^{m'_1 + m_{12}} \frac{1}{4\pi} \sum_{n_1 n_{23} s_1 s_{23}} (2n_1 + 1)(2n_{23} + 1) (l'_1, l_1, q_{12}, q_{31})^{\frac{1}{2}} \begin{pmatrix} l'_1 & l_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\times \begin{pmatrix} q_{12} & q_{31} & n_{23} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n_1 & n_{23} & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & l_1 & n_1 \\ -m'_1 & m_1 & s_1 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_{23} \\ -m_{12} & m_{31} & s_{23} \end{pmatrix} \\ &\times \begin{pmatrix} q_{12} & q_{31} & n_{23} \\ -m_{12} & m_{31} & s_{23} \end{pmatrix} \begin{pmatrix} n_1 & n_{23} & 0 \\ s_1 & s_{23} & 0 \end{pmatrix}. \end{aligned}$$

and with the relation,

$$\begin{pmatrix} a & b & 0 \\ \alpha & \beta & 0 \end{pmatrix} = (-1)^{a-\alpha} \delta_{a,b} \delta_{\alpha,-\beta} (2a+1)^{-1/2} \quad (\text{B.4})$$

the integral reduces to

$$\int A_1 d\Omega_1 = (-1)^{m_1+m_{12}} \frac{1}{4\pi} \sum_{n_1} (2n_1+1) (l'_1, l_1, q_{12}, q_{31})^{\frac{1}{2}} \begin{pmatrix} l'_1 & l_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_1 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} l'_1 & l_1 & n_1 \\ -m'_1 & m_1 & m'_1 - m_1 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_1 \\ -m_{12} & m_{31} & m_1 - m'_1 \end{pmatrix}.$$

Following a similar procedure for the  $A_2$  and  $A_3$  integrals, we get

$$\int A_2 d\Omega_2 = (-1)^{m_2+m_{23}} \frac{1}{4\pi} \sum_{n_2} (2n_2+1) (l'_2, l_2, q_{12}, q_{23})^{\frac{1}{2}} \begin{pmatrix} l'_2 & l_2 & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{23} & q_{12} & n_2 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} l'_2 & l_2 & n_2 \\ -m'_2 & m_2 & m'_2 - m_2 \end{pmatrix} \begin{pmatrix} q_{23} & q_{12} & n_2 \\ -m_{23} & m_{12} & m_2 - m'_2 \end{pmatrix},$$

and

$$\int A_3 d\Omega_3 = (-1)^{m_3+m_{31}} \frac{1}{4\pi} \sum_{n_3} (2n_3+1) (l'_3, l_3, q_{31}, q_{23})^{\frac{1}{2}} \begin{pmatrix} l'_3 & l_3 & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{31} & q_{23} & n_3 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} l'_3 & l_3 & n_3 \\ -m'_3 & m_3 & m'_3 - m_3 \end{pmatrix} \begin{pmatrix} q_{31} & q_{23} & n_3 \\ -m_{31} & m_{23} & m_3 - m'_3 \end{pmatrix}.$$

Now, substituting these evaluated integrals into Eq. (B.2), we obtain

$$\tilde{I} = (-1)^{m_1+m_2+m_3} (l_1, l_2, l_3, l'_1, l'_2, l'_3)^{\frac{1}{2}} \sum_{m_{12}m_{23}m_{31}} \sum_{n_1n_2n_3} (-1)^{m_{12}+m_{23}+m_{31}} (n_1, n_2, n_3) \\ \times \begin{pmatrix} l'_1 & l_1 & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & l_2 & n_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_3 & l_3 & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} q_{23} & q_{12} & n_2 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} q_{31} & q_{23} & n_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & l_1 & n_1 \\ -m'_1 & m_1 & m'_1 - m_1 \end{pmatrix} \begin{pmatrix} q_{12} & q_{31} & n_1 \\ -m_{12} & m_{31} & m_1 - m'_1 \end{pmatrix}$$

$$\begin{aligned}
& \times \begin{pmatrix} l'_2 & l_2 & n_2 \\ -m'_2 & m_2 & m'_2 - m_2 \end{pmatrix} \begin{pmatrix} q_{23} & q_{12} & n_2 \\ -m_{23} & m_{12} & m_2 - m'_2 \end{pmatrix} \begin{pmatrix} q_{31} & q_{23} & n_3 \\ -m_{31} & m_{23} & m_3 - m'_3 \end{pmatrix} \\
& \times \begin{pmatrix} l'_3 & l_3 & n_3 \\ -m'_3 & m_3 & m'_3 - m_3 \end{pmatrix}, \tag{B.5}
\end{aligned}$$

and using the relation

$$\begin{aligned}
& \sum_{\alpha\beta\gamma} (-1)^{A+B+C+\alpha+\beta+\gamma} \begin{pmatrix} A & B & c \\ \alpha & -\beta & \gamma' \end{pmatrix} \begin{pmatrix} B & C & \alpha \\ \beta & -\gamma & \alpha' \end{pmatrix} \begin{pmatrix} C & A & b \\ \gamma & -\alpha & \beta' \end{pmatrix} \\
& = \left\{ \begin{matrix} a & b & c \\ A & B & C \end{matrix} \right\} \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix} \tag{B.6}
\end{aligned}$$

this may be further simplified to Eq. (2.36).



# Appendix C

## Derivation of the Backward Recursion Relation

We begin by considering

$$F(1, s+1+p; s+1; z) = \sum_{n=0}^{\infty} \frac{(1)_n (s+1+p)_n}{n! (s+1)!} z^n, \quad (\text{C.1})$$

where  $(a)_n = a(a+1)(a+2)\cdots(a+n-1)$  and  $(a)_0 = 1$ . Next, we make use of the fact that

$$\begin{aligned} (a)_n &= (a)(a+1)(a+2)\cdots(a+n-1) \\ &= \frac{(a+n-1)!}{(a-1)!}, \end{aligned} \quad (\text{C.2})$$

to rewrite Eq. (C.1) as

$$\begin{aligned} F(1, s+1+p; s+1; z) &= \sum_{n=0}^{\infty} \frac{n!(s+p+n)!s!}{n!(s+p)!(s+n)!} z^n \\ &= \frac{s!}{(s+p)!} \sum_{n=0}^{\infty} \frac{(s+p+n)!}{(s+n)!} z^n \end{aligned} \quad (\text{C.3})$$

Now, let us consider

$$F(1, s + p; s; z) = \frac{(s-1)!}{(s-1+p)!} \sum_{N=0}^{\infty} \frac{(s-1+p+N)!}{(s-1+N)!} z^N. \quad (\text{C.4})$$

Letting  $N - 1 = n$ , (C.4) becomes

$$\begin{aligned} F(1, s + p; s; z) &= \frac{(s-1)!}{(s-1+p)!} \sum_{n=-1}^{\infty} \frac{(s+p+n)!}{(s+n)!} z^{n+1} \\ &= \frac{(s-1)!}{(s-1+p)!} z \sum_{n=-1}^{\infty} \frac{(s+p+n)!}{(s+n)!} z^n \\ &= \frac{(s-1)!}{(s-1+p)!} z \left[ \frac{(s+p-1)!}{(s-1)!} z^{-1} + \sum_{n=0}^{\infty} \frac{(s+p+n)!}{(s+n)!} z^n \right]. \quad (\text{C.5}) \end{aligned}$$

Finally, using (C.3), we get

$$\begin{aligned} F(1, s + p; s; z) &= 1 + \frac{(s-1)!}{(s-1+p)!} z \frac{(s+p)!}{s!} F(1, s+1+p; s+1; z) \\ &= 1 + \frac{s+p}{s} z F(1, s+1+p; s+1; z), \quad (\text{C.6}) \end{aligned}$$

which is the relation we seek.

# Appendix D

## The General Form of the Integral Involved in the Calculation of $\epsilon_n^{(1)}$

The general form of the integrals (3.31), (3.32), and (3.33) may be expressed as

$$\langle \Psi | \frac{1}{r_{ij}} | \Psi \rangle = \iiint R_{n_1 l_1}^*(r_1) R_{n_2 l_2}^*(r_2) R_{n_3 l_3}^*(r_3) Y_{l_1 m_1}^*(\hat{r}_1) Y_{l_2 m_2}^*(\hat{r}_2) Y_{l_3 m_3}^*(\hat{r}_3) \frac{1}{r_{ij}} R_{n_1 l_1'}(r_1) \times R_{n_2 l_2'}(r_2) R_{n_3 l_3'}(r_3) Y_{l_1' m_1'}(\hat{r}_1) Y_{l_2' m_2'}(\hat{r}_2) Y_{l_3' m_3'}(\hat{r}_3) d^3 r_1 d^3 r_2 d^3 r_3. \quad (\text{D.1})$$

In this Appendix, the general form of the angular part of this integral is determined and the essential integral relations for the evaluation of the radial part are given.

To split up the radial and angular part of (D.1), we begin by making use of the expansion

$$\frac{1}{r_{ij}} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \theta_{ij}), \quad (\text{D.2})$$

where  $\theta_{ij}$  is the angle between  $r_i$  and  $r_j$  and  $r_{<}$  is the lesser and  $r_{>}$  the greater of  $r_i$  and  $r_j$ . This expansion may be rewritten as

$$\frac{1}{r_{ij}} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \left( \frac{4\pi}{2k+1} \right) \sum_{q=-k}^k Y_{kq}^*(\hat{r}_i) Y_{kq}(\hat{r}_j), \quad (\text{D.3})$$

where we have made use of the spherical harmonic addition theorem. Now, substituting (D.3) into (D.1), we obtain

$$I = \sum_{k=0}^{\infty} R_{ij}^{(k)}(n_1 l_1, n_2 l_2, n_3 l_3, n'_1 l'_1, n'_2 l'_2, n'_3 l'_3) \left( \frac{4\pi}{2k+1} \right) \sum_{q=-k}^k \tilde{I}, \quad (\text{D.4})$$

where

$$R_{ij}^{(k)} = \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \int_0^{\infty} r_3^2 dr_3 R_{n_1 l_1}^*(r_1) R_{n_2 l_2}^*(r_2) R_{n_3 l_3}^*(r_3) \frac{r^k}{r^{k+1}} R_{n'_1 l'_1}(r_1) R_{n'_2 l'_2}(r_2) R_{n'_3 l'_3}(r_3), \quad (\text{D.5})$$

and

$$\tilde{I} = \iiint Y_{l_1 m_1}^*(\hat{r}_1) Y_{l_2 m_2}^*(\hat{r}_2) Y_{l_3 m_3}^*(\hat{r}_3) Y_{kq}^*(\hat{r}_i) Y_{kq}(\hat{r}_j) Y_{l'_1 m'_1}(\hat{r}_1) Y_{l'_2 m'_2}(\hat{r}_2) Y_{l'_3 m'_3}(\hat{r}_3) d\Omega_1 d\Omega_2 d\Omega_3, \quad (\text{D.6})$$

where  $d\Omega = \sin \theta d\theta d\varphi$ .

## D.1 Evaluation of the Angular Part

For the angular integral (D.6) let us set  $i = 1$  and  $j = 3$ , and rewrite it as

$$\tilde{I} = \int A_1 d\Omega_1 \int A_2 d\Omega_2 \int A_3 d\Omega_3, \quad (\text{D.7})$$

where

$$A_1 = Y_{l_1 m_1}^*(\hat{r}_1) Y_{kq}^*(\hat{r}_1) Y_{l'_1 m'_1}(\hat{r}_1), \quad (\text{D.8})$$

$$A_2 = Y_{l_2 m_2}^*(\hat{r}_2) Y_{l'_2 m'_2}(\hat{r}_2), \quad (\text{D.9})$$

and

$$A_3 = Y_{l_3 m_3}^*(\hat{r}_3) Y_{kq}(\hat{r}_3) Y_{l'_3 m'_3}(\hat{r}_3). \quad (\text{D.10})$$

Rewriting (D.8), we have

$$A_1 = (-1)^{m'_1} Y_{l_1 m_1}^*(\hat{r}_1) \left[ Y_{kq}^*(\hat{r}_1) Y_{l'_1 m'_1}^*(\hat{r}_1) \right]$$

and with the complex conjugate of relation (B.3), this becomes

$$\begin{aligned} A_1 &= (-1)^{m'_1} \sum_{\lambda_1=|k-l'_1|}^{k+l'_1} \sum_{\mu_1=-\lambda_1}^{\lambda_1} (-1)^{q-m'_1} \left[ \frac{(k, l'_1, \lambda_1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} k & l'_1 & \lambda_1 \\ q & -m'_1 & \mu_1 \end{pmatrix} \begin{pmatrix} k & l'_1 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\times Y_{l_1 m_1}^*(\hat{r}_1) Y_{\lambda_1 \mu_1}(\hat{r}_1). \end{aligned} \quad (\text{D.11})$$

Now using the orthonormal relation for the spherical harmonics

$$\int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta Y_{lm}^*(\hat{r}) Y_{l'm'}(\hat{r}) = \delta_{l,l'} \delta_{m,m'} \quad (\text{D.12})$$

together with (D.11), we have

$$\begin{aligned} \int A_1 d\Omega_1 &= (-1)^q \sum_{\lambda_1 \mu_1} \left[ \frac{(k, l'_1, \lambda_1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} k & l'_1 & \lambda_1 \\ q & -m'_1 & \mu_1 \end{pmatrix} \begin{pmatrix} k & l'_1 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \delta_{l_1, \lambda_1} \delta_{m_1 \mu_1} \\ &= (-1)^q \left[ \frac{(k, l'_1, l_1)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} k & l'_1 & l_1 \\ q & -m'_1 & m_1 \end{pmatrix} \begin{pmatrix} k & l'_1 & l_1 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (\text{D.13})$$

Similarly,

$$\int A_3 d\Omega_3 = (-1)^q \left[ \frac{(k, l'_3, l_3)}{4\pi} \right]^{\frac{1}{2}} \begin{pmatrix} k & l'_3 & l_3 \\ q & -m'_3 & m_3 \end{pmatrix} \begin{pmatrix} k & l'_3 & l_3 \\ 0 & 0 & 0 \end{pmatrix}, \quad (\text{D.14})$$

and

$$\int A_2 d\Omega_2 = \int Y_{l_2 m_2}^*(\hat{r}_2) Y_{l'_2 m'_2}(\hat{r}_2) d\Omega_2 = \delta_{l_2, l'_2} \delta_{m_2, m'_2}. \quad (\text{D.15})$$

Substituting (D.13), (D.14), and (D.15) into (D.7), we get

$$\begin{aligned} \tilde{I} = & (-1)^{2q}(l_1, l'_1, l_3, l'_3)^{\frac{1}{2}} \frac{(2k+1)}{4\pi} \begin{pmatrix} k & l'_1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & l'_1 & l_1 \\ q & -m'_1 & m_1 \end{pmatrix} \\ & \times \begin{pmatrix} k & l'_3 & l_3 \\ q & -m'_3 & m_3 \end{pmatrix} \begin{pmatrix} k & l'_3 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \delta_{l_2, l'_2} \delta_{m_2, m'_2}. \end{aligned} \quad (\text{D.16})$$

Now without loss of generality, we will choose  $m = 0$  for the wavefunctions, so that

$$\begin{aligned} \tilde{I}_0 = & (l_1, l'_1, l_3, l'_3)^{\frac{1}{2}} \frac{(2k+1)}{4\pi} \begin{pmatrix} k & l'_1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & l'_1 & l_1 \\ q & 0 & 0 \end{pmatrix} \\ & \times \begin{pmatrix} k & l'_3 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & l'_3 & l_3 \\ q & 0 & 0 \end{pmatrix} \delta_{l_2, l'_2} \delta_{m_2, m'_2}. \end{aligned} \quad (\text{D.17})$$

Equation (D.17) is the general equation for the angular part of integral (D.4), and with this equation (D.4) may be written as

$$I = \sum_{k=0}^{\infty} R_{ij}^{(k)} \sum_{q=-k}^k \tilde{I}_0. \quad (\text{D.18})$$

## D.2 Integral Relations for the Evaluation of the Radial Part

In this section, the general integral relations for the evaluation of the radial integral (D.5) are presented. To begin, we note that Eq. (D.5) is of the form

$$F_{mn}^{(k)} = \int_0^\infty \int_0^\infty \int_0^\infty f(r_l, r_m, r_n) \frac{r_{\leq}^k}{r_{>}^{k+1}} dr_l dr_m dr_n, \quad (\text{D.19})$$

where  $r_> = \max(r_m, r_n)$ , and  $r_< = \min(r_m, r_n)$ . To evaluate this integral, it must be separated in the following way

$$\int_0^\infty \int_0^\infty \int_0^\infty f(r_l, r_m, r_n) \frac{r_<^k}{r_>^{k+1}} dr_l dr_m dr_n = \int_0^\infty f(r_l) dr_l \int_0^\infty f(r_m) dr_m \times \left[ \frac{1}{r_m^{k+1}} \int_0^{r_m} f(r_n) r_n^k dr_n + r_m^k \int_{r_m}^\infty f(r_n) \frac{1}{r_n^{k+1}} dr_n \right]. \quad (\text{D.20})$$

Next, the evaluation of (D.20) is carried out with the use of the following integral relations

$$\int_0^\infty r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}, \quad (\text{D.21})$$

$$\int_0^{r'} r^n e^{-\alpha r} dr = \frac{e^{-\alpha r'}}{(-\alpha)} \left[ r'^n - \frac{n r'^{n-1}}{(-\alpha)} + \frac{n(n-1) r'^{n-2}}{(-\alpha)^2} - \dots - \frac{(-1)^n n!}{(-\alpha)^n} \right] - \frac{(-1)^n n!}{(-\alpha)^{n+1}}, \quad (\text{D.22})$$

and

$$\int_{r'}^\infty r^n e^{-\alpha r} dr = -\frac{e^{-\alpha r'}}{(-\alpha)} \left[ r'^n - \frac{n r'^{n-1}}{(-\alpha)} + \frac{n(n-1) r'^{n-2}}{(-\alpha)^2} - \dots - \frac{(-1)^n n!}{(-\alpha)^n} \right]. \quad (\text{D.23})$$

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## VITA AUCTORIS

**NAME:** Mauro Tambasco

**PLACE OF BIRTH:** Toronto, Ontario

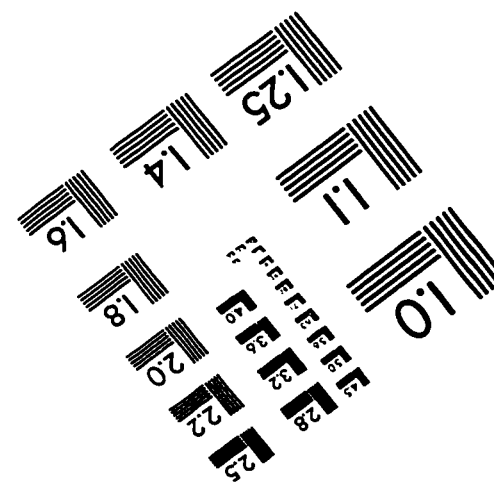
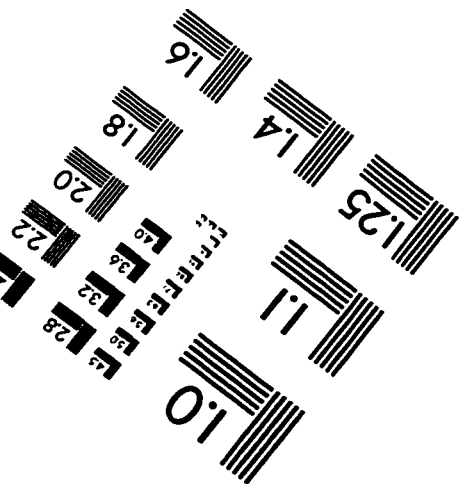
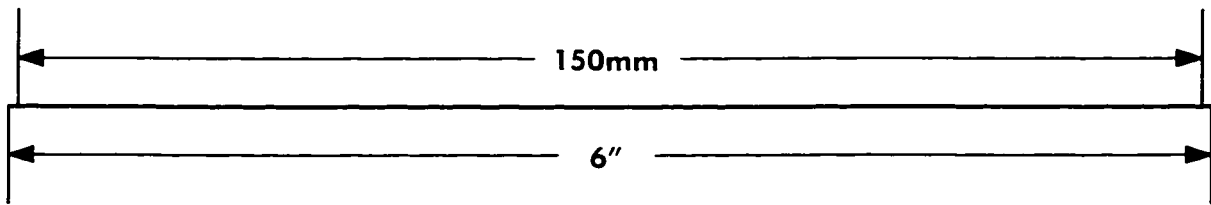
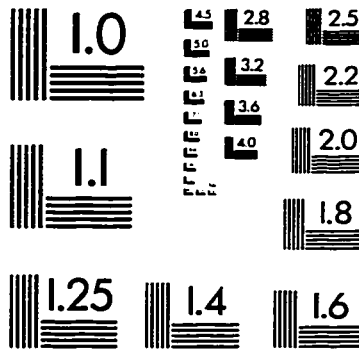
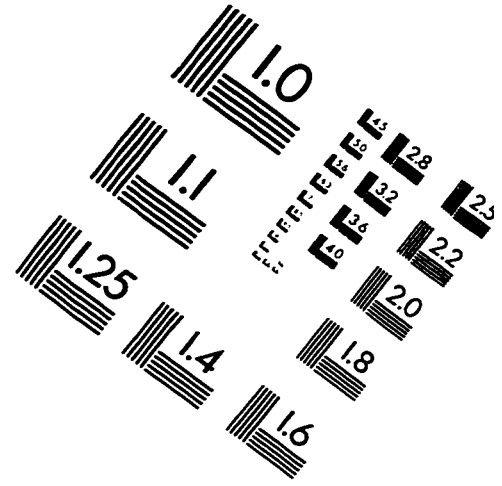
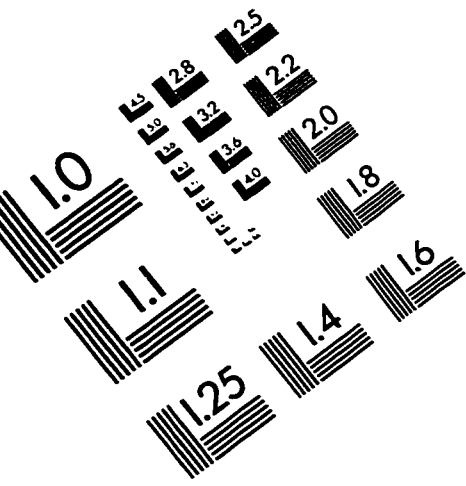
**YEAR OF BIRTH:** 1971

**EDUCATION:** Jarvis Collegiate Institute, Toronto  
1985-1990

University of Toronto, Toronto, Ontario  
1990-1994 B.Sc.

University of Windsor, Windsor, Ontario  
1995-1997 M.Sc.

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