INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®

UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

DIMENSIONAL PERTURBATION THEORY OF THE TWO-ELECTRON ATOM FOR STATES WITH ARBITRARY ANGULAR MOMENTUM

A Dissertation
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
Doctor of Philosophy

By
John Charles Carzoli
Norman, Oklahoma
2000

UMI Number: 9988509

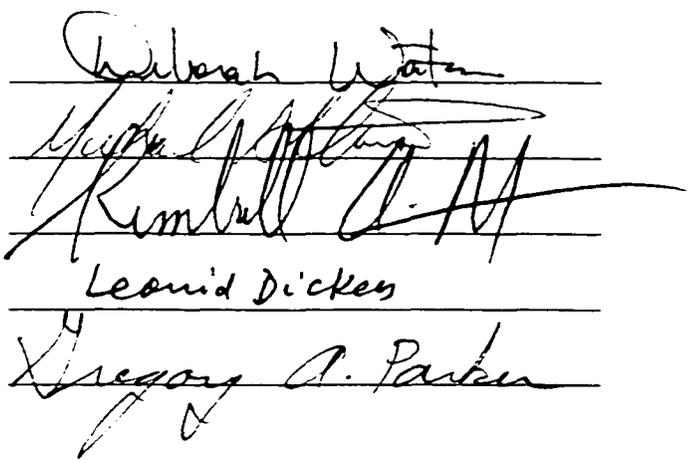
UMI Microform 9988509

Bell & Howell Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

DIMENSIONAL PERTURBATION THEORY OF THE TWO-ELECTRON ATOM FOR STATES WITH ARBITRARY ANGULAR MOMENTUM

A Dissertation APPROVED FOR THE
DEPARTMENT OF PHYSICS AND ASTRONOMY

By



Dedication

To my seven brothers and sisters, my mom and dad, my fifteen nieces and nephews, and to my very best friend Tricia.

YABOPMN!

Acknowledgements

I would like to thank my family and friends for encouraging me and motivating me to finish this, my advisor Dr. Deborah K. Watson for allowing me to begin a teaching career while in the middle of my research, and my committee for their help and constructive criticism. I would also like to thank God for all the opportunities He has given me.

Contents

Abstract

Dimensional Perturbation Theory (DPT) has been applied to many systems including the hydrogen atom, hydrogen atom in a magnetic field, H_2^+ molecule and the helium atom. Only S-wave states, and interdimensionally degenerate P^e states, have, up until now, been studied for the helium atom. Here we outline the procedures and discuss the results of a formalism that generalizes the Schwartz expansion of the wavefunction to N-electrons with arbitrary total orbital angular momentum and arbitrary spatial dimension. We present results specifically for $^{1,3}P^o$ states of helium and their interdimensionally degenerate $^{3,1}D^o$ counterparts.

Chapter 1

Background

1.1 Introduction

The helium atom is perhaps the most studied atom because of its simple structure yet complicated spectral features. In the early days of quantum mechanics the "old quantum theory" could not even calculate the ground state energy satisfactorily. This failure provided an impetus for further development of quantum mechanics. As the "new quantum theory" was developed, more accurate results for the ground and singly excited state energies were calculated, and the agreement with experiment was, at best, satisfactory. With the advent of computers the calculated energies agreed more closely with experiment, however, experimental resolution increased faster than computational accuracy and in 1963 a high resolution experiment by Madden and Codling [1] showed that the spectral structure of doubly excited helium was not very well understood. Further development in computational techniques ensued and by the late 1980's a much clearer understanding of the helium atom had developed.

In this first chapter we begin in Sec. 1.2.1 with a brief discussion of the "old" quantum theory followed by a glimpse of the beginnings of the "new" quantum theory as applied to the helium atom. The basic spectral structure based on an independent particle model will then be discussed in Sec. 1.3.1 followed by a brief overview, in Sec. 1.4.1, of the popular numerical methods used to solve the two-electron problem. In Sec. 1.5 we describe a way to represent the two-electron wavefunction, called the Schwartz expansion, as a product of two functions one being a function solely

of internal coordinates. This expansion is necessary in order to derive a tractable set of differential equations when calculating states with non-zero orbital angular momentum. Finally, in Sec. 1.6.1 we outline dimensional perturbation theory (DPT) and summarize the case for states with zero total orbital angular momentum.

Chapter 2 discusses the generalization of the Schwartz expansion for a two-electron atom with arbitrary angular momentum and arbitrary dimension, D [2, 3, 4, 5]. This generalization is a major achievement that extends the work of Schwartz [6] and Breit [7]. In Sec. 2.2.1 this generalization is presented for the specific case of P^o states but the resulting computer code, written by the author (see Ch. 3), is capable of calculating states of *any* angular momentum. In Sec. 2.2.2 the generalized Schrödinger equation and Hamiltonian are presented followed by a discussion of the large dimension limit. Finally, in Sec. 2.3 we derive an expansion of the Schrödinger equation in terms of the perturbation parameter $\delta = 1/(D + t)$ where t is related to the angular momentum. Section 2.3 ends with a set of perturbation equations one can use to solve for the wavefunction and energy coefficients exactly up to a specified order in δ. These perturbation equations are an infinite set of coupled inhomogeneous differential matrix equations.

In Ch. 3 a method for solving the above-mentioned perturbation equations, called the matrix method, is presented. Previously the matrix method had been discussed in detail only for states with zero total angular momentum and one degree of freedom [8]. It has also been discussed for states with three degrees of freedom but not in as great of detail [9]. In Sec. 3.1 I present a detailed discussion of the matrix method for states with zero total angular momentum followed, in Sec. 3.2, by the application of the matrix method to states of arbitrary total angular momentum. In Sec. 3.3.1 the computer code, written to solve the resulting matrix method perturbation equations, is discussed. This code is an extension of a code for S-wave states [9] to states with arbitrary total orbital angular momentum. The extension of the S-wave code was quite a formidable task due to the complexity and size of the tensors introduced through the matrix method and due to the large number of additional terms in the

Hamiltonian, which includes a complicated off-diagonal coupling term that is not present in the S-wave case.

Finally, Ch. 4 discusses the results of the first application of the generalized Schwartz expansion to states of the two-electron atom with non-zero total orbital angular momentum. The complexity of the helium spectrum for doubly excited states quickly becomes apparent when one tries to sum the energy series for these states. To sum even the lowest few P^o states one needs to consider other states that may be influencing the convergence of these lowest states. Analysis of the singularity structure of the energy function is discussed in Sec. 4.1 followed by a discussion of methods used to sum the energy series that results from the perturbation expansion of the Schrödinger equation. It is then found that we need to consider structure that is more complex than simply poles, and in Sec. 4.3 we discuss branch points and how they arise in the energy function. In the last section we discuss summation of the wavefunction and consider how the wavefunction evolves as one moves from large dimension to the physical dimension, $D = 3$.

1.2 The Two-Electron Atom

1.2.1 The Hamiltonian

Consider an atom consisting of a nucleus of charge Ze and mass M and two electrons of mass m. Neglecting all forces except Coulomb forces, and separating out the center of mass motion, the Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{r_1}^2 - \frac{\hbar^2}{2\mu}\nabla_{r_2}^2 - \frac{\hbar^2}{M}\nabla_{r_1}\cdot\nabla_{r_2} - \frac{Ze^2}{(4\pi\varepsilon_0)\,r_1} - \frac{Ze^2}{(4\pi\varepsilon_0)\,r_2} + \frac{e^2}{(4\pi\varepsilon_0)\,r_{12}}\right]\psi(\mathbf{r}_1,\mathbf{r}_2) = E\,\psi(\mathbf{r}_1,\mathbf{r}_2)\,, \tag{1.1}$$

where $\mu = mM/(m+M)$ is the reduced mass of an electron with respect to the nucleus and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the interelectron separation (see Figure 1.1). For the remainder of this thesis we will consider the infinite nuclear mass approximation

where $\mu = m$ and the mass polarization term $(-\hbar^2/M)\nabla_{r_1} \cdot \nabla_{r_2}$ is zero. In atomic units, the Schrödinger equation becomes

$$H\,\psi(\mathbf{r}_1, \mathbf{r}_2) = E\,\psi(\mathbf{r}_1, \mathbf{r}_2)\,. \tag{1.2}$$

where the Hamiltonian is given by

$$H = -\frac{1}{2}\nabla^2_{r_1} - \frac{1}{2}\nabla^2_{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \tag{1.3}$$

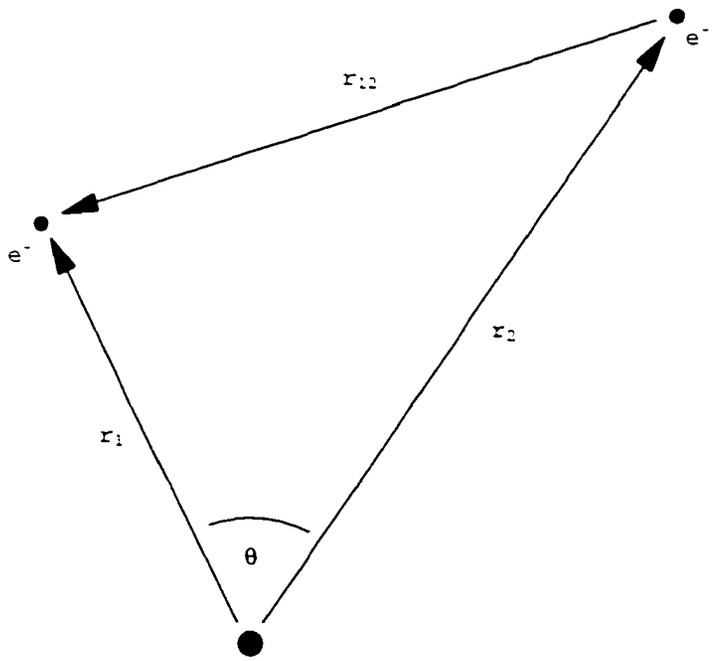


Figure 1.1: The coordinates of the two-electron atom in the infinite nuclear mass approximation.

1.2.2 Early Calculations of the Ground State

The beginnings of quantum theory were based more on a semiclassical approach, sometimes referred to as Bohr-Sommerfeld quantization, where the electron of an atom, such as hydrogen, was considered to move along a periodic Keplerian orbit. This description of the hydrogen atom, as every student of quantum theory should

know, yielded very accurate results and quite satisfactorily explained the full spectrum of the hydrogen atom. However, there were problems. As experimental resolution increased it was realized that certain lines, originally thought to be single lines, actually consisted of multiple lines very close together. The Bohr model could not account for these discrepancies, but it was a very good start.

With enthusiasm, Bohr applied this technique to the helium atom [10] in 1913, theorizing that the two electrons orbited the nucleus opposite one another on the same periodic orbit. He was quite dismayed by the results, which gave an ionization energy of the ground state that was about 4 eV higher than the then-accepted value of about 24.5 eV. Many leading theoretical physicists struggled with the problem of calculating the ground state energy of the helium atom for the next several years. A good review of this struggle is discussed by Mehra and Rechenberg [11].

It wasn't until the wave theory of quantum mechanics was developed by Heisenberg and Schrödinger that successful calculations of the ground state energy of helium were obtained. Heisenberg's first application of this "new" quantum mechanics to the helium atom was published in 1926 [12]. Within the next two years several methods were developed and the calculated ground state energy was greatly improved. These methods included a first order perturbation theory by Unsöld [13]; a molecule-like description in which one electron is treated as being in the presence of two fixed centers of charge $-e$ and $+e$ by Slater [14] (similar methods are still used today to describe doubly excited states); and variational techniques by Kellner [15], who used a Ritz variational method, and Hylleraas [16], who used a trial wavefunction with 38 variational parameters. For a more complete review of the methods used for low-lying states of helium see Bethe and Salpeter [17].

Even with the success of the "new" quantum theory, the "old" quantum theory was to find new life about 50 years later. In the early 1980's Leoplod et. al [18, 19] argued that for very high, doubly excited states of the helium atom the electrons should behave like classical particles. They should have Kepler type orbits somewhat similar to the orbits of planets around the sun. This is exactly what Bohr and Sommerfeld assumed for the ground state, but their theory failed miserably. Percival

coined the phrase "planetary atoms" to refer to such high, doubly excited atoms and through his work was born the semiclassical approach to studying such states.

The theory is called "semi"-classical because it uses concepts from both classical and quantum mechanics. A purely classical treatment of these highly excited atoms results in an unstable atom. Usually the classical, two-electron atom autoionizes after only a few revolutions of the electrons around the nucleus. One electron gives some energy to the other electron allowing it to escape, leaving an atom with a single electron in a much lower energy state. Classically there is no lowest energy of the singly ionized two-electron atom. That allows the remaining electron to give up as much energy as is required to ionize the atom. Thus the classical two-electron atom is unstable for all initial energies.

Incorporating quantum ideas, such as a minimum energy, into the classical model of the atom not only gives a stable atom, but actually gives very accurate energies for high, doubly excited states. The semiclassical approach will not be discussed further in this thesis, but a nice review was published by Tanner et al [20].

1.3 The Basic Spectral Structure of the Helium Atom

1.3.1 Introduction

We begin our discussion of the spectral features of the helium atom by considering the exact symmetries that allow us to specify each state by a set of good quantum numbers. We begin by noticing that the Hamiltonian, Eq. (1.3), commutes with the total orbital angular momentum operator $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$: the atom has rotational symmetry, and the total orbital angular momentum is conserved. This gives rise to two good quantum numbers, the total orbital angular momentum quantum number L, and its projection along the z-axis, M_L. Furthermore, the Hamiltonian also commutes with the exchange operator, also known as the "pairwise particle interchange operator" and denoted by $\hat{P}_{12}$, which takes $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ and $\mathbf{r}_2 \rightarrow \mathbf{r}_1$. The eigenstates of the

exchange operator are either symmetric or antisymmetric with respect to exchange. The requirement that the total wavefunction (spatial and spin) be antisymmetric with respect to exchange leads to the pairing of the spatially symmetric wavefunctions with singlet ($S = 0$) spin functions, and the spatially antisymmetric wavefunctions with triplet ($S = 1$) spin functions. Thus the total spin S and its z-component M_s can be used to label the states. Finally, the Hamiltonian commutes with the parity operator, which takes $\mathbf{r}_1 \rightarrow -\mathbf{r}_1$ and $\mathbf{r}_2 \rightarrow -\mathbf{r}_2$. Thus the wavefunctions are eigenfunctions of the parity operator with eigenvalues $\pi = \pm 1$. In terms of the individual electron orbital angular momentum quantum number l_i, the parity is given by $\pi = (-1)^{l_1+l_2}$. The $\pi = +1$ states are called "even" states and the $\pi = -1$ states are called "odd" states. They are designated with an "e" or an "o" respectively. These three symmetries lead to the notation $^{2S+1}L^{\pi}$, called a term symbol (assuming LS coupling).

1.3.2 The Independent Particle Model

We begin our analysis with the independent particle model. In this model the Hamiltonian is written as

$$H = H_0 + H'$$

where the zero-order, unperturbed Hamiltonian is

$$H_0 = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} \tag{1.4}$$

and the perturbation,

$$H' = \frac{1}{r_{12}},$$

is the electron-electron interaction. If we ignore this term and notice that the zero-order Hamiltonian H_0 is a sum of hydrogenic Hamiltonians then we can write the Schrödinger equation as

$$H_0\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = E^{(0)}\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2). \tag{1.5}$$

where $\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ is a product of hydrogenic wavefunctions

$$\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n_1,l_1,m_1}(\mathbf{r}_1)\,\psi_{n_2,l_2,m_2}(\mathbf{r}_2)\,. \tag{1.6}$$

and the energy is a sum of hydrogenic energies, in a.u..

$$E^{(0)}_{n_1,n_2} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right). \tag{1.7}$$

Exchanging the indices of the two electrons in the wavefunction $\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ we obtain

$$\psi^{(0)}(\mathbf{r}_2, \mathbf{r}_1) = \psi_{n_1,l_1,m_1}(\mathbf{r}_2)\,\psi_{n_2,l_2,m_2}(\mathbf{r}_1)\,. \tag{1.8}$$

which is degenerate with $\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$. This type of degeneracy is called exchange degeneracy.

According to the Pauli exclusion principle the total spatial wavefunction must be either symmetric or antisymmetric with respect to interchange of electrons. The full spatial part of the wavefunction must then be a linear combination of wavefunctions (1.6) and (1.8). Thus, the correct zero-order spatial wavefunction in the independent particle model is

$$\psi^{(0)}_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1,l_1,m_1}(\mathbf{r}_1)\,\psi_{n_2,l_2,m_2}(\mathbf{r}_2) \pm \psi_{n_1,l_1,m_1}(\mathbf{r}_2)\,\psi_{n_2,l_2,m_2}(\mathbf{r}_1)\right]. \tag{1.9}$$

The factor $1/\sqrt{2}$ ensures normalization, while the (+) sign gives the symmetric state and the (−) sign gives the antisymmetric state. To obtain the full wavefunction, $\psi^{(0)}_-$ is then multiplied by a symmetric spin wavefunction and $\psi^{(0)}_+$ is multiplied by the antisymmetric spin function. Thus $\psi^{(0)}_-$ corresponds to a spin triplet and $\psi^{(0)}_+$ corresponds to a spin singlet. The singlet and triplet states are still degenerate, but if we include the perturbation $1/r_{12}$ this degeneracy will be removed. The only states that do not have degenerate triplet and singlet wavefunctions are states where both electrons have quantum numbers $n_1 = n_2$, $l_1 = l_2$, and $m_1 = m_2$. From Eq. (1.9) it is clear that the triplet state is zero and only the singlet state remains. In

fact, the early observation that the helium atom did not have a triplet ground state provided evidence that led Pauli to formulate his exclusion principle. No two identical particles can have the same set of quantum numbers, and, since in the ground state both electrons have the same spatial quantum numbers, they must then have opposite spin, allowing only a singlet state.

The energy spectrum of helium in the independent particle model is shown is Figure 1.2. The horizontal axis labels the principal quantum number $N = n_1$ of electron one. We will use N to designate the principal quantum number of the inner electron for excited states of the two-electron atom. Notice that there are several series (called Rydberg series), one for each value of N, with n_2 going from N to infinity. For $N = 1$ we have the ground state and all of the singly excited states. The ground state is at $E_0^{(0)} = -4$ a.u., compared to the experimental value of about $E_{\rm exp} = -2.90$ a.u., and the series approaches $E = -2$ a.u. as $n_2 \to \infty$, corresponding to an ionization energy of $I_1 = 2$ a.u., as compared to the experimental value of $I_{1_{\rm exp}} = 0.90$ a.u.

The remaining series, $N > 1$, correspond to doubly excited states. As is seen in the energy spectrum, all of the doubly excited states lie above the first ionization threshold at I_1. In other words, the energies of the doubly excited states lie higher than the ground state energy of the He^+ ion. Thus all of the doubly excited states lie in the continuum of the $He^+(N = 1) + e^-$ ion. When we consider the term $1/r_{12}$ we find that, since it is a strictly repulsive term, it can only raise the energy levels so that even in the real helium atom (and in all two electron atoms) the doubly excited states lie in the continuum. As $n_2 \to \infty$ each series for $N > 1$ approaches the energy of an excited state of the He^+ ion where the remaining electron has a principal quantum number of N. The energies of the He^+ ion are unaffected by the $1/r_{12}$ repulsion term and so the ionization thresholds for each Rydberg series of the He atom remain fixed while all other energies move up when the $1/r_{12}$ term is introduced.

In this simple independent particle model the energy levels can be labeled by $(N; n)$ where N and n are principal quantum numbers for the inner and outer electrons, respectively, and a particular Rydberg series is labeled by $(N; N, N+1, \ldots, \infty)$.

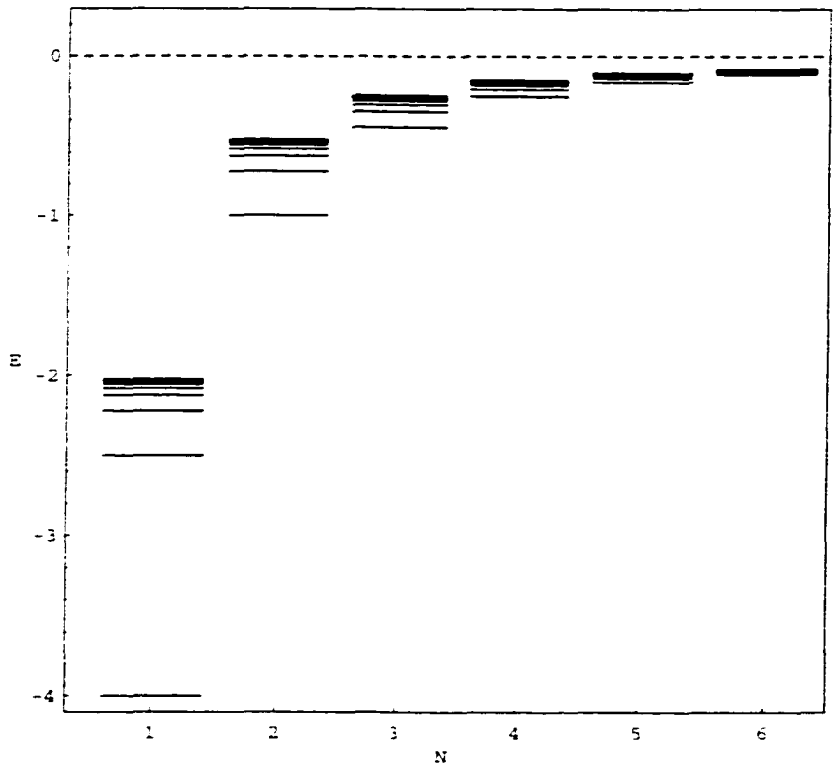


Figure 1.2: Energy levels, in atomic units, of the helium atom in the independent particle model. Each series corresponds to one electron with principal quantum number N and the other electron with principal quantum number $n = N, N+1, \ldots$. The series $N = 1$ consists of all singly excited states, while all other series represent doubly excited states embedded in the $He^+(N = 1) + e^-$ continuum.

We can also label individual states with hydrogenic designations such as $1s2p$ or $2p3d$, etc. The energy for a given N and n may be highly degenerate because of the possible values of l_1, m_{l_1}, l_2, m_{l_2}, L, M_L, S, and, M_s. For example, the states $1s2s\ ^1S^e$, $1s2s\ ^3S^e$, $1s2p\ ^1P^o$, and $1s2p\ ^3P^o$ are all degenerate in the independent particle model.

1.3.3 Central Field Approximation

We can improve on the basic independent particle model discussed above by considering how one electron may effect the motion of the other electron by screening the nuclear charge. As an example, we assume that each electron "feels" a central

potential $V(r_i)$ due to the average motion of the other electron. This extra potential is introduced by writing the Hamiltonian as

$$H = \bar{H}_0 + \bar{H}'$$

where

$$\bar{H}_0 = -\frac{1}{2}\nabla_{r_1}^2 - \frac{Z}{r_1} + V(r_1) - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_2} + V(r_2)$$

and

$$\bar{H}' = \frac{1}{r_{12}} - V(r_1) - V(r_2).$$

$V(r)$ is chosen such that the effect of $\bar{H}'$ is small compared to $\bar{H}_0$ so that $\bar{H}'$ may be treated as a perturbation. This model is still an independent particle model but it does take into account an effect of one electron on the other. The potential $V(r)$ depends only on the radial distance from the nucleus, so this model is called a central field approximation.

If we ignore the term $\bar{H}'$ then the Schrödinger equation will be separable and the wavefunction may be written as a product of spherical harmonics and a radial function. This radial function will not be hydrogenic unless $V(r)$ is a coulomb potential. Hence the energy levels will no longer be degenerate in l_1 and l_2 but will still be degenerate in L, M_L, S, and M_s. Then each Rydberg series in Fig. 1.2 will be split into several series which depend on l_1, and l_2, and are labeled as $(N, l_1; n = N, \ldots, \infty, l_2)$

For the ground and singly excited states we have $(1,0; n = 1, 2, 3, \ldots, \infty, l_2)$ and when l_2 is specified we can assign term symbols, obtaining singlet and triplet states. When the $1/r_{12}$ repulsion term is included in the Hamiltonian the singlet states are found to lie significantly higher in energy than the triplet states due to an exchange repulsion or exchange force. This arises because the singlet spatial wavefunctions are non-zero when $\mathbf{r}_1 = \mathbf{r}_2$; this allows the electrons to be closer together, which in turn raises the energy because of their mutual repulsion. As $n \to \infty$ the $(1,0; n, l_2)$ Rydberg series approaches the first ionization threshold I_1 at $-Z^2/2$ a.u. which equals the energy of the He^+ ground state (~ -54.42 eV).

The Rydberg series for doubly excited states approach ionization thresholds I_N corresponding to the energies of the excited $He^+(N)$ atom given by $-Z^2/(2N^2)$ a.u. All of the doubly excited states lie above the first ionization threshold and are thus embedded in the $He^+(1) + e^-$ continuum. In general, a particular doubly excited state is embedded in the continuum of at least one energetically lower Rydberg series. Thus the doubly excited states are resonances that can decay via autoionization through the electron-electron interaction. However, the $\pi = (-1)^{L+1}$ states below the $N = 2$ threshold are bound states since there are no $\pi = (-1)^{L+1}$ states below the $N = 1$ threshold. Autoionization does not happen with singly excited states because the $N = 1$ electron, being in its ground state, can not transfer energy to the outer electron.

Specifically, for S^e states there are N different Rydberg series converging to each ionization threshold. Each series corresponds to the possible configurations for fixed N that would yield S^e states. As an example, for $N = 3$ we can have $3sns$, $3pnp$, $3dnd$ with $n \geq 3$. As a further example, the P^o states have $2N - 1$ Rydberg series approaching the $He^+(N)$ threshold. For example, for $N = 2$ we have $2s(n \geq 2)p$, $2p(n > 2)s$, and $2pnd$.

The study of high doubly excited states of helium by Madden and Codling [1] revealed that the simple independent particle angular momentum quantum numbers l_1 and l_2 discussed above are not appropriate for states associated with overlapping Rydberg series. For $N \geq 4$ an increasing number of Rydberg series overlap, and to a greater extent, as N increases. This causes the independent particle configurations to mix to a greater and greater extent as the energy approaches the double ionization threshold, $E = 0$. This mixing is caused by the electron-electron interaction and can thus only be modeled by a theory that includes electron correlation. Electron correlation becomes increasingly important for high, doubly excited states. For a low-lying doubly excited state electron correlation is still important and there may be significant mixing between independent particle states, but there may be a single dominant independent particle configuration that can be used to classify the state.

1.4 Numerical Approaches To The Two Electron Atom

1.4.1 Variational methods

An excellent review of variational methods for singly excited states is given by Drake [21], which we briefly review here. These variational methods yield some of the most precise calculations for bound states of the two electron atom. We begin by choosing any normalizable trial wavefunction, with appropriate symmetry, and calculate

$$E_{\rm tr} = \frac{\langle \Psi_{\rm tr} | \, H \, | \Psi_{\rm tr} \rangle}{\langle \Psi_{\rm tr} | \, \Psi_{\rm tr} \rangle}. \tag{1.10}$$

$E_{\rm tr}$ is an upper bound for the lowest energy state with the same symmetry chosen for $\Psi_{\rm tr}$. The question is, what do we choose for the wavefunction $\Psi_{\rm tr}$? The general idea is to choose a trial wavefunction which contains several parameters that can be varied to obtain a minimum for $E_{\rm tr}$. Usually one chooses a basis set and then writes the trial wavefunction as a linear combination of the basis functions. For example, the basis functions

$$\chi_p(\alpha, \beta) = r_1^i r_2^j r_{12}^k \, e^{-\alpha r_1 - \beta r_2}$$

where p is an index that labels distinct combinations of the non-negative integers i, j, and k, and α and β are constants. This choice of basis set is called a Hylleraas basis set [16]. The trial wavefunction can then be written as

$$\Psi_{\rm tr} = \sum_{p=1}^{N} c_p \, \chi_p(\alpha, \beta).$$

Substituting this wavefunction into Eq. (1.10) we have

$$E_{\rm tr} = \frac{\sum_{p=1}^{N} \sum_{p'=1}^{N} c_p c_{p'}^* \, \langle \chi_{p'} | \, H \, | \chi_p \rangle}{\sum_{q=1}^{N} \sum_{q'=1}^{N} c_q c_{q'}^* \, \langle \chi_{q'} | \, \chi_q \rangle}.$$

Differentiating with respect to c_p and setting the result equal to zero gives

$$\frac{\partial E_{\rm tr}}{\partial c_p} = 0 = \frac{\sum_{p'=1}^{N} c_{p'}^{*} \langle \chi_{p'} | H | \chi_p \rangle}{\sum_{q=1}^{N} \sum_{q'=1}^{N} c_q c_{q'}^{*} \langle \chi_{q'} | \chi_q \rangle} - \frac{\sum_{p=1}^{N} \sum_{p'=1}^{N} c_p c_{p'}^{*} \langle \chi_{p'} | H | \chi_p \rangle}{\left[\sum_{q=1}^{N} \sum_{q'=1}^{N} c_q c_{q'}^{*} \langle \chi_{q'} | \chi_q \rangle\right]^2} \sum_{q'=1}^{N} c_{q'}^{*} \langle \chi_{q'} | \chi_p \rangle$$

or

$$\sum_{p'=1}^{N} c_{p'}^{*} \langle \chi_{p'} | H | \chi_p \rangle - \frac{\sum_{p=1}^{N} \sum_{p'=1}^{N} c_p c_{p'}^{*} \langle \chi_{p'} | H | \chi_p \rangle}{\sum_{q=1}^{N} \sum_{q'=1}^{N} c_q c_{q'}^{*} \langle \chi_{q'} | \chi_q \rangle} \sum_{q'=1}^{N} c_{q'}^{*} \langle \chi_{q'} | \chi_p \rangle = 0$$

which gives

$$\sum_{p'=1}^{N} c_{p'}^{*} \langle \chi_{p'} | H | \chi_p \rangle = E_{\rm tr} \sum_{q'=1}^{N} c_{q'}^{*} \langle \chi_{q'} | \chi_p \rangle .$$

There are N of these equations, one for each p from $p = 1$ to N. Thus the set of equations can be written as the matrix eigenvalue equation

$$\mathbf{Hc} = \lambda \mathbf{Oc}.$$

where $\mathbf{c}$ is a column of coefficients c_p and $\mathbf{H}$ and $\mathbf{O}$ are matrices having elements $H_{pq} = \langle \chi_p | H | \chi_q \rangle$ and $O_{pq} = \langle \chi_p | \chi_q \rangle$. There are N eigenvalues λ_i the lowest of which gives an upper bound to the exact energy.

The variational method has been used extensively by several authors [22, 23, 24] to obtain highly precise values for the low-lying states of helium. Many variations on the wavefunction expansion have been tried with varying success. A popular and more accurate method is to use a double basis set where the set consists of Hylleraas functions with differing values of α and β.

1.4.2 The molecular adiabatic approach for doubly excited states

Molecules are often studied using the Born-Oppenheimer approximation which treats the internucleus distance as a slowly changing variable compared to the interelectron

and electron-nucleus distances. The molecule is then essentially two or more nuclei fixed in space with the electrons moving through their total potential. The energies are then found by studying the adiabatic potential energy curve. In 1986 Feagin and Briggs [25] applied this technique to atoms by considering the interelectron distance to be adiabatic.

One starts with a two electron Hamiltonian in molecular Jacobi coordinates

$$H = -\nabla_R^2 - \frac{1}{4}\nabla_r^2 - \frac{Z}{|\mathbf{R}/2 - \mathbf{r}|} - \frac{Z}{|\mathbf{R}/2 + \mathbf{r}|} + \frac{1}{R},$$

where $\mathbf{R} = \mathbf{r}_{12}$ is the interelectron distance and $\mathbf{r} = (\rho, z, \varphi)$ is a vector pointing from the center of mass of the two electrons to the nucleus. Treating $\mathbf{R}$ as a slow variable may seem strange at first since the light electrons should move fast compared to the heavy nucleus. But, when we refer to mass we must refer to the reduced masses involved. The Laplacian terms in the Hamiltonian are multiplied by a fraction whose denominator is proportional to the mass. Since the denominators multiplying the two Laplacians in the above Hamiltonian are the same order of magnitude (not orders of magnitude different, as for an electron and nucleus) we see that it could be reasonable to assume that $\mathbf{R}$ is a slow variable compared to $\mathbf{r}$. Furthermore, the success of this method does not hinge so much on requiring one variable to be slow, but rather it allows a quasi-separability of the system in the variables $\mathbf{r}$ and $\mathbf{R}$.

The next step is to expand the wavefunction as a sum over products of rotational, $D^{L,S,I}_{Mm}(\alpha, \beta, \gamma)$, vibrational, $f^{L}_{im}(R)$, and molecular orbital, $\psi^{L}_{im}(\rho, z; R)$ wavefunctions. The wavefunction is then substituted into the Schrödinger equation with the above Hamiltonian and integrated over $\mathbf{r}$ and the Euler angles that take one from the lab frame to the body-fixed frame. This results in a set of coupled differential equations for the vibrational wavefunctions. In the adiabatic approximation the expansion of the wavefunction is limited to one term. We then have a single differential equation for a single vibrational wavefunction. Transforming to prolate spheroidal coordinates gives

$$\left(-\frac{d^2}{dR^2} + U^{L}_{n_\lambda, n_\mu, m}(R) - E_{\bar{n}}\right) f_{\bar{n}}(R) = 0.$$

The eigenvalues of this equation give the energies of the doubly excited state resonances. In the process of deriving this equation several quantum numbers have been introduced. The exact quantum numbers L, M, S, M_s, and π are the usual angular momentum and parity quantum numbers, while $\bar{n}$, n_λ, n_μ, and m are new quantum numbers introduced through the molecular adiabatic approximation. The quantum number $\bar{n}$ performs the same task as the hydrogenic quantum number n of the outermost electron. In other words, $\bar{n}$ specifies the excitation of the outermost electron along a single Rydberg series. In terms of the hydrogenic quantum numbers $\bar{n} = n - N$.

There are many advantages to the molecular adiabatic approximation. It allows one to derive propensity rules for radiative and nonradiative transitions, such as autoionization and dipole transitions, based on the approximate quantum numbers. It also allows one to better understand the structure and decay widths of very highly excited states where $n >> N$ called planetary states. Unfortunately, this method is not very useful for low-lying excited states where both hydrogenic quantum numbers are small.

1.4.3 Complex Rotation

The complex rotation method allows one to calculate resonant energies, widths, cross sections and wavefunctions of autoionizing states by making use of bound state methods. The radial coordinates are scaled according to $r \rightarrow r\exp(i\theta)$ and the momenta are scaled as $p \rightarrow p\exp(-i\theta)$. The rotated Hamiltonian is then diagonalized in a basis set of real square-integrable wavefunctions, and eigenvalues $E_n - i\Gamma_n/2$ are obtained. The resonance energy is E_n and the width is obtained from Γ_n.

This method was first employed by Doolan et al. in 1974 [26] for doubly excited states of helium. Since then it has been extensively employed by numerous authors such as Ho, Wintgen, Burgers et al. and Richter et al. [27, 28, 29, 30, 31]. Extensive lists of energies and widths of various states of the helium atom are given in the above references as well as in Ref. [32].

1.4.4 The hyperspherical adiabatic approach

In the hyperspherical adiabatic approach we first introduce hyperspherical coordinates through the hyperradius $R = (r_1^2 + r_2^2)^{1/2}$, where r_1 and r_2 are the electron-nucleus distances, and the hyperangle $\alpha = \tan^{-1}(r_2/r_1)$. The two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are replaced by the six coordinates R and Ω, where $\Omega = (\alpha, \theta_1, \phi_1, \theta_2, \phi_2)$ denotes the five angles, with respect to the laboratory frame, with θ_i and ϕ_i being the spherical angles of electron i. We can eliminate first-order derivatives in the Schrödinger equation, Eq. (1.2) by introducing the square root of a portion of the volume element, $d\mathbf{r}_1\, d\mathbf{r}_2 = R^5(\sin\alpha\cos\alpha)^2 d\hat{r}_1\, d\hat{r}_2$ into the wavefunction

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(R, \Omega)/(R^{5/2}\sin\alpha\cos\alpha)$$

so that $\psi(R, \Omega)$ satisfies

$$\left(-\frac{d^2}{dR^2} + \frac{\Lambda^2}{R^2} + \frac{2C}{R} + 2E\right)\psi(R, \Omega) = 0. \tag{1.11}$$

E is the total energy in atomic units and Λ^2 is the grand angular momentum operator given by

$$\Lambda^2 = \left(-\frac{d^2}{d\alpha^2} + \frac{\mathbf{l}_1^2}{\cos^2\alpha} + \frac{\mathbf{l}_2^2}{\sin^2\alpha}\right) - \frac{1}{4}. \tag{1.12}$$

where $\mathbf{l}_i$ is the angular momentum operator for electron i. Also, C/R is the total Coulomb potential with C given by

$$C(\alpha, \theta) = -\frac{Z}{\cos\alpha} - \frac{Z}{\sin\alpha} + \frac{1}{(1 - \sin 2\alpha\cos\theta)^{1/2}}. \tag{1.13}$$

where θ is the angle between the two electrons with respect to the nucleus and Z is the nuclear charge.

Some features of this potential are interesting to note. When $\alpha \to 0$ ($r_2 \to \infty$) and $\alpha \to \pi/2$ ($r_1 \to \infty$) there are deep valleys corresponding to strong Coulomb attraction between the nucleus and the near electron. There is a steep spike when $\alpha = \pi/4$ ($r_1 = r_2$) and $\theta = 0$ corresponding to the strong repulsion of the two

electrons when they are near. Finally there is a saddle point at $\alpha = \pi/4$ and $\theta = \pi$. The potential decreases as α moves away from $\pi/4$ but increases as θ moves away from π.

The eigenfunctions of the Λ^2 operator are called hyperspherical harmonics, $u_{[k]}(\Omega)$, where $[k]$ denotes the set of quantum numbers (l_1, l_2, m) with l_i being the orbital angular momentum quantum number of electron i and m being related to polynomial functions in the angle α. The hyperspherical harmonics are functions on the hypersphere in six dimensions and are simultaneous eigenfunctions of Λ^2, $\mathbf{l}_1^2$, $\mathbf{l}_2^2$, L^2 and L_z and form a complete set.

The wavefunction can then be expanded as a sum of hyperspherical harmonics as

$$\psi(R, \Omega) = \sum_{[k]} F_{[k]}(R)\, u_{[k]}(\Omega),$$

and substituted into Eq. (1.11) to obtain a set of second-order hyperradial differential equations for $F_{[k]}(R)$. Attempts were made to solve these equations but the convergence of the wavefunction expansion was very slow [33, 34]. This lead to the adiabatic approximation first applied by Macek [35] where he expanded the wavefunction as

$$\psi(R, \Omega) = \sum_{\mu} F_\mu(R)\, \Phi_\mu(R; \Omega).$$

When this expansion is substituted into Eq. (1.11) we obtain an equation for the "channel functions" $\Phi_\mu(R; \Omega)$

$$\left[\frac{\Lambda^2}{R^2} + \frac{C}{R}\right] \Phi_\mu(R; \Omega) = U_\mu(R)\, \Phi_\mu(R; \Omega). \tag{1.14}$$

and a set of coupled equations for the hyperradial functions $F_\mu(R)$

$$\begin{aligned} &\left(-\frac{d^2}{dR^2} + U_\mu(R) - 2E\right) F_\mu(R) \\ &= \sum_\nu \left(2\left\langle \Phi_\mu \left| \frac{d}{dR} \right| \Phi_\nu \right\rangle \frac{d}{dR} + \left\langle \Phi_\mu \left| \frac{d^2}{dR^2} \right| \Phi_\nu \right\rangle\right) F_\nu(R). \end{aligned} \tag{1.15}$$

In the adiabatic approximation $\Phi_\mu(R;\Omega)$ is assumed to be a slowly varying function of R and Eq. (1.14) is solved at fixed R to form a potential curve, $U_\mu(R)$. The adiabatic approximation is valid if the off-diagonal coupling terms $\left\langle \Phi_\mu \left| \frac{d}{dR} \right| \Phi_\nu \right\rangle$ and $\left\langle \Phi_\mu \left| \frac{d^2}{dR^2} \right| \Phi_\nu \right\rangle$ are small so that in a zeroth order approximation the right hand side of Eq. (1.15) is zero. The index μ, associated with the potential $U_\mu(R)$, can then be used to define a new set of quantum numbers used to identify doubly excited states in each channel. The hyperradial functions give information about the size of the state while the channel functions give information about the internal motion and overall rotation of the state.

The adiabatic approximation fails near avoided crossings where the off-diagonal coupling terms may be large. One technique to circumvent these problems is called the hyperspherical close coupling (HSCC) method. In this method the hyperradius is broken down into sectors and within each sector the channel functions $\Phi_\mu(R_a;\Omega)$ are fixed and chosen to satisfy Eq. (1.14) at R_a where R_a is a point within the sector. The wavefunctions are then matched at the sector boundaries. For an excellent review of these techniques see Ref. [36].

Macek showed that there are three potential curves for $^1P^o$ states below the $He^+(N = 2)$ threshold whose energy levels agree very well with the three known Rydberg series. This was the first indication that treating the hyperradius as an adiabatic variable was at least approximately valid and that individual Rydberg series can be associated with an individual hyperspherical potential curve and the energy levels in a particular Rydberg series can be found by calculating the eigenvalues from the corresponding curve.

In addition, since the number of curves that approach the $He^+(N)$ threshold, $2N-1$ for P^o states, increase rapidly as N increases we can reproduce the complexity of the helium spectrum even for N as low as $N = 5$. It is found that the minimum of the potential curves for low N are above the asymptotic limit of the $(N-1)$th curve so that the energy levels of each curve never overlap. This is no longer true for larger N, i.e. $N \geq 5$. For these "large" values of N, energy levels from many adiabatic potential curves may overlap resulting in strong mixing of the corresponding states.

In this region electron correlation plays a large role in understanding the spectrum and experimental results are resolved well only for states with N less than 6 or 7 (see Figs. 4.2 and 4.9 in Ref. [36]).

A major advantage of the hyperspherical adiabatic approach is the identification of approximate quantum numbers, identified collectively as μ, for doubly excited states of two-electron atoms. Each potential curve can be designated by quantum numbers K, T, and A using the notation $(K,T)^A$. The index μ equals the set $\{(K,T)^A, N, L, S, \pi\}$, where N refers to the asymptotic limit of the curve, i.e. the energy of the $He^+(N)$ ion. L and S are the total orbital and spin angular momentum quantum numbers and π is the parity. The K, T, and A quantum numbers do not arise from the hyperspherical adiabatic method nor are they needed to compute the various energies. Procedures for assigning these quantum numbers to states calculated via the hyperspherical adiabatic method were developed by Lin [36, 37].

The original definitions of the K and T quantum numbers were formulated by Herrick and Sinanoglu [38]. They constructed doubly excited state basis functions (DESB) from products of hydrogenic basis functions to study the helium atom. From the expansion of their wavefunctions they derived the following limits on K and T for a given L and N

$$T = 0, 1, 2, \ldots, \min(L, N-1), \qquad K = N-1-T, N-3-T, \ldots, -(N-1-T). \tag{1.16}$$

For states with $\pi = (-1)^{L+1}$, $T = 0$ is not allowed. The meaning of the K, T, and A quantum numbers can be understood by considering the wavefunction in the body frame. The results are that T can be considered as the projection of the total orbital angular momentum, L, along the interelectronic axis. The K quantum number is related to the angle between the two electrons. For each N, states with $K = N-1$ have the largest angle between the two electrons. To a good approximation K can be related to the bending vibrational quantum number $\nu = N - K - 1$. Finally, the quantum number A refers to the body frame wavefunction's symmetry with respect

to electron exchange. When the angle $\alpha \rightarrow \pi/2 - \alpha$ ($r_1 \leftrightarrow r_2$) the body frame wavefunction has symmetry

$$A = \pi(-1)^{S+T} \qquad \text{if} \qquad K > L - N. \tag{1.17}$$

The $A = +1$ states have an antinode at $\alpha = \pi/4$ ($r_1 = r_2$), and the $A = -1$ states have a node at $\alpha = \pi/4$. Not all doubly excited states have this symmetry. These states are labeled as $A = 0$ and the K and T quantum numbers are then just used as labels and do not retain their original meaning. The rule that Lin has derived is

$$A = 0 \qquad \text{if} \qquad K \leq L - N. \tag{1.18}$$

An interesting feature of the helium spectrum is that if one fixes the K, T, A, and N quantum numbers and plots the energy levels of the states by letting L increase from zero one finds that the spacing of the states resembles the spacing of the rotor series of a molecule. Furthermore, for states with $T \neq 0$ there are two rotor series that are nearly degenerate. This near degeneracy is similar to Λ-doubling in a molecule and is called it T-doubling. Finally, the $A = 0$ states do not give rise to this rotor pattern (See Fig. 4.12 in Ref. [36]). The $A = 0$ states are not described by a molecular picture but are easily calculated by the hyperspherical adiabatic approach since this approach does not assume a molecular structure at any order, unlike the molecular adiabatic approach discussed above.

Two other advantages of the hyperspherical adiabatic approach is that electron correlation is included at lowest order and since a series of states can be calculated from a single potential curve, their corresponding wavefunctions are already orthogonal. This aids in calculating various cross-sections and expectation values.

1.4.5 Dimensional scaling

The first step in dimensional scaling is to derive a D-dimensional Schrödinger equation. This can be accomplished by writing the wavefunction in such a way that it is

a product of two functions, one of which depends only on the internal coordinates. One can then obtain a D-dimensional Schrödinger equation that can then be scaled in such a way that the limit $D \to \infty$ gives a finite energy. In the $D \to \infty$ limit all dynamical terms in the Hamiltonian disappear and the electrons are stationary in the infinite dimensional potential. This limit is then used as a zeroth order perturbation theory and can be developed into a full dimensional perturbation theory with the addition of more terms. This method is the focus of this dissertation. We begin by considering a way to write the wavefunction that will be useful when one goes to large dimension.

1.5 The Two-Electron wavefunction: The Schwartz Expansion

In 1961 Charles Schwartz [6] published a paper on the Lamb shift in the helium atom and in an appendix he vaguely demonstrated how one might write the wavefunction of a two-electron atom with a total angular momentum L as a finite sum rather than the usual infinite sum over all possible values of l_1 and l_2. Earlier, in 1930, G. Breit [7] derived the same results for $L = 1$ states but his method is difficult to extend to higher L. Here we will present the Schwartz expansion, filling in a few of the gaps in his appendix and applying the results to ${}^{1,3}S^e$ and ${}^{1,3}P^o$ states. We will also adjust notation slightly by writing the radial coordinate of the i^{th} electron as r_i and the Cartesian coordinates as $(r_i)_j$ where $j = 1, 2, 3$.

The usual way one would write the spatial wavefunction for two electrons with total orbital angular momentum L is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; L, M) = \sum_{l_1, l_2} \psi(l_1, l_2, L, M) f_{l_1 l_2}(r_1, r_2) . \tag{1.19}$$

where

$$\psi(l_1, l_2, L, M) = \sum_{m_1, m_2} Y_{m_1}^{l_1}(1) Y_{m_2}^{l_2}(2) \langle l_1, m_1, l_2, m_2 | L, M \rangle . \tag{1.20}$$

and the subscripts are particle indices. Equation (1.19) is an infinite sum which would normally be truncated at some point. Schwartz avoids this by extracting functions of the scalar

$$r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$$

and combines these with the $f_{l_1,l_2}(r_1, r_2)$. Equation (1.19) then becomes a finite sum

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; L, M) = \sum_{\{l_1,l_2\}} \psi(l_1, l_2, L, M) F_{l_1,l_2}(r_1, r_2, r_{12}). \tag{1.21}$$

where we are now summing over the restricted set $\{l_1, l_2\}$ with either (A): $l_1 + l_2 = L$ or (B): $l_1 + l_2 = L + 1$ and $|l_1 - l_2| \leq L$. The parity, π, of the states is given by $\pi = (-1)^{l_1+l_2}$. Thus states with parity $\pi = (-1)^L$ correspond to condition (A) and states with parity $\pi = (-1)^{L+1}$ correspond to condition (B).

As an example, for S-wave, $L = 0$, we are restricted to $l_1 = l_2 = 0$. We have

$$\begin{aligned}\Psi(\mathbf{r}_1, \mathbf{r}_2; 0, 0) &= \psi(0, 0, 0, 0) F_{0,0}(r_1, r_2, r_{12}) \\ &= \mathcal{Y}_0^0(1)\mathcal{Y}_0^0(2) F_{0,0}(r_1, r_2, r_{12}) \equiv F(r_1, r_2, r_{12}).\end{aligned}$$

The full spatial wavefunction must then be symmetrized and so we define $\tilde{F}(r_1, r_2, r_{12}) \equiv F(r_2, r_1, r_{12})$ and finally we have

$$\Psi\left({}^{1,3}S^e\right) = F(r_1, r_2, r_{12}) \pm \tilde{F}(r_1, r_2, r_{12}). \tag{1.22}$$

The plus sign is taken for the singlet state since the singlet spin wavefunction is antisymmetric. Also, there are no odd-parity S states in three dimensions since condition (B) above would require $\{l_1, l_2\} = \{0, 1\}$ or $\{1, 0\}$ which would violate $|l_1 - l_2| \leq L$.

Now for P-wave states, $L = 1$, and we have either $\{l_1, l_2\} = \{1, 0\}$ or $\{0, 1\}$ for odd parity or $\{l_1, l_2\} = \{1, 1\}$ for even parity. Considering odd parity states Eq. (1.21) becomes

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; 1, M) = \psi(1, 0, 1, M) F_{1,0}(r_1, r_2, r_{12}) + \psi(0, 1, 1, M) F_{0,1}(r_1, r_2, r_{12}). \quad (1.23)$$

Eq. (1.20) gives, for $M = 1$,

$$\psi(1, 0, 1, 1) = \mathcal{Y}_1^1(1)\mathcal{Y}_0^0(2) \qquad \text{and} \qquad \psi(0, 1, 1, 1) = \mathcal{Y}_0^0(1)\mathcal{Y}_1^1(2);$$

for $M = 0$,

$$\psi(1, 0, 1, 0) = \mathcal{Y}_0^1(1)\mathcal{Y}_0^0(2) \qquad \text{and} \qquad \psi(0, 1, 1, 0) = \mathcal{Y}_0^0(1)\mathcal{Y}_0^1(2);$$

and for $M = -1$,

$$\psi(1, 0, 1, -1) = \mathcal{Y}_{-1}^1(1)\mathcal{Y}_0^0(2) \qquad \text{and} \qquad \psi(0, 1, 1, -1) = \mathcal{Y}_0^0(1)\mathcal{Y}_{-1}^1(2);$$

where all Clebsch-Gordon coefficients happen to be 1.

We define $F \equiv F_{1,0}(r_1, r_2, r_{12})$ and $\tilde{F} \equiv F_{0,1}(r_1, r_2, r_{12})$, and since $\mathcal{Y}_0^0$ is a constant, it can be absorbed into F and $\tilde{F}$. This allows us to write Eq. (1.23) as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2; 1, M) = \mathcal{Y}_M^1(1) F \pm \mathcal{Y}_M^1(2) \tilde{F},$$

where we have included the minus sign to symmetrize the wavefunction for the triplet state.

A general P^o state can be written as a linear combination of this wavefunction for each value of M. Without specifying the coefficients of the linear combination, we can write the wavefunction as a spherical tensor of rank-1 giving

$$\Psi\left({}^{1,3}P^o\right) = \begin{pmatrix} Y_1^{-1}(1) \\ Y_0^{-1}(1) \\ Y_{-1}^{-1}(1) \end{pmatrix} F \pm \begin{pmatrix} Y_1^{-1}(2) \\ Y_0^{-1}(2) \\ Y_{-1}^{-1}(2) \end{pmatrix} \tilde{F}. \tag{1.24}$$

This spherical tensor can be transformed to a Cartesian tensor via a unitary transformation. In this case we have

$$\frac{1}{r_i}\left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \mathbf{U} \begin{pmatrix} Y_1^{-1}(i) \\ Y_0^{-1}(i) \\ Y_{-1}^{-1}(i) \end{pmatrix},$$

where

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 & 1 \\ i & 0 & i \\ 0 & \sqrt{2} & 0 \end{pmatrix}.$$

($i = \sqrt{-1}$ in the matrix $\mathbf{U}$.) Operating on Eq. (1.24) with $\mathbf{U}$ gives

$$\Psi\left({}^{1,3}P^o\right) = \frac{1}{r_1}\left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} F \pm \frac{1}{r_2}\left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \tilde{F}$$

Absorbing the factor $\frac{1}{r_1}\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}$ into F and $\frac{1}{r_2}\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}$ into $\tilde{F}$ and writing the wavefunction in terms of Cartesian vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ gives

$$\Psi\left({}^{1,3}P^o\right) = \mathbf{r}_1 F \pm \mathbf{r}_2 \tilde{F} = \hat{\mathbf{r}}_1 r_1 F \pm \hat{\mathbf{r}}_2 r_2 \tilde{F}. \tag{1.25}$$

This can be written in matrix form as

$$\Psi\left({}^{1,3}P^o\right) = [\mathbf{W}]^T \mathbf{F}, \tag{1.26}$$

where

$$\mathbf{F} = \begin{pmatrix} F \\ \pm\tilde{F} \end{pmatrix} \qquad \text{and} \qquad \mathbf{W} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \end{pmatrix}.$$

Alternatively the wavefunction can also be written in component form as

$$\Psi_j \left({}^{1,3}P^o \right) = (r_1)_j F \pm (r_2)_j \tilde{F} \qquad \text{where} \qquad j = 1, 2, 3.$$

To extend this wavefunction to D-dimensions, as will be required when we discuss dimensional perturbation theory, one might think to simply let j range from 1 to D. This is almost true, but it is not just a simple extension of j. We will return to the Schwartz expansion in Sec. 2.2.1 where we discuss its generalization to D-dimensions.

1.6 Dimensional Perturbation Theory and Dimensional Scaling

1.6.1 The helium atom in three dimensions

Before delving into the world of arbitrary dimension we will first review the three dimensional helium atom. Since we are treating the nucleus as infinitely massive we can consider the laboratory and body-fixed reference frames as having their origins at the nucleus. In the lab frame there are six degrees of freedom, three Euler angles that take one from the lab frame to the body-fixed frame, and three internal degrees of freedom. The three internal degrees of freedom, $\{r_1, r_2, r_{12}\}$, (or $\{r_1, r_2, \theta\}$) consist of two electron-nucleus distances and one electron-electron distance (or one inter-electron angle). The two electrons and the nucleus form a plane which we can take to be the zx-plane, or the xy-plane, etc. of the body-fixed frame. The helium atom thus occupies a two-dimensional subspace of the three-dimensional world.

The wavefunction in the body-fixed frame is a function of $\{r_1, r_2, r_{12}\}$ (F and $\tilde{F}$ in the previous section), while the wavefunction in the lab frame, Ψ, is a function of the three internal coordinates as well as the three Euler angles. One may transform

from the body frame to the lab frame using Wigner rotation matrices which depend on the Euler angles. We then obtain a sum consisting of products of functions of the internal coordinates times functions of the Euler angles (see Eq. (1.22) for S-wave and Eq. (1.25) for P-wave). We have in effect factored out the internal degrees of freedom from the Euler angles. Upon inserting this wavefunction into the Schrödinger equation, we obtain a set of coupled differential equations for the internal coordinates which can, in principle, be solved.

When we consider the helium atom in D-dimensions we will have $2D$ degrees of freedom: they will consist of $2D-3$ Euler angles and, again, three internal degrees of freedom. The three internal degrees of freedom define a plan and the D-dimensional helium atom will again occupy a two-dimensional subspace of the D-dimensional world.

The wavefunction for S-wave states of the helium atom is independent of the Euler angles (see Eq. (1.22)) and thus has the same form in the lab frame as in the body frame. The wavefunction for any state for which $L \neq 0$ will depend in some way on the Euler angles. To transform from the lab frame to the body frame we use generalized Wigner rotation matrices which will depend on the $2D-3$ Euler angles and are D-dimensional. Thus, the dimension of the rotation matrices grows as D increases and so do the number of coupled differential equations. When we consider the limit $D \to \infty$, as is required by dimensional perturbation theory, we would expect the dimension of the matrices to also go to infinity. This will lead to an intractable set of differential equations, making the solution of the perturbation equations nearly impossible. We will return to the problem of $L \neq 0$ later, but first we need to review the techniques employed for S-wave states.

1.6.2 Outline of dimensional scaling and DPT

The general procedures for dimensional scaling and dimensional perturbation theory are as follows:[2, 3, 4, 5, 39, 40, 9, 41, 42, 43]

1. Derive an expansion for the wavefunction as a product of two functions, one being a known function of the generalized Euler angles and internal coordinates and the other being a function only of the internal coordinates. For S^e states the full wavefunction is already factored: it is already a function only of the internal coordinates and does not depend on the Euler angles. For higher angular momentum states we will use the generalized Schwartz expansion to achieve this factorization.

2. Insert the factored wavefunction into the Schrödinger equation and derive a differential equation, depending only on the internal coordinates, allowing continuation in D.

3. Incorporate a factor of the square root of the Jacobian into the wavefunction. This eliminates some first order derivatives and introduces new terms into the effective potential allowing there to be a lower bound to the effective potential as $D \to \infty$.

4. Re-scale the radial coordinates r_i and energy E so they remain finite as $D \to \infty$.

$$\tilde{r}_i = \frac{r_i}{D^2} = \delta^2 r_i \qquad \tilde{E} = D^2 E = \frac{E}{\delta^2}.$$

where

$$\delta = \frac{1}{D}.$$

5. At this point, as $D \to \infty$, the derivative terms vanish and the effective potential approaches a minimum. The large D limit is thus an "electrostatic" problem with the electrons frozen into a rigid configuration, called the *Lewis structure*, at the minimum of the effective potential defined by $\tilde{r}_i = r_m$ and $\theta = \theta_m$. The minimum of the effective potential gives the zeroth order energy, $\varepsilon_\infty \equiv V_{\rm eff}(r_m, r_m, \theta_m)$, in our perturbation expansion.

6. To calculate higher order corrections to the energy and wavefunction we allow for movement about the $D \to \infty$ Lewis structure equilibrium positions. To do so we introduce displacement coordinates x_1, x_2, and y through

$$\tilde{r}_i = r_m + \delta^{\frac{1}{2}} x_i \qquad \text{and} \qquad \theta = \theta_m + \delta^{\frac{1}{2}} \frac{\sqrt{2}}{r_m} y, \tag{1.27}$$

and symmetry coordinates x and q_1 through

$$x = \frac{1}{\sqrt{2}} (x_1 + x_2) \qquad \text{and} \qquad q_1 = \frac{1}{\sqrt{2}} (x_1 - x_2) . \tag{1.28}$$

We then expand the Hamiltonian, wavefunction, and energy as power series in $\delta^{1/2}$

$$H' = \sum_{j=0}^{\infty} \delta^{\frac{j}{2}} H'_j, \qquad \Phi = \sum_{p=0}^{\infty} \delta^{\frac{p}{2}} \Phi_p, \tag{1.29}$$

and

$$\tilde{E} = V_{\text{eff}}(r_m, r_m, \theta_m) + \delta \sum_{j=0}^{\infty} \delta^j \varepsilon_{2j}. \tag{1.30}$$

Finally, we plug these expansions into the Schrödinger equation and equate powers of $\delta^{1/2}$ to obtain a set of coupled differential equations in $\{q_1, x, y\}$.

7. The first order energy correction ε_0 is given by the δ order equation

$$H'_2 \Phi_0 = \varepsilon_0 \Phi_0.$$

The Hamiltonian, H'_2, becomes a three dimensional simple harmonic oscillator Hamiltonian if we transform to normal coordinates $q_1 = \frac{1}{\sqrt{2}}(x_1 - x_2)$, $q_2 \approx \frac{1}{\sqrt{2}}(x_1 + x_2)$, and $q_3 \approx y$. Thus q_1 corresponds to an antisymmetric stretch mode while q_2 and q_3 correspond approximately to the symmetric stretch and bending vibration modes respectively. These small oscillations about the Lewis structure are called *Langmuir vibrations*.

The zeroth order wavefunction Φ_0 is then a product of three simple harmonic oscillator wavefunctions, while the energy correction, ε_0, is a sum of three simple

harmonic oscillator energies. We call ε_0 the "harmonic order" correction to the energy and H_2' the harmonic order Hamiltonian.

8. Finally, once the zeroth and first order energies and the zeroth order wavefunction are found one may solve the coupled differential equations developed in step 6 by a number of different methods. We will limit our discussion to the matrix method which is currently the method of choice for multiple degrees of freedom [8].

The above steps will first be demonstrated for S-wave states and then for higher angular momentum states in the next chapter.

1.6.3 S-wave states and the extension to D dimensions

We will discuss the S-wave perturbation expansion in detail because many of the equations we will arrive at will be identical to equations used in the perturbation expansion for higher angular momentum states. Beginning with Step 1 we simply do nothing since the S-wave wavefunction is a function of the internal coordinates only. We then proceed to Step 2 and derive a differential equation in terms of the internal coordinates allowing continuation in D. We do this by writing the Hamiltonian in D-dimensions by starting with a D-dimensional Laplacian in Cartesian coordinates. x_k $(k = 1, 2, \ldots, D)$.

$$\nabla_D^2 \equiv \sum_{k=1}^{D} \frac{\partial^2}{\partial x_k^2}. \tag{1.31}$$

and defining the radial coordinate r as

$$r \equiv \left[\sum_{k=1}^{D} x_k^2 \right]^{\frac{1}{2}}.$$

In polar coordinates there are one radial coordinate and $D-1$ angles denoted by Ω_{D-1} and the Cartesian coordinates, x_k, are defined by $x_k = r f_k(\Omega_{D-1})$. The f_k consist of cosines and sines of the angles $\theta_1, \theta_2, \ldots, \theta_{D-1}$. In two dimensions there is one radial coordinate, r, and one angle, θ_1. We then have $x_1 = r\cos\theta_1$ and $x_2 = r\sin\theta_1$, with

$0 \leq \theta_1 \leq 2\pi$. In three dimensions we have the usual spherical polar coordinates r, $\theta_1 = \phi$, and $\theta_2 = \theta$. We can then write $x_1 = r\cos\theta_1 \sin\theta_2$, $x_2 = r\sin\theta_1 \sin\theta_2$, $x_3 = r\cos\theta_2$ with $0 \leq \theta_2 \leq \pi$. And in four dimensions we have $x_1 = r\cos\theta_1 \sin\theta_2 \sin\theta_3$, $x_2 = r\sin\theta_1 \sin\theta_2 \sin\theta_3$, $x_3 = r\cos\theta_2 \sin\theta_3$, $x_4 = r\cos\theta_3$ with $0 \leq \theta_3 \leq \pi$. The extension to D-dimensions is straight forward. The Laplacian in polar coordinates becomes

$$\nabla_D^2 = \frac{1}{r^{D-1}}\frac{\partial}{\partial r}(r^{D-1}\frac{\partial}{\partial r}) - \frac{L_{D-1}^2}{r^2},$$

where L_{D-1}^2 is a generalized orbital angular momentum operator and a function of the $D-1$ angles. As discussed by Herschbach [44], L_{D-1}^2 can be written in terms of a sequence of generalized orbital angular momentum operators of lower dimension:

$$\begin{aligned} L_1^2 &= -\frac{\partial^2}{\partial\theta_1^2}, \\ L_2^2 &= -\frac{1}{\sin\theta_2}\frac{\partial}{\partial\theta_2}\left(\sin\theta_2\frac{\partial}{\partial\theta_2}\right) + \frac{L_1^2}{\sin^2\theta_2}, \end{aligned}$$

etc., or in general

$$L_k^2 = -\frac{1}{\sin^{k-1}\theta_k}\frac{\partial}{\partial\theta_k}\left(\sin^{k-1}\theta_k\frac{\partial}{\partial\theta_k}\right) + \frac{L_{k-1}^2}{\sin^2\theta_k}.$$

with $k = 2, 3, \ldots, D-1$ and $0 \leq \theta_k \leq \pi$.

For S-states the wavefunction depends only on the internal coordinates $\{r_1, r_2, r_{12}\}$, or $\{r_1, r_2, \theta\}$, where θ is the angle between r_1 and r_2. In atomic units the Schrödinger equation is written as

$$\left[-\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + V(r_1, r_2, \theta)\right]\Psi = E\Psi.$$

The sum of the two D-dimensional Laplacians was worked out by Hill [45] and is

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{r_1^{D-1}}\frac{\partial}{\partial r_1}(r_1^{D-1}\frac{\partial}{\partial r_1}) + \frac{1}{r_2^{D-1}}\frac{\partial}{\partial r_2}(r_2^{D-1}\frac{\partial}{\partial r_2}) - \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)L_{D-1}^2.$$

L^2_{D-1} depends on $D-1$ angles of which all are separable (do not appear in the potential V) except the angle θ. Thus, L^2_{D-2} will be a constant of the motion and so we write

$$L^2_{D-1} = -\frac{1}{\sin^{D-2}\theta}\frac{\partial}{\partial\theta}\left(\sin^{D-2}\theta\frac{\partial}{\partial\theta}\right) + \frac{L^2_{D-2}}{\sin^2\theta}$$

with L^2_{D-2} being replaced by its eigenvalue $L(L+D-3)$ which is zero for S-states. This completes step 2.

The next step is to incorporate a square root of the Jacobian

$$J_D = (r_1 r_2)^{D-1}\sin^{D-1}\theta$$

into the wavefunction, $\Psi = J_D^{-1/2}\Phi$, which allows us to write

$$(T + U + V)\,\Phi = E\Phi$$

with derivatives appearing only in

$$T = -\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2}\right) - G^+\frac{\partial^2}{\partial\theta^2}$$

while dimensional dependence appears only in the centrifugal term

$$U = \frac{1}{4}\left[\frac{(D-2)(D-4)}{\sin^2\theta} - 1\right]G^+.$$

We also have

$$V = -\frac{1}{r_1} - \frac{1}{r_2} + \lambda\left[r_1^2 + r_2^2 - 2r_1 r_2\cos\theta\right]^{-1/2},$$

where we have introduced $\lambda = 1/Z$ and $G^+ = (r_1^{-2} + r_2^{-2})/2$. In addition, the energy units of E are atomic units divided by Z^2 and distance units are atomic units multiplied by Z.

Notice that the centrifugal term, U, becomes infinite as $D \to \infty$. We proceed with Step 4 to remedy this by introducing a suitable scaling of the distance units. If we

let $\tilde{r}_i = \delta^2 r_i$, with $\delta = 1/D$, and let $\tilde{E} = D^2 E$ then we have the dimensional scaled Schrödinger equation

$$\left[\delta^2 T\left(\tilde{r}_1, \tilde{r}_2, \theta\right) + \tilde{U}\left(\tilde{r}_1, \tilde{r}_2, \theta\right) + \tilde{V}\left(\tilde{r}_1, \tilde{r}_2, \theta\right)\right] \Phi = \tilde{E}\Phi. \tag{1.32}$$

where

$$\tilde{U} = \frac{1}{4}\left[\frac{(1-2\delta)(1-4\delta)}{\sin^2\theta} - \delta^2\right] G^{-}\left(\tilde{r}_1, \tilde{r}_2\right).$$

In the kinetic term of Eq. (1.32) we see that the dimension D appears as an effective mass.

In the limit $D \to \infty$ the electrons become infinitely heavy and stationary at the minimum of the effective potential

$$\tilde{V}_{\text{eff}}\left(\tilde{r}_1, \tilde{r}_2, \theta\right) = \frac{1}{4\sin^2\theta} G^{+}\left(\tilde{r}_1, \tilde{r}_2\right) + \tilde{V}\left(\tilde{r}_1, \tilde{r}_2, \theta\right).$$

Continuing with Step 5, the dimensional scaled Schrödinger equation becomes, as $D \to \infty$,

$$\tilde{V}_{\text{eff}}\left(\tilde{r}_1, \tilde{r}_2, \theta\right) \Phi = \varepsilon_\infty \Phi.$$

where ε_∞ is the energy at the minimum of the effective potential. This then provides a zeroth order perturbation theory for the D-dimensional helium atom. To solve for ε_∞ we need to specify which minimum of the effective potential we wish to expand about. We choose a symmetric minimum where $\tilde{r}_1 = \tilde{r}_2 = r_m$ and $\theta = \theta_m$. We then find

$$\begin{aligned} c_m &= \cos\theta_m = -2\bar{\lambda}\left[\left(1+\bar{\lambda}^2\right)^{1/2} + \bar{\lambda}\right], \\ r_m &= \frac{1}{4}\left(1+c_m\right)^{-2}, \\ \varepsilon_\infty &\equiv \tilde{V}_{\text{eff}}\left(r_m, r_m, \theta_m\right) = \frac{-4\left(1+c_m\right)^3}{\left(1-c_m\right)}. \end{aligned} \tag{1.33}$$

with $\bar{\lambda} = \sqrt{2}\lambda/16$. This symmetric minimum exists for $Z > Z_0 \simeq 1.2279$. For smaller values of Z the atom ionizes as $D \to \infty$. Therefore, to study H^- one could introduce

a D dependence into the nuclear charge in such a way that $Z = 1$ when $D = 3$ [46]. The geometry of the helium atom at $D \to \infty$ is called the *Lewis structure*. For $Z = 2$ we find that $\theta_m \simeq 95.3°$ and $\varepsilon_\infty = -2.737769133$.

The choice of the point of the effective potential to expand about is not arbitrary. The only requirement is that it be a stationary point so that the first order correction to the energy comes from harmonic oscillations about the expansion point. We chose to expand about a symmetric minimum in the hopes that our results would better describe doubly excited states. Our zeroth order helium atom has its two electrons at equal distances from the nucleus unlike a singly excited state where, on average, one electron is further from the nucleus. In other words, the choice of expansion points depends on the physical properties of the system you are trying to model. Another possible expansion point might be a saddle point. Expansion about saddle points would result in complex energy coefficients, allowing one to calculate resonance positions and widths. Our symmetric minimum gives real energy coefficients not enabling us to calculate resonance widths.

Next, to determine the first order correction to the energy, ε_0, we proceed to Step 6 and introduce dimensional scaled displacement coordinates x_1, x_2, and y and symmetry coordinates x and q_1, which represent symmetric and antisymmetric stretches respectively. Substituting these coordinates into Eq. (1.32) gives a Hamiltonian that can be expanded in powers of $\delta^{1/2}$.

$$\begin{aligned} H' &= \delta\left(-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial q_1^2}\right) - G^+(x,q_1)\,\frac{r_m^2}{2}\frac{\partial^2}{\partial y^2}\right) \\ &\quad +\frac{1}{4}\left(\frac{(1-2\delta)(1-4\delta)}{\sin^2\theta}-\delta^2\right)G^+(x,q_1) \\ &\quad -\frac{1}{\tilde{r}_1}-\frac{1}{\tilde{r}_2}+\frac{\lambda}{\sqrt{\tilde{r}_1^2+\tilde{r}_2^2-2\tilde{r}_1\tilde{r}_2\cos\theta}}. \end{aligned}$$

After expanding the Hamiltonian in powers of $\delta^{1/2}$ we find that the zeroth order term is simply the energy at the minimum of the effective potential, $\varepsilon_\infty \equiv V_{\text{eff}}(r_m, r_m, \theta_m)$. The first order term, of order $\delta^{1/2}$, is zero since it is the first derivative of the effective potential evaluated at r_m and θ_m, which define a minimum. The δ-order term is the

first term to contain derivatives and, for reasons that will become apparent later, we call it the harmonic order Hamiltonian, H_2'. It is given by

$$H_2' = -\frac{1}{2}\left(\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + u\,x^2 + w\,y^2 + v\,xy + \frac{1}{2}\omega_1^2\,q_1^2 - \frac{3}{2r_m^2\,s_m^2}. \tag{1.34}$$

where

$$u = \frac{1}{r_m^3}\left[\frac{3}{8r_m\,s_m^2} - 1 + \frac{\lambda}{2\left[2\left(1-c_m\right)\right]^{1/2}}\right]. \tag{1.35}$$

$$v = \frac{1}{2r_m^3}\left[\frac{1}{r_m\,s_m^2\,t_m} + \frac{\lambda\,s_m}{\left[2\left(1-c_m\right)\right]^{3/2}}\right], \tag{1.36}$$

$$w = \frac{1}{2r_m^3}\left[\frac{1}{r_m\,s_m^2}\left(\frac{3}{s_m^2} - 2\right) + \frac{\lambda\left(3+c_m\right)}{\left[2\left(1-c_m\right)\right]^{3/2}}\right]. \tag{1.37}$$

and

$$\omega_1^2 = \frac{2}{r_m^3}\left[\frac{3}{8r_m\,s_m^2} - 1 - \frac{\lambda\left(1+c_m\right)}{2\left[2\left(1-c_m\right)\right]^{\frac{3}{2}}}\right]. \tag{1.38}$$

where $s_m = \sin\theta_m$ and $t_m = \tan\theta_m$.

We can separate the coordinates x and y in Eq. (1.34) by transforming to normal coordinates. This is accomplished by setting

$$u\,x^2 + w\,y^2 + v\,xy = \frac{1}{2}\omega_2^2\,q_2^2 + \frac{1}{2}\omega_3^2\,q_3^2.$$

or in matrix notation

$$\begin{pmatrix} x & y \end{pmatrix}\begin{pmatrix} 2u & v \\ v & 2w \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} q_2 & q_3 \end{pmatrix}\begin{pmatrix} \omega_2^2 & 0 \\ 0 & \omega_3^2 \end{pmatrix}\begin{pmatrix} q_2 \\ q_3 \end{pmatrix}.$$

We then diagonalize the matrix on the left obtaining the eigenvalues

$$\omega_2^2 = (u+w) - \sqrt{(w-u)^2 + 4v^2} \tag{1.39}$$

and

$$\omega_3^2 = (u+w) + \sqrt{(w-u)^2 + 4v^2}. \tag{1.40}$$

and the eigenfunctions

$$q_2 = -x\sin\chi + y\cos\chi \qquad \text{and} \qquad q_3 = x\cos\chi + y\sin\chi, \tag{1.41}$$

where χ is given by

$$\tan\chi = \frac{(w-u)\left[1+\sqrt{1+\left(\frac{2v}{w-u}\right)^2}\right]}{2v}. \tag{1.42}$$

χ is approximately 90 degrees, so from equations (1.27), (1.28) and (1.41) we see that q_1 corresponds to the antisymmetric stretch mode while q_2, and q_3 correspond approximately to the symmetric stretch and bending vibration modes respectively.

Finally, the δ-order Hamiltonian becomes

$$H_2' = -\frac{1}{2}\left(\frac{\partial^2}{\partial q_1^2}+\frac{\partial^2}{\partial q_2^2}+\frac{\partial^2}{\partial q_3^2}\right)+\frac{1}{2}\omega_1^2 q_1^2+\frac{1}{2}\omega_2^2 q_2^2+\frac{1}{2}\omega_3^2 q_3^2-\frac{3}{2r_m^2 s_m^2}. \tag{1.43}$$

and the first order energy correction is simply a sum of three one-dimensional simple harmonic oscillator energies plus a constant

$$\varepsilon_0 = \omega_1\left(n_a+\frac{1}{2}\right)+\omega_2\left(n_s+\frac{1}{2}\right)+\omega_3\left(n_\theta+\frac{1}{2}\right)-\frac{3}{2r_m^2 s_m^2}. \tag{1.44}$$

while the zeroth order wavefunction is a product of three one-dimensional simple harmonic oscillator eigenfunctions

$$\Phi_0 = h_{n_a}\left(\omega_1^{1/2}q_1\right)h_{n_s}\left(\omega_2^{1/2}q_2\right)h_{n_\theta}\left(\omega_3^{1/2}q_3\right). \tag{1.45}$$

This completes Step 7.

To complete Step 8 we reconsider the Schrödinger equation after transforming to normal coordinates.

$$H'\Phi\left(q_1,q_2,q_3\right) = \tilde{E}\Phi\left(q_1,q_2,q_3\right),$$

with

$$
\begin{aligned}
H' &= \delta\left(-\frac{1}{2}\left(\cos^2\chi\frac{\partial^2}{\partial q_3^2}-2\sin\chi\cos\chi\frac{\partial^2}{\partial q_2\partial q_3}+\sin^2\chi\frac{\partial^2}{\partial q_2^2}+\frac{\partial^2}{\partial q_1^2}\right)\right. \\
&\quad \left.-G^+\left(q_1,q_2,q_3\right)\frac{r_m^2}{2}\left(\cos^2\chi\frac{\partial^2}{\partial q_2^2}+2\sin\chi\cos\chi\frac{\partial^2}{\partial q_2\partial q_3}+\sin^2\chi\frac{\partial^2}{\partial q_3^2}\right)\right) \\
&\quad +\frac{1}{4}\left(\frac{(1-2\delta)(1-4\delta)}{\sin^2\theta}-\delta^2\right)G^+\left(q_1,q_2,q_3\right) \\
&\quad -\frac{1}{\tilde{r}_1}-\frac{1}{\tilde{r}_2}+\frac{\lambda}{\tilde{r}_{12}}
\end{aligned}
\tag{1.46}
$$

where

$$
\lambda=\frac{1}{Z},\qquad \delta=\frac{1}{D},\qquad G^+\left(q_1,q_2,q_3\right)=\frac{1}{2}\left(\frac{1}{\tilde{r}_1^2}+\frac{1}{\tilde{r}_2^2}\right). \tag{1.47}
$$

and

$$
\begin{aligned}
\tilde{r}_1 &= r_m+\delta^{1/2}\frac{1}{\sqrt{2}}\left(q_3\cos\chi-q_2\sin\chi+q_1\right). \\
\tilde{r}_2 &= r_m+\delta^{1/2}\frac{1}{\sqrt{2}}\left(q_3\cos\chi-q_2\sin\chi-q_1\right). \\
\theta &= \theta_m+\delta^{1/2}\frac{\sqrt{2}}{r_m}\left(q_2\cos\chi+q_3\sin\chi\right), \\
\tilde{r}_{12} &= \left[\tilde{r}_1^2+\tilde{r}_2^2-2\tilde{r}_1\tilde{r}_2\cos\theta\right]^{1/2}.
\end{aligned}
\tag{1.48}
$$

Expanding G^+ and the various potential terms as power series in $\delta^{1/2}$ gives us a kinetic term

$$
\begin{aligned}
T &= -\frac{\delta}{2}\left(\frac{\partial^2}{\partial q_1^2}+\frac{\partial^2}{\partial q_2^2}+\frac{\partial^2}{\partial q_3^2}\right) \\
&\quad +\sum_{j=3}^{\infty}\delta^{j/2}\sum_{k=0}^{(j-2)/2}\sum_{l=0}^{j-2-2k}T_{j,k,l}\;q_1^{2k}\;q_2^{l}\;q_3^{j-2-2k-l} \\
&\quad \times\left(\cos^2\chi\frac{\partial^2}{\partial q_2^2}+2\sin\chi\cos\chi\frac{\partial^2}{\partial q_2\partial q_3}+\sin^2\chi\frac{\partial^2}{\partial q_3^2}\right).
\end{aligned}
\tag{1.49}
$$

and the effective potential term

$$
U = \sum_{j=0}^{\infty}\delta^{j/2}\sum_{k=0}^{j/2}\sum_{l=0}^{j-2k}U1_{j,k,l}\;q_1^{2k}\;q_2^{l}\;q_3^{j-2k-l}
$$

$$+\sum_{j=2}^{\infty}\delta^{j/2}\sum_{k=0}^{(j-2)/2}\sum_{l=0}^{j-2-2k} U2_{j,k,l}\, q_1^{2k}\, q_2^{l}\, q_3^{j-2-2k-l}$$
$$+\sum_{j=4}^{\infty}\delta^{j/2}\sum_{k=0}^{(j-4)/2}\sum_{l=0}^{j-4-2k} U3_{j,k,l}\, q_1^{2k}\, q_2^{l}\, q_3^{j-4-2k-l}. \qquad (1.50)$$

which are combined to give the Hamiltonian

$$H' = \sum_{j=0}^{\infty} H'_j \delta^{j/2} \qquad \text{where.} \qquad H'_j = T_j + U_j. \qquad (1.51)$$

Next. we expand the wavefunction and energy as power series in $\delta^{1/2}$

$$\Phi\,(q_1, q_2, q_3) = \sum_{p=0}^{\infty} \Phi_p \delta^{\,p/2}, \qquad \text{and} \qquad \tilde{E} = V_{\text{eff}}(r_m, r_m, \theta_m) + \delta \sum_{j=0}^{\infty} \varepsilon_{2j} \delta^{\,j}. \quad (1.52)$$

where $V_{\text{eff}}(r_m, r_m, \theta_m)$ is the value of the minimum of the effective potential, as $D \to \infty$. such that $\tilde{r}_1 = \tilde{r}_2 \equiv r_m$. and $\theta = \theta_m$.

Substituting these expansions into the Schrödinger equation gives

$$\sum_{j=0}^{\infty} H'_j \delta^{j/2} \sum_{p=0}^{\infty} \Phi_p \delta^{p/2} = \sum_{p=0}^{\infty} \Phi_p \delta^{p/2} \left(V_{\text{eff}}(r_m, r_m, \theta_m) + \delta \sum_{j=0}^{\infty} \varepsilon_{2j} \delta^{j} \right). \qquad (1.53)$$

The δ^0 term gives $H'_0 \Phi_0 = V_{\text{eff}}(r_m, r_m, \theta_m)\Phi_0$ which simply says that $H'_0 = V_{\text{eff}}(r_m, r_m, \theta_m)$. which is the energy at the minimum of the effective potential; in other words. it is the energy as $D \to \infty$ of the D-dimensional helium atom. The $\delta^{1/2}$ term gives $(H'_0\Phi_1 + H'_1\Phi_0) = V_{\text{eff}}(r_m, r_m, \theta_m)\Phi_1$ but H'_1 contains only effective potential terms and is the derivative of the effective potential evaluated at its minimum. Thus. $H'_1 = 0$. and we are left with $H'_0\Phi_1 = V_{\text{eff}}(r_m, r_m, \theta_m)\Phi_1$ which gives us no new information. Since $H'_0 = V_{\text{eff}}(r_m, r_m, \theta_m)$ and $H'_1 = 0$. Eq. (1.53) can now be written as

$$\sum_{j=2}^{\infty} H'_j \delta^{j/2} \sum_{p=0}^{\infty} \Phi_p \delta^{p/2} = \delta \sum_{p=0}^{\infty} \Phi_p \delta^{p/2} \sum_{j=0}^{\infty} \varepsilon_j \delta^{j/2} \qquad (1.54)$$

with $\varepsilon_{2j+1} = 0$. After a change of variables and some rearranging we can write

$$\sum_{p=0}^{\infty} \delta^{j/2} \sum_{l=0}^{p} (H_l - \varepsilon_l)\, \Phi_{p-l} = 0.$$

where $H_l = H'_{l+2}$. This then leads us to an infinite set of coupled inhomogeneous differential equations

$$\sum_{l=0}^{p} (H_l - \varepsilon_l)\, \Phi_{p-l} = 0 \qquad p = 0, 1, 2, \ldots \tag{1.55}$$

The method we used to solve these equations is called the matrix method and will be discussed later. For $p = 0$ Eq. (1.55) gives the zeroth order Schrödinger equation. $H_0\Phi_0 = \Phi_0\varepsilon_0$. Identifying H_0 with H'_2 we find, as in Eq. (1.43)

$$H_0 = -\frac{1}{2}\left(\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2} + \frac{\partial^2}{\partial q_3^2}\right) + \frac{1}{2}\omega_1^2 q_1^2 + \frac{1}{2}\omega_2^2 q_2^2 + \frac{1}{2}\omega_3^2 q_3^2 - \frac{3}{2r_m^2 s_m^2}.$$

This zeroth order Schrödinger equation is clearly a three dimensional harmonic oscillator equation and thus the energy and wavefunction are given by Eqs. (1.44) and (1.45). The h_ν in Eq. (1.45) are the harmonic oscillator eigenfunctions

$$h_\nu(x) = \left(\frac{1}{2^\nu \nu! \pi^{1/2}}\right)^{1/2} \mathrm{H}_\nu(x) \exp\left(-\frac{1}{2}x^2\right). \tag{1.56}$$

The H_ν are the Hermite polynomials of degree ν. The normalization of the h_ν has been chosen such that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Phi_0^2(q_1, q_2, q_3)\, dq_1 dq_2 dq_3 = 1.$$

The zeroth order wavefunction, Eq. (1.45), describes harmonic oscillations about the $D \to \infty$ limit of the helium atom. Thus we refer to $\{n_a, n_s, n_\theta\}$ as the large dimension quantum numbers and we refer to H_0 as the harmonic order, rather than zeroth order, Hamiltonian. The large dimension states are designated by the ket

$|n_a, n_s, n_\theta\rangle$ and they evolve into known states of the helium atom as higher order terms are included in the Hamiltonian and as $D \to 3$.

1.6.4 Large order quantum numbers

The large dimension limit provides a set of approximate quantum numbers, $\{n_a, n_s, n_\theta\}$, to label states when $D = 3$. We would like to relate these quantum numbers to quantum numbers used in the literature to describe $D = 3$ states of the helium atom. Several examples have been discussed so far. There is the set $\{\bar{n}, n_\lambda, n_\mu, m\}$ used in the molecular adiabatic approach, the set $\{K, T, A\}$ used in the hyperspherical adiabatic approach, and the set $\{N, l_N, n, l_n\}$ used in the independent particle approach.

Loeser and Herschbach [47] have demonstrated how the large dimension quantum numbers can be related to single particle quantum numbers in the limit $Z \to \infty$. They found that states in the large dimension limit (harmonic states) can be written as linear combinations of singly and doubly excited independent particle states. It was not clear which state the large dimension state becomes as D is decreased to 3. Some insight can be gained by noting that classically, the potential ridge riding symmetric stretch states, states with large electron density for $r_1 = r_2$ for large D, tend to become unstable as $D \to 3$ due to strong interactions at the triple collision point. These states tend to "fall off" of the potential ridge and become states with unequal excitation when $D = 3$. From this analysis one finds a relationship between the large dimension and single particle quantum numbers

$$N = \lfloor n_a/2 \rfloor + n_\theta + 1 \tag{1.57}$$

$$n = N + n_s + (n_a - 2\lfloor n_a/2 \rfloor), \tag{1.58}$$

where $\lfloor x \rfloor$ denotes the integer part of x. The quantum numbers n_a and n_s describe radial excitation while n_θ describes angular excitation, which leads to the correspondence for $L = 0$ states

$$l_N = l_n = n_\theta \tag{1.59}$$

and the spin is given by

$$S = 1 - (-1)^{n_a}. \tag{1.60}$$

Thus, singly excited states ($N = 1$) have $n_\theta = 0$ and $n_a < 2$ so that $|0n_s0\rangle$ corresponds to $1sns\ ^1S^e$ with $n = n_s + 1$, and $|1n_s0\rangle$ corresponds to $1sns\ ^3S^e$ with $n = n_s + 2$.

As an example, Loeser and Herschbach suggested that the state $|020\rangle$ corresponds to a linear combination of $D = 3$ states such as $1s3s\ ^1S^e$ and $2s^2\ ^1S^e$. With the quantum number correspondences listed above this state should become the $1s3s\ ^1S^e$ state at $D = 3$, agreeing with the classical argument that the symmetric stretch states should fall off of the potential ridge as $D \to 3$ becoming states with unequal excitation between the two electrons.

Correspondences between the large dimension and the $\{K, T\}$ quantum numbers have also been discussed. The T quantum number is the projection of the total orbital angular momentum onto an axis parallel to the interelectron axis. Thus for $L = 0$ states we must have $T = 0$. The K quantum number is related to excitation in the vibrational mode with the relationship [48]

$$\begin{aligned} K &= N - 2n_\theta - 1 - T \\ &= \lfloor n_a/2 \rfloor - n_\theta \qquad \text{for } L = 0. \end{aligned} \tag{1.61}$$

The correspondences for states with $L \neq 0$ have not been completely worked out yet.

1.6.5 Interdimensional Degeneracies

The existence of states in one particular dimension being degenerate with different states in a different dimension was first discussed by Herrick and Stillinger in 1975 [49, 50]. Using the results of Breit [7] and Schwartz [6] they started by writing a P^e state in terms of an S^e state. Breit and Schwartz found that P^e states could be written as

$$\Psi = P\,\chi(r_1, r_2, \theta)$$

with

$$P = x_1 y_2 - x_2 y_1,$$

where x and y are two Cartesian coordinates of a space-fixed frame and the subscripts distinguish the coordinates of the two electrons. The function χ is a function only of the internal coordinates and so must be an S^e state. Herrick and Stillinger then evaluated the commutator $[\Delta_D^{(1)} + \Delta_D^{(2)}, P]$ where $\Delta_D^{(i)}$ is the D-dimensional Laplacian for electron i. They obtained

$$\left(-\frac{1}{2}\Delta_D^{(1)} - \frac{1}{2}\Delta_D^{(2)} + V - E\right) P\chi = P\left(-\frac{1}{2}\Delta_{D+2}^{(1)} - \frac{1}{2}\Delta_{D+2}^{(2)} + V - E\right)\chi.$$

Thus if $P\chi$ is an eigenstate of the D-dimensional Schrödinger equation with eigenvalue E then χ is an eigenstate of the $(D+2)$-dimensional Schrödinger equation with the same eigenvalue E. In other words, χ, an S^e state, evaluated at $D = 5$ has the same energy as $P\chi$, a P^e state, at $D = 3$. In addition, since P is antisymmetric with respect to electron interchange then $P\chi$ and χ have opposite spin. Thus, for every ${}^{1,3}S^e$ state at $D = 5$ there is a ${}^{3,1}P^e$ state at $D = 3$ with the same energy. These exact degeneracies are called interdimensional degeneracies. Similar exact degeneracies exist between ${}^{1,3}P^o$ states at $D = 5$ and ${}^{3,1}D^o$ states at $D = 3$.

At $D = 5$ the lowest S^e state is the ground state with an energy of -0.71a.u.[39, 40, 9] This state is degenerate with the lowest P^e state at $D = 3$. The $D = 5$ first ionization threshold is given by the energy of the He^+ ground state at $D = 5$. The energies of the He^+ atom are given by

$$E_{He^+} = -2(N + \Delta)^{-2} \quad \text{in a.u.}$$

where $\Delta \equiv \frac{1}{2}(D-3)$ and N is the principal quantum number of the remaining electron. Thus the first ionization threshold at $D = 5$ is at -0.5 a.u., which is degenerate with the second ionization threshold at $D = 3$, and the first ionization threshold at $D = 3$ is at -2.0 a.u. Thus, at $D = 3$, all singly excited states lie below -2.0 a.u. so the P^e state at -0.71 a.u. $(D = 3)$ must be a doubly excited state.

Indeed, there can be no P^e singly excited states. More importantly, the P^e state at $D = 3$ is a bound state, since there are no lower P^e states for it to autoionize to, and it is degenerate with a $D = 5$, S^e bound state.

At $D = 5$ the lowest P^o state lies at about -0.56 a.u., which is a singly excited bound state. This state is degenerate with a D^o state at $D = 3$ which is doubly excited (its energy is between the first and second ionization thresholds at $D = 3$), as well as bound, since there are no D^o states below the $D = 3$ first ionization threshold for it to decay to.

To summarize, all S^e (P^o) states at $D = 5$ are degenerate with doubly excited P^e (D^o) states at $D = 3$ and if the S^e (P^o) state at $D = 5$ is a bound state so too will the P^e (D^o) state at $D = 3$ be a bound state. Also, for $D = 5$ all states above -0.5 a.u. are autoionizing resonances and can decay into the continuum. These states are degenerate with states at $D = 3$ that are also autoionizing. Thus, bound states are degenerate with bound states and autoionizing states are degenerate with autoionizing states.

Taking advantage of these interdimensional degeneracies allows one to write code to find the energies of two states at $D = 3$ by calculating an energy series for one state. For example a single series can then be summed at $D = 3$ to obtain a P^o energy or it can be summed at $D = 5$ to obtain a $D = 3$ D^o energy. This is exactly what has been done to obtain $D = 3$ P^e states and this is what we will do to obtain $D = 3$ D^o states in Chapter 4.

1.6.6 Fermi Resonances

Recall the harmonic order energy

$$\varepsilon_0 = \omega_1 \left(n_a + \frac{1}{2} \right) + \omega_2 \left(n_s + \frac{1}{2} \right) + \omega_3 \left(n_\theta + \frac{1}{2} \right) - \frac{3}{2 r_m^2 s_m^2}.$$

As can be seen from Eqs. (1.35)-(1.40), ω_1, ω_2, and ω_3 are functions of λ. In Fig. (1.6.6) we plot the $\omega's$ versus λ. First notice that ω_1, the antisymmetric stretch frequency, is zero at $\lambda_0 = 0.8143894$ corresponding to $Z_0 = 1.227914$. As discussed

on page 33. when $Z < Z_0$ the two electron atom ionizes so that we must include some δ dependence into the nuclear charge in order to study the H^- ion.

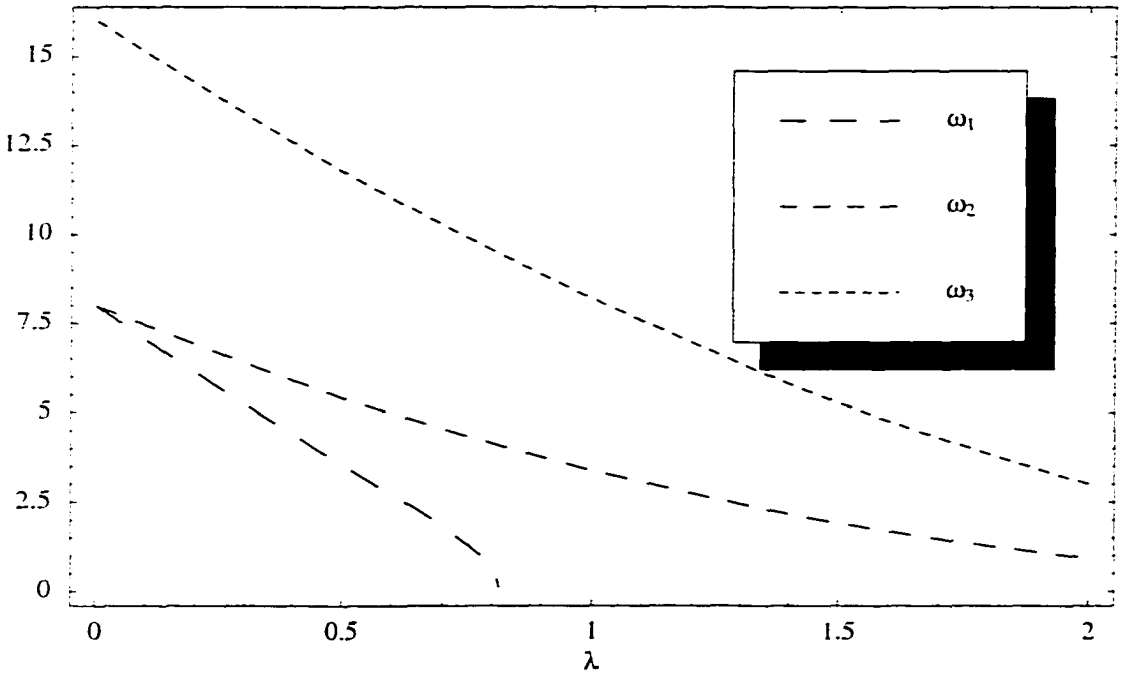


Figure 1.3: ω_1, ω_2, and ω_3 as functions of λ.

Since the harmonic frequencies are functions of λ we can look for values of λ where ratios of different frequencies are rational numbers. For example, when $\lambda = \lambda^* \equiv 0.6369$ we find $\omega_2/\omega_1 = 2$. For this value of λ we find that the states $|010\rangle$ and $|200\rangle$ are degenerate at harmonic order. These degeneracies, which arise from the harmonic frequencies being commensurate, are called Fermi resonances. In Fig. (1.6.6) we plot the harmonic order energy verses λ for several states.

We can consider the energy function of the states of helium as being a function of both λ and δ. When $\lambda = \lambda^*$, zeroth order perturbation theory gives energy functions of the $|010\rangle$ and $|200\rangle$ states that are degenerate. It is a general result of perturbative eigenvalue problems that when two eigenvalues are degenerate at zeroth order in δ their eigenvalues as a function of the perturbation parameter δ will share a square-root branch point at $\delta = 0$. As λ moves away from λ^* the zeroth order energies are

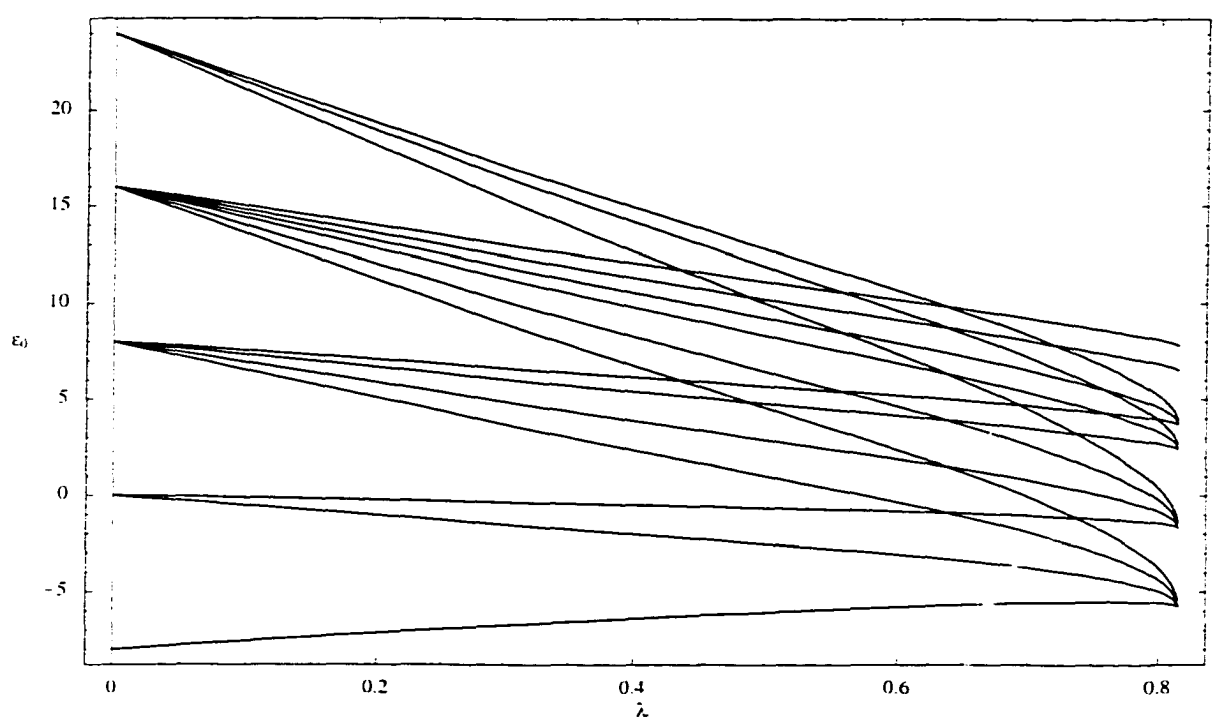


Figure 1.4: Harmonic order energies as functions of λ. The order of the states from lowest to highest is $|000\rangle$, $|100\rangle$, $|010\rangle$, $|200\rangle$, $|110\rangle$, etc. Notice the degeneracy at $\lambda = 0.6369$ for the $|010\rangle$ and $|200\rangle$ states.

no longer degenerate and the branch point moves away from the origin usually as a pair of complex conjugate branch points.

A simple example should clarify this. Bender and Orszag [51] consider the "simplest eigenvalue problem of all." Consider the two real 2×2 matrices

$$A = \begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix} \quad \text{and} \quad B = \begin{pmatrix} x & z \\ z & y \end{pmatrix}.$$

If we wanted to find the eigenvalues of the sum of these two matrices we could multiply B by the parameter δ and express the two eigenvalues as power series in δ. One power series will have a zeroth order coefficient equal to a, and the other will have a zeroth order coefficient equal to b. We would then find the eigenvalues of $A + \delta B$ using perturbation theory.

This problem can also be solved exactly by diagonalizing the matrix $A + \delta B$, i.e. by solving $A + \delta B - I\varepsilon = 0$ where I is the 2×2 unit matrix. We find

$$\varepsilon_{\pm} = \frac{1}{2}\left(a + b + \delta x + \delta y \pm \left[(a - b + \delta x - \delta y)^2 + 4\delta^2 z^2\right]^{1/2}\right)$$

These eigenvalues are functions of δ and are analytic except where the term in the square root is zero. Thus the functions $\varepsilon_{\pm}(\delta)$ have a pair of complex conjugate branch points at

$$\delta_{\pm} = \frac{(a - b)(y - x \pm 2i\,z)}{(y - x)^2 + 4z^2}.$$

The radius of convergence of $\varepsilon_{\pm}$ is equal to $|\delta_{\pm}|$.

The two eigenvalue functions ε_+ and ε_- are analytic continuations of each other. Analytically continuing around either branch point changes the sign of the square root term in the eigenvalue function and hence the two eigenvalues exchange character. This is called a level crossing. The two single valued eigenvalue functions ε_+ and ε_- can be considered to form a single two-valued function $\varepsilon(\delta)$ which is defined on a two sheeted Riemann surface. On one surface $\varepsilon(\delta) = \varepsilon_+$ while on the other surface $\varepsilon(\delta) = \varepsilon_-$.

Now consider the zeroth order eigenvalues a and b to be functions of some other parameter λ. If for some $\lambda = \lambda^*$, $a(\lambda^*) = b(\lambda^*) \equiv c$ then the radius of convergence will go to zero as $\lambda \to \lambda^*$ and the branch points will coalesce at the origin. This example illustrates what has been found for the helium atom for S states [9] as well as for P^o states as we will see in Chapter 4. Also, for an enlightening discussing on branch points and the Barbanis Hamiltonian see Ref. [52].

The zeroth order eigenvalues corresponding to a and b are the harmonic order coefficients ε_0 which are functions of $\lambda = 1/Z$. When $\lambda = \lambda^*$ two or more states have degenerate zeroth order energies and hence share a square root branch point at the origin. As λ moves from λ^* to $\lambda = 1/2$ these branch points move away from the origin possibly increasing the radius of convergence. As the energy function of these connected states are analytically continued beyond the radius of convergence (i.e. summed at point $\delta = 1/3$ perhaps, corresponding to $D = 3$) the characters of

the states are exchanged. This exchange is also seen by the presence of an avoided crossing between the two states.

For example ratio and root tests for the energy series for the $|010\rangle$ and $|200\rangle$ states show a radius of convergence of $\delta_c \simeq 0.0118$. Furthermore, quadratic Padé analysis (able to model the singularity structure of the energy series including branch points) suggests a square root branch point at $\delta_s = -0.011386007$ shared by both energy series. This branch point is thought to arise from the $\omega_2/\omega_1 = 2$ Fermi resonance which occurs at $\lambda = \lambda^* \equiv 0.6369$. Thus, the energy functions for these two states could be modeled in the form

$$E_{010}(\delta) = f(\delta) + g(\delta)\sqrt{\delta - \delta_s}$$

and

$$E_{200}(\delta) = f(\delta) - g(\delta)\sqrt{\delta - \delta_s}.$$

Each energy is thus considered to be a separate branch of a two-valued function. When these two energy series are added term by term and then analyzed using quadratic Padé approximants the branch point is no longer present. The states have a certain character for large D but as D is decreased to $D = 3$ the states are seen to exchange character due to the above mentioned shared branch point. Analysis of the wavefunction at large and small D also show this exchange of character.

Looking again at Fig. 1.6.6 we see that for higher lying states the number of Fermi Resonances increases rapidly. Thus we would expect higher lying states to have many square root branch points in their energy functions and thus exchange character several times as we go from large D, to $D = 3$. The increasing number of branch points also makes summation of the energy series more difficult. To accurately sum these series we must somehow remove or account for these branch points. We will see in Chapter 4 that this behavior exists for higher angular momentum states as well and can actually be more complex.

Chapter 2

The D-Dimensional Helium Atom For $L \neq 0$.

2.1 Introduction

The derivation of tractable perturbation equations requires an expansion of the wavefunction in which the rotational degrees of freedom, which multiply with increasing D, are isolated within known basis functions so that perturbation equations purely in terms of internal coordinates may be derived for the unknown expansion coefficients. For S-wave states this is fairly simple [39, 40, 9], thus to date DPT studies have focused for the most part on S^e states and their interdimensionally degenerate P^e counterparts (see Sec. 1.6.5).

During the past five years Dunn and Watson have published a series of four papers [2, 3, 4, 5], which detail the extension of the DPT formalism to higher angular momentum states for multi-electron atoms. This work completes and generalizes earlier work by Schwartz [6, 53] and others [7] who worked solely in 3 dimensions. References [2, 3] describe, in detail, the derivation of a finite expansion for the D-dimensional, N-electron wavefunction using D-dimensional rotational invariance implemented through the group theoretic method of irreducible tensors. The resulting wavefunction expansion leaves the expansion coefficients dependent only on a finite number of internal coordinates. In Ref. [4], application of the Hamiltonian to this wavefunction expansion for the atomic two-electron system results in a tractable set of differential equations which allow continuation in the dimension D, i.e. allow a perturbation theory which uses D as its parameter. These differential equations

also clearly reveal the complete set of exact interdimensional degeneracies for the two-electron system generalizing the work of Herrick and Stillinger[49, 50], Doren and Herschbach [41, 42, 43] and Goodson et. al.[54] who identified a few particular interdimensional degeneracies. Finally, in Ref. [5], these differential equations are solved in the large dimension limit and a zeroth order solution is obtained about which a perturbation series can be developed. This enables the methods of DPT to be extended to all higher angular momentum states of two-electron systems. (For a different treatment of higher angular momentum DPT as applied to molecules see reference [55]).

The goal of this dissertation is to present the first application of this extensive formalism. For our initial system we have chosen to study excited states of the helium atom. We begin in the next section by summarizing the results and procedures outlined in Refs. [4, 5]. We begin with a brief discussion of the generalized Schwartz expansion as applied to states with P^o symmetry. We then outline the procedures for dimensional scaling and dimensional perturbation theory for arbitrary angular momentum, deriving a set of perturbation equations as was done in Sec. 1.6.3 for S-states. After having obtained a suitable zeroth order approximation we then outline, in Ch. 3, the procedure for solving the perturbation equations to any order. Finally, in Ch. 4, we present the results for various P^o states and their interdimensionally degenerate D^o counterparts.

The results of this research serve to validate the correctness of the formalism for two-electron atomic states with arbitrary total orbital angular momentum developed by Dunn and Watson. We are now confident that the formalism should be correct for an arbitrary number of electrons as well. The formalism is now being used to study Bose-Einstein condensates and can, without too much effort, be used to study more complex systems such as many electron atoms.

2.2 Two-Electron Hamiltonian And Large-D Limit

The two-electron Hamiltonian in D-dimensions for arbitrary angular momentum is derived in Ref. [4] by specializing the wavefunction expansion of Refs. [2, 3] to a two-electron system. Reference [5] then discusses the large D limit of the Hamiltonian. Here we present a summary of the results of Refs. [2, 3], specifically, we consider the generalized Schwartz expansion for the wavefunctions of P^o states, then we summarize the results of Refs. [4, 5] and discuss the application of the equations to the calculation of the ${}^{1,3}P^o$ states that are the focus of this dissertation.

2.2.1 The D-Dimensional Schwartz Expansion

We begin by summarizing the generalized Schwartz expansion, the results of Refs. [2, 3], specifically for P^o states. The D-dimensional Schwartz expansion for two electrons is given by Eq. (1) of Ref. [4]

$$\Psi^{\Gamma}_{\{I_t\}}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\mu_1,\mu_2;\varsigma(\mu_1+\mu_2=t)} W^{t;\Gamma;\varsigma}_{t;\mu_1,\mu_2;\{I_t\}}(\mathbf{r}_1,\mathbf{r}_2)\, f^{\Gamma,\varsigma}_{\mu_1,\mu_2}(r_1,r_2,r_{12}) \qquad (2.1)$$

Γ labels the irreducible representation of the D-dimensional orthogonal group $O(D)$, the group of rotations and reflections in D-dimensions. (Recall that the Spherical Harmonics Y_{lm} transform under irreducible representations of $O(3)$.) We concern ourselves only with those irreducible representations that survive down to $D = 3$. These representations may be denoted by a Young diagram with γ_i boxes in the i^{th} row, $1 \le i \le 2$, and γ_2 is restricted to be 0 or 1. Young diagrams determine a particular symmetry with respect to permutation. Γ is then taken to be the partition $\Gamma = [\gamma_1, \gamma_2]$. In three dimensions the $\Gamma = [\gamma_1]$ ($\gamma_2 = 0$) states are the $L = \gamma_1$, $\pi = (-1)^L$ states and the $\Gamma = [\gamma_1, 1]$ states are the $L = \gamma_1$, $\pi = (-1)^{L+1}$ states. Also $t = \gamma_1 + \gamma_2 = \mu_1 + \mu_2$. For example, the P^o states would have $L = \gamma_1 = 1$ and $\pi = -1$. This would imply that the P^o states would transform under the irreducible representation denoted by $\Gamma = [1]$, (i.e. $\gamma_1 = 1$, $\gamma_2 = 0$.) Similarly, D^o states would be represented by $\Gamma = [2, 1]$.

Now consider the indices in Eq. (2.1) for P^o states. First of all, the set of indices $\{I_t\} = \{i_1, i_2, \ldots, i_t\}$ becomes just one index, i, since $t = 1$ for the P^o states. Thus the wavefunction is a first rank tensor. This index i ranges from 1 to D. The sum over ς is a sum over standard Young tableau of the group of permutations of t objects, S_t. Since $t = 1$, S_1 is just the identity and there is only one standard tableau, thus the sum over ς gives just one term. Finally, the sum over μ_1 and μ_2 results in just two terms since $\mu_1 + \mu_2 = t = 1$ which gives $(\mu_1, \mu_2) = (1, 0)$ or $(0, 1)$. Now we can rewrite the Schwartz expansion as

$$\Psi_i^{\Gamma}(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{W}^{\Gamma}_{1;1,0;i}(\mathbf{r}_1, \mathbf{r}_2) f^{\Gamma}_{1,0}(r_1, r_2, r_{12}) + \mathcal{W}^{\Gamma}_{1;0,1;i}(\mathbf{r}_1, \mathbf{r}_2) f^{\Gamma}_{0,1}(r_1, r_2, r_{12}), \quad (2.2)$$

with $i = 1, 2, \ldots D$.

What is $\mathcal{W}$? In general $\mathcal{W}$ is given by

$$\mathcal{W}^{\Gamma;\varsigma}_{t;\mu_1,\mu_2;\{I_t\}}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\{J_{\mu_1}\},\{J_{\mu_2}\}} {}^{\Gamma\Gamma}_{\varsigma}\bar{D}^{tt\{J_{\mu_1}\},\{J_{\mu_2}\}}_{tt\{I_t\}} M^{\mu_1,\mu_2}_{\{J_{\mu_1}\},\{J_{\mu_2}\}}(\mathbf{r}_1, \mathbf{r}_2). \quad (2.3)$$

$\mathcal{W}_t$ is a rank-t homogeneous polynomial/tensor with each tensor index ranging from 1 to D. Since $t = 1$, $\mathcal{W}_1$ is a column of homogeneous polynomials. M is a tensor with the set of indices $\{J_{\mu_1}\} = j_1, j_2, \ldots, j_{\mu_1}$ and $\{J_{\mu_2}\} = j_1, j_2, \ldots, j_{\mu_2}$ with $1 \le j_i \le D$. Since $\mu_1 + \mu_2 = t$ is the number of indices on M, then M is also a rank-t tensor and, like $\mathcal{W}$, the tensor indices of M range from 1 to D. Again, since $t = 1$, M is a column vector, like $\mathcal{W}$. In other words, when $(\mu_1, \mu_2) = (1, 0)$ we have $\{J_{\mu_1}\} = j_1 \equiv j$ and $\{J_{\mu_2}\} = \emptyset$, similarly, when $(\mu_1, \mu_2) = (0, 1)$ we have $\{J_{\mu_1}\} = \emptyset$ and $\{J_{\mu_2}\} = j_1 \equiv j$. Finally, the operator $\bar{D}$ has t indices given by $\{J_{\mu_1}\}, \{J_{\mu_2}\}$ and another t indices given by $\{I_t\}$ and is thus a rank-$2t$ tensor. $\bar{D}$ is simply a matrix when $t = 1$.

Since the set of indices $\{J_{\mu_1}\}, \{J_{\mu_2}\}$ is really just one index when $t = 1$, the multiple sum in Eq. (2.3) becomes just one sum and $\mathcal{W}_1$ becomes

$$\mathcal{W}^{\Gamma;\varsigma}_{1;\mu_1,\mu_2;i}(\mathbf{r}_1, \mathbf{r}_2) = \sum_j {}^{\Gamma\Gamma}_{\varsigma}\bar{D}^{11\,j}_{11\,i} M^{\mu_1,\mu_2}_j(\mathbf{r}_1, \mathbf{r}_2) \quad (2.4)$$

The operator ${}^{\Gamma\Gamma}_{\rho\kappa}\bar{D}^{11}_{11}$ turns out to be the identity matrix and so we can write ${}^{\Gamma\Gamma}_{\varsigma}\bar{D}^{11\,j}_{11\,i} = \delta_{ij}$ and Eq. (2.4) becomes

$$W^{\Gamma}_{1;\mu_1,\mu_2;j}(\mathbf{r}_1,\mathbf{r}_2) = M^{\mu_1,\mu_2}_{j}(\mathbf{r}_1,\mathbf{r}_2)$$

M is defined as

$$M^{\mu_1,\mu_2}_{\{J_{\mu_1}\},\{J_{\mu_2}\}}(\mathbf{r}_1,\mathbf{r}_2) = T^{\mu_1}_{\{J_{\mu_1}\}}(\mathbf{r}_1)\,T^{\mu_2}_{\{J_{\mu_2}\}}(\mathbf{r}_2)\,.$$

where

$$T^{\mu_i}_{\{J_{\mu_i}\}}(\mathbf{r}_i) = (r_i)_{j_1}(r_i)_{j_2}\cdots(r_i)_{j_{\mu_i}}\,.$$

The $(r_i)_j$ are the Cartesian components of the D-dimensional position vector $\mathbf{r}_i$ of the i^{th} electron. When $\mu_i = 0$, T^0 is the identity. When $\mu_i = 1$, $T^1_j = (r_i)_j$. We can now write

$$W^{\Gamma}_{1;1,0;j}(\mathbf{r}_1,\mathbf{r}_2) = (r_1)_j \qquad \text{and} \qquad W^{\Gamma}_{1;0,1;j}(\mathbf{r}_1,\mathbf{r}_2) = (r_2)_j\,.$$

Substituting into Eq. (2.2) we have

$$\Psi^{\Gamma}_{j}(\mathbf{r}_1,\mathbf{r}_2) = (r_1)_j\ f^{\Gamma}_{1,0}(r_1,r_2,r_{12}) + (r_2)_j\ f^{\Gamma}_{0,1}(r_1,r_2,r_{12})\,.$$

We can write this wavefunction as a column

$$\Psi^{\Gamma}(\mathbf{r}_1,\mathbf{r}_2) = \begin{pmatrix} (r_1)_1 \\ (r_1)_2 \\ \vdots \\ (r_1)_D \end{pmatrix} f^{\Gamma}_{1,0}(r_1,r_2,r_{12}) + \begin{pmatrix} (r_2)_1 \\ (r_2)_2 \\ \vdots \\ (r_2)_D \end{pmatrix} f^{\Gamma}_{0,1}(r_1,r_2,r_{12})\,. \qquad (2.5)$$

or in Cartesian vector notation as

$$\Psi^{\Gamma}(\mathbf{r}_1,\mathbf{r}_2) = \mathbf{r}_1\, f^{\Gamma}_{1,0}(r_1,r_2,r_{12}) \pm \mathbf{r}_2\, f^{\Gamma}_{0,1}(r_1,r_2,r_{12})\,.$$

This last form is identical to that derived by Schwartz in 1961 except for the fact that the vectors $\mathbf{r}_i$ contain D components. Also, we have properly symmetrized the wavefunction with the + sign for the singlet state and the − sign for the triplet state.

If we define $F_1 = f^{\Gamma}_{1,0}(r_1, r_2, r_{12})$, and $F_2 = f^{\Gamma}_{0,1}(r_1, r_2, r_{12})$, the wavefunction can be written as

$$\Psi^{\Gamma}(\mathbf{r}_1, \mathbf{r}_2) = \mathbf{r}_1 F_1 \pm \mathbf{r}_2 F_2 = \hat{\mathbf{r}}_1 r_1 F_1 \pm \hat{\mathbf{r}}_2 r_2 F_2. \tag{2.6}$$

Or, if we define the following column vectors

$$\mathbf{F}^{\Gamma} = \begin{pmatrix} F_1 \\ \pm F_2 \end{pmatrix} \qquad \text{and} \qquad \mathbf{W}^{\Gamma} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \end{pmatrix},$$

we can write the wavefunction as

$$\Psi^{\Gamma} = \left[\mathbf{W}^{\Gamma}\right]^T \mathbf{F}^{\Gamma}. \tag{2.7}$$

This is exactly the same form as Eq. (1.26) for the Schwartz expansion of the P^o wavefunction in three dimensions. Notice that $\mathbf{W}^{\Gamma}$ is a known function of internal coordinates and Euler angles while the function $\mathbf{F}^{\Gamma}$ is a function of the internal coordinates only. Thus our goal of factoring the wavefunction as discussed above has been achieved and we now need to solve for $\mathbf{F}^{\Gamma}$. Even though we have summarized the generalized Schwartz expansion for P^o states, Eq. (2.7) is true for any state of any two electron atom. $\mathbf{W}^{\Gamma}$ will always be a column vector but the number, and the functional form of, the elements will vary. The function $\mathbf{F}^{\Gamma}$ will also be a column vector for all states and will depend only on the internal coordinates.

We now will change notation slightly to make the angular momentum and parity quantum numbers more explicit in our equations. Rather than writing Ψ^{Γ} we will write $\Psi^{L,\pi}$ and wherever else there appeared a Γ we will simply replace it with L, π. Now that we have succeeded in writing the wavefunction as a product of two functions, one of which depends only on the internal coordinates and the other is a known function of the Euler angles and internal coordinates, we proceed to step 2

of the general DPT procedures and derive a differential equation for the unknown functions $\mathbf{F}^{L,\pi}$.

2.2.2 The Schrödinger Equation

The generalized Schwartz expansion of two electron atoms in D dimensions was developed in Refs. [2, 3] and is given by

$$\Psi^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2) = \left[\mathbf{W}^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2)\right]^T \mathbf{F}^{L,\pi}(r_1, r_2, r_{12}) . \tag{2.8}$$

as discussed above, where L is the angular momentum and π is the parity. $\left[\mathbf{W}^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2)\right]^T$ is the transpose of the column vector $\mathbf{W}^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2)$ of basis functions and $\mathbf{F}^{L,\pi}(r_1, r_2, r_{12})$ is the column vector of expansion coefficients. The scalar quantities r_1 and r_2 are the electron-nucleus distances while r_{12} is the inter-electron separation.

In Ref. [4] the wavefunction expansion of Eq. (2.8) is introduced into the Schrödinger equation

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right) \Psi^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2) = E\, \Psi^{L,\pi}(\mathbf{r}_1, \mathbf{r}_2) . \tag{2.9}$$

resulting in a system of coupled differential equations [4]

$$\bar{\mathbf{H}}_{L,\pi} \mathbf{F}^{L,\pi} = E\, \mathbf{F}^{L,\pi}, \tag{2.10}$$

where the matrix differential operator, $\bar{\mathbf{H}}_{L,\pi}$, is

$$\begin{aligned}
&\bar{\mathbf{H}}_{L,\pi}(r_1, r_2, r_{12}) = \\
&\left(-\frac{1}{2}\frac{\partial^2}{\partial r_1^2} - \frac{1}{2}\frac{\partial^2}{\partial r_2^2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{r_{12}^2 + r_1^2 - r_2^2}{2 r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}}\right. \\
&\left. - \frac{r_{12}^2 + r_2^2 - r_1^2}{2 r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} - \frac{Z}{r_1} - \frac{Z}{r_2} - \frac{1}{r_{12}}\right) \mathbf{I}_x \\
&- \frac{(D - 1 + L + \gamma_2)\mathbf{I}_x + \mathbf{L}_x}{2 r_1}\frac{\partial}{\partial r_1}
\end{aligned}$$

$$\begin{array}{c} -\dfrac{(D-1+L+\gamma_2)\mathbf{I}_x+\mathbf{L}_x}{2r_2}\dfrac{\partial}{\partial r_2} \\ -\dfrac{(D-1+L+\gamma_2)\mathbf{I}_x+\mathbf{S}_x}{2r_{12}}\dfrac{\partial}{\partial r_{12}}. \end{array} \tag{2.11}$$

with $x = L - \gamma_2$ and $\gamma_2 = (\frac{1}{2}(\pi + (-1)^{L+1}))^2$ which yields $\gamma_2 = 0$ for states with $\pi = (-1)^L$ and $\gamma_2 = 1$ for states with $\pi = (-1)^{L+1}$[56].

$\mathbf{I}_x$ is a $(x+1) \times (x+1)$ dimensional unit matrix and $\mathbf{L}_x$ and $\mathbf{S}_x$ are $(x+1) \times (x+1)$ dimensional matrices given by

$$\mathbf{L}_x = \begin{pmatrix} x & 0 & 0 & \cdots & 0 & 0 \\ 0 & x-2 & 0 & \cdots & 0 & 0 \\ 0 & 0 & x-4 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & -(x-2) & 0 \\ 0 & 0 & 0 & \cdots & 0 & -x \end{pmatrix} \tag{2.12}$$

and

$$\mathbf{S}_x = \begin{pmatrix} 0 & 1 & 0 & \cdots & 0 & 0 \\ x & 0 & 2 & \cdots & 0 & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & \cdots & 2 & 0 & x \\ 0 & 0 & \cdots & 0 & 1 & 0 \end{pmatrix} \tag{2.13}$$

2.2.3 The Pauli Principle

The system we are modeling consists of two identical fermions. Therefore the complete wavefunction must be totally antisymmetric under interchange of the two electrons. For a singlet state the spatial wavefunction must be symmetric while for the triplet state it must be antisymmetric. It has been shown that this antisymmetry is ensured when the column vector $\mathbf{F}^{L,\pi}$ satisfies the following constraint (see reference [4])

$$\mathbf{F}^{L,\pi}(r_1, r_2, r_{12}) = (-1)^{S+\gamma_2}\mathbf{N}_x\,\mathbf{F}^{L,\pi}(r_2, r_1, r_{12})\,, \tag{2.14}$$

where S is the total spin and the $(x+1) \times (x+1)$ dimensional matrix $\mathbf{N}_x$ is

$$\mathbf{N}_x = \begin{pmatrix} 0 & 0 & \cdots & 0 & 1 \\ 0 & 0 & \cdots & 1 & 0 \\ \vdots & \vdots & \iddots & \vdots & \vdots \\ 0 & 1 & \cdots & 0 & 0 \\ 1 & 0 & \cdots & 0 & 0 \end{pmatrix}. \tag{2.15}$$

2.2.4 Interdimensional Degeneracies

Equations (2.10), (2.11) and (2.14) show the complete spectrum of exact interdimensional degeneracies between the $\pi = (-1)^L$ and $\pi = (-1)^{L+1}$ states. The differential equations are invariant under the replacement

$$\begin{aligned} &L + \gamma_2;\ \pi = (-1)^L;\ (2S+1) = 3, 1;\ D \Leftrightarrow \\ &L + \gamma_2 + 2;\ \pi = (-1)^{L+1};\ (2S+1) = 1, 3;\ D - 2 \end{aligned} \tag{2.16}$$

For instance, the ${}^{3,1}P^o$ states calculated at $D = 5$ give the ${}^{1,3}D^o$ states at $D = 3$. Recall our discussion in Sec. 1.6.5.

2.2.5 The Large Dimension Limit

The goal in this section is to transform the Schrödinger equation to obtain an exact solution in the $D \to \infty$ limit. We begin by regularizing the large Z limit with the transformation $r_i \to r_i/Z$ and $E \to Z^2 E$ and we define $\lambda = 1/Z$.

Next we transform from the variables $\{r_1, r_2, r_{12}\}$ to $\{r_1, r_2, \theta\}$, where θ is the angle subtended by the two electrons at the nucleus. This transformation eliminates the derivative cross-terms in the Hamiltonian, $\bar{\mathbf{H}}_{L,\pi}$.

Finally we rewrite Eq. (2.10) as

$$\tilde{\mathbf{H}}_{L,\pi}(r_1, r_2, \theta)\,\mathbf{\Phi}^{L,\pi}(r_1, r_2, \theta) = E\,\mathbf{\Phi}^{L,\pi}(r_1, r_2, \theta)\,. \tag{2.17}$$

with

$$\tilde{\mathbf{H}}_{L,\pi}(r_1, r_2, \theta) = \tilde{\mathbf{J}}^{\frac{1}{2}}\,\tilde{\mathbf{H}}_{L,\pi}\,\tilde{\mathbf{J}}^{-\frac{1}{2}}. \tag{2.18}$$

$$\mathbf{\Phi}^{L,\pi} = \tilde{\mathbf{J}}^{\frac{1}{2}}\,\mathbf{F}^{L,\pi}. \tag{2.19}$$

$$\begin{aligned}
&\tilde{\mathbf{J}} = r_1^{[(L+\gamma_2)\mathbf{I}_x+\mathbf{L}_x]}\,r_2^{[(L+\gamma_2)\mathbf{I}_x-\mathbf{L}_x]}\,\sin^{(L+\gamma_2)}\theta\,J, \text{ and} \\
&J = r_1^{(D-1)}r_2^{(D-1)}\sin^{(D-2)}\theta,
\end{aligned} \tag{2.20}$$

where J is the Jacobian. The matrix differential operator $\tilde{\mathbf{H}}_{L,\pi}$ becomes

$$\tilde{\mathbf{H}}_{L,\pi}(r_1, r_2, \theta) = \tilde{\mathbf{T}} + \frac{1}{\delta^2}\tilde{\mathbf{U}} + \tilde{V}\mathbf{I}_x + \frac{1}{\delta}\tilde{\mathbf{W}}. \tag{2.21}$$

where $\delta = 1/(D + L + \gamma_2)$.

Every term in Eq. (2.21) is a function of $\{r_1, r_2, \theta\}$. The terms $\tilde{\mathbf{T}}$, $\tilde{\mathbf{U}}$, and $\tilde{V}\mathbf{I}_x$ contain the matrices $\mathbf{I}_x$ and/or $\mathbf{L}_x$ and hence are diagonal matrix operators. The term $\tilde{\mathbf{W}}$ is a tridiagonal matrix operator with zero diagonal. Furthermore, all the terms except $\tilde{V}$ are δ dependent. The terms $\tilde{\mathbf{T}}$ and $\tilde{\mathbf{W}}$ are kinetic terms (i.e. contain derivatives) while $\tilde{V}$ is the Coulomb potential term and $\tilde{\mathbf{U}}$ is an additional "potential" term with factors of $1/r_i^2$. These terms are given by

$$\begin{aligned}
\tilde{\mathbf{T}}(r_1, r_2, \theta) \;=\; &\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2}\right) - G^{+}\frac{\partial^2}{\partial\theta^2}\right]\mathbf{I}_x \\
&-G^{-}\cot\theta\,\frac{\partial}{\partial\theta}\,\mathbf{L}_x,
\end{aligned} \tag{2.22}$$

$$\tilde{\mathbf{U}}(r_1, r_2, \theta) \;=\; \frac{1}{4}\left[\left\{\frac{(1-2\delta)(1-4\delta)}{\sin^2\theta} - \delta^2\right\}\mathbf{I}_x + \delta^2\,\mathbf{L}_x\right]G^{+}$$

$$+\frac{\delta}{2}\frac{1-2\delta}{\sin^2\theta}\,\mathbf{L}_x\,G^-. \tag{2.23}$$

$$\tilde{V}^-(r_1,r_2,\theta) = -\frac{1}{r_1}-\frac{1}{r_2}+\lambda\left[r_1^2+r_2^2-2r_1r_2\cos\theta\right]^{-1/2}. \tag{2.24}$$

$$\tilde{\mathbf{W}} = \frac{\tilde{\mathbf{M}}_x(r_1,r_2)}{r_1r_2\sin\theta}\left(\delta\frac{\partial}{\partial\theta}-\frac{1}{2}\frac{1-2\delta}{\tan\theta}\right). \tag{2.25}$$

where

$$\begin{aligned}\tilde{\mathbf{M}}_x(r_1,r_2) &= \left(\frac{r_1}{r_2}\right)^{\frac{\mathbf{L}_x}{2}}\mathbf{S}_x\left(\frac{r_1}{r_2}\right)^{-\frac{\mathbf{L}_x}{2}} \\ &= \begin{bmatrix} 0 & \frac{r_1}{r_2} & 0 & 0 & \cdots & 0 \\ x\frac{r_2}{r_1} & 0 & 2\frac{r_1}{r_2} & 0 & \cdots & 0 \\ 0 & (x-1)\frac{r_2}{r_1} & 0 & 3\frac{r_1}{r_2} & \cdots & 0 \\ 0 & 0 & (x-2)\frac{r_2}{r_1} & 0 & \ddots & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & x\frac{r_1}{r_2} \\ 0 & 0 & 0 & 0 & \frac{r_2}{r_1} & 0 \end{bmatrix}.\end{aligned} \tag{2.26}$$

and

$$G^- = \frac{1}{2}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right).$$

2.2.6 Lewis Structure

To consider the large dimension limit we scale the coordinates and energy as we did for S-wave

$$\tilde{r}_i = \delta^2 r_i. \qquad \tilde{E} = \frac{E}{\delta^2}. \tag{2.27}$$

and introduce these into Eq. (2.17) to obtain

$$\begin{aligned}&\Big[\delta\left\{\delta\tilde{\mathbf{T}}(\tilde{r}_1,\tilde{r}_2,\theta)+\tilde{\mathbf{W}}(\tilde{r}_1,\tilde{r}_2,\theta)\right\} \\ &+\tilde{\mathbf{U}}(\tilde{r}_1,\tilde{r}_2,\theta)+\tilde{V}^-(\tilde{r}_1,\tilde{r}_2,\theta)\,\mathbf{I}_x\Big]\,\mathbf{\Phi}^{L,\pi} = \tilde{E}\mathbf{\Phi}^{L,\pi}.\end{aligned} \tag{2.28}$$

Notice that as $\delta \to 0$ ($D \to \infty$) the derivative terms disappear and so the electrons are stationary at the minimum of the effective potential given by $\mathbf{V}_{\text{eff}}(\tilde{r}_1, \tilde{r}_2, \theta) = \tilde{\mathbf{U}}_0(\tilde{r}_1, \tilde{r}_2, \theta) + \tilde{V}(\tilde{r}_1, \tilde{r}_2, \theta)\mathbf{I}_x$ where $\tilde{\mathbf{U}}_0(\tilde{r}_1, \tilde{r}_2, \theta)$, a multiple of the unit matrix, is the $\delta \to 0$ limit of $\tilde{\mathbf{U}}(\tilde{r}_1, \tilde{r}_2, \theta)$. Explicitly, the $D \to \infty$ potential is given by

$$\mathbf{V}_{\text{eff}}(\tilde{r}_1, \tilde{r}_2, \theta) = \left[\frac{1}{4}\frac{1}{\sin^2\theta}G^+ - \frac{1}{\tilde{r}_1} - \frac{1}{\tilde{r}_2} + \lambda\left[\tilde{r}_1^2 + \tilde{r}_2^2 - 2\tilde{r}_1\tilde{r}_2\cos\theta\right]^{-1/2}\right]\mathbf{I}_x.$$

We again choose to expand about a symmetric minimum where $\tilde{r}_1 = \tilde{r}_2 = r_m$, and $\theta = \theta_m$. This "frozen" structure is again called the *Lewis structure*. Notice that this Lewis structure is independent of angular momentum, since the large D potential only contains the matrix $\mathbf{I}_x$ and not the matrices $\mathbf{L}_x$ or $\mathbf{S}_x$ whose elements change as angular momentum is changed. This is also evident since $\mathbf{V}_{\text{eff}}(\tilde{r}_1, \tilde{r}_2, \theta)$ is exactly the same as S-wave large D effective potential multiplied by the unit matrix $\mathbf{I}_x$. Hence, the values of r_m and θ_m are given by the same equations as in the S-wave case

$$c_m = \cos\theta_m = -2\bar{\lambda}\left[\left(1 + \bar{\lambda}^2\right)^{\frac{1}{2}} + \bar{\lambda}\right] \tag{2.29}$$

and

$$r_m = \frac{1}{4}(1 + c_m)^{-2}, \text{ where } \bar{\lambda} = \frac{\sqrt{2}\lambda}{16}. \tag{2.30}$$

while ε_∞ is again given by

$$\varepsilon_\infty = -4\frac{(1 + c_m)^3}{(1 - c_m)} = -\frac{1}{4r_m^2 s_m^2}. \tag{2.31}$$

Again note that the results of the large D limit, equations (2.29) through (2.31) hold for any value of the total orbital angular momentum. Furthermore, the term $\tilde{V}$, containing all of the electron correlation, has no overall factor of δ and hence has a contribution at zeroth order. In other words, electron correlation effects are included at the lowest order of DPT unlike other perturbation methods which include electron correlation only at higher orders.

2.2.7 The Langmuir Vibrations

The next step in developing a perturbation expansion of the Schrödinger equation is to allow for small oscillations, called Langmuir vibrations, about the Lewis structure positions. To investigate these oscillations and obtain a zeroth order solution to the wavefunction we introduce the dimensionally scaled displacement coordinates x_1, x_2 and y through the transformations given by Eq. (1.27). When the displacement coordinates are substituted into the Hamiltonian we find that $\tilde{\mathbf{U}}$ and $\tilde{V}$ remain unchanged, except that $\tilde{r}_i$ and θ are functions of x_i, y, and δ, but $\tilde{\mathbf{T}}$ and $\tilde{\mathbf{W}}$ change slightly due to the presence of derivative terms. The Hamiltonian becomes

$$\tilde{\mathbf{H}} = \delta^2\tilde{\mathbf{T}}(x_1, x_2, y) + \delta\,\tilde{\mathbf{W}}(x_1, x_2, y) + \tilde{\mathbf{U}}(x_1, x_2, y) + \tilde{V}(x_1, x_2, y)\,\mathbf{I}_x,$$

where

$$\begin{aligned}\delta^2\tilde{\mathbf{T}}(x_1, x_2, y) &= \delta\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - G^+\frac{r_m^2}{2}\frac{\partial^2}{\partial y^2}\right]\mathbf{I}_x \\ &\quad -\delta^{3/2}G^-\cot\theta\,\frac{r_m}{\sqrt{2}}\frac{\partial}{\partial y}\,\mathbf{L}_x,\end{aligned}$$

and

$$\delta\,\tilde{\mathbf{W}}(x_1, x_2, y) = \frac{\tilde{\mathbf{M}}_x(\tilde{r}_1, \tilde{r}_2)}{\tilde{r}_1\tilde{r}_2\sin\theta}\left(\delta^{3/2}\frac{r_m}{\sqrt{2}}\frac{\partial}{\partial y} - \frac{\delta}{2}\frac{1-2\delta}{\tan\theta}\right).$$

Now since $\tilde{r}_i$, and θ are functions of displacement coordinates and δ we can expand the Hamiltonian and wavefunction, $\mathbf{\Phi}^{L,\pi}(\tilde{r}_1, \tilde{r}_2, \theta)$, in powers of $\delta^{\frac{1}{2}}$ while $\tilde{E}$ is expressed as a power series in δ as we did in the S-wave case, see Eqs. (1.30) and (1.29). The coefficients of $\delta^{1/2}$ in these expansions are no longer simply functions of the displacement coordinates but are matrices, in the case of the Hamiltonian, or column vectors, in the case of the wavefunction. These expansions are then substituted into Eq. (2.28) and by equating coefficients of $\delta^{1/2}$ we obtain a set of equations for ε_i and $\mathbf{\Phi}_i^{L,\pi}$.

The coefficients of δ^0 give the large D energy ε_∞ as derived above but we get no information about $\mathbf{\Phi}_0$. The coefficient of $\delta^{1/2}$ in the Hamiltonian is zero since this

coefficient is the first derivative of the effective potential with respect to $\delta^{1/2}$ evaluated at $\delta^{1/2} = 0$ which is at the minimum of the potential. Finally, the coefficient of δ, i.e. second order in $\delta^{1/2}$, gives us a coupled differential equation for ε_0 and $\mathbf{\Phi}_0$. Specifically

$$\begin{aligned} \tilde{\mathbf{H}}_2(x_1, x_2, y)\, \mathbf{\Phi}_0^{L,\pi}(x_1, x_2, y) &= \Big[\tilde{\mathbf{T}}_2(x_1, x_2, y) + \tilde{\mathbf{U}}_2(x_1, x_2, y) + \tilde{\Gamma}_2(x_1, x_2, y)\, \mathbf{I}_x \\ + \tilde{\mathbf{W}}_2(x_1, x_2, y)\Big]\ \mathbf{\Phi}_0^{L,\pi}(x_1, x_2, y) &= \varepsilon_0\ \mathbf{\Phi}_0^{L,\pi}(x_1, x_2, y)\,. \end{aligned} \tag{2.32}$$

where $\tilde{\mathbf{T}}_2$, $\tilde{\mathbf{U}}_2$ and $\tilde{\Gamma}_2\mathbf{I}_x$ are diagonal (they are simply scalar functions of $\{x_1, x_2, y\}$ multiplied by the unit matrix $\mathbf{I}_x$) and $\tilde{\mathbf{W}}_2$ multiplies the non-diagonal matrix $\mathbf{S}_x$ and is independent of the displacement coordinates. The term $\tilde{\mathbf{W}}_2$ thus serves to couple the $(x+1)$ differential equations in Eq. (2.32).

Equation (2.32) is invariant under the substitution $x_1 \leftrightarrow x_2$ so if we transform to symmetry coordinates using Eq. (1.28) the variable q_1 separates from the other variables and we are left with x and y still coupled. The δ order Schrödinger equation becomes

$$\tilde{\mathbf{H}}_2(q_1, x, y)\, \mathbf{\Phi}_0^{L,\pi}(q_1, x, y) = \varepsilon_0 \mathbf{\Phi}_0^{L,\pi}(q_1, x, y)\,. \tag{2.33}$$

where

$$\begin{aligned} \tilde{\mathbf{H}}_2(q_1, x, y) = \Bigg[-\frac{1}{2}\left(\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + u\,x^2 + v\,xy + w\,y^2 \\ + \frac{1}{2}\omega_1^2 q_1^2 - \frac{3}{2r_m^2 s_m^2}\Bigg]\mathbf{I}_x - \frac{\mathbf{S}_x}{2r_m^2 s_m t_m}. \end{aligned} \tag{2.34}$$

and u, v, w and ω_1^2 are the same functions given by Eqs. (1.35) and (1.38).

We can then separate x and y by transforming to normal coordinates using the transformation of Eq. (1.41) where χ is again given by Eq. (1.42). χ is approximately 90 degrees so from Eqs. (1.27), (1.28) and (1.41) we see that q_1 corresponds

to the antisymmetric stretch mode while q_2, and q_3 correspond approximately to the symmetric stretch and bending vibration modes respectively.

At this point the full Hamiltonian is given by

$$\tilde{\mathbf{H}} = \delta^2\tilde{\mathbf{T}} + \delta\,\tilde{\mathbf{W}} + \tilde{\mathbf{U}} + \tilde{\Gamma}\mathbf{I}_x$$

where

$$\begin{aligned}\delta^2\tilde{\mathbf{T}} &= \delta\left[-\frac{1}{2}\left(\cos^2\chi\frac{\partial^2}{\partial q_3^2} - 2\sin\chi\cos\chi\frac{\partial^2}{\partial q_2\partial q_3} + \sin^2\chi\frac{\partial^2}{\partial q_2^2} + \frac{\partial^2}{\partial q_1^2}\right)\right. \\ &\quad \left. -G^+(q_1,q_2,q_3)\,\frac{r_m^2}{2}\left(\cos^2\chi\frac{\partial^2}{\partial q_2^2} + 2\sin\chi\cos\chi\frac{\partial^2}{\partial q_2\partial q_3} + \sin^2\chi\frac{\partial^2}{\partial q_3^2}\right)\right]\mathbf{I}_x \\ &\quad -\delta^{3/2}G^-(q_1,q_2,q_3)\cot\theta\frac{r_m}{\sqrt{2}}\left(\sin\chi\frac{\partial}{\partial q_3} + \cos\chi\frac{\partial}{\partial q_2}\right)\mathbf{L}_x. \qquad (2.35)\end{aligned}$$

$$\delta\tilde{\mathbf{W}} = \frac{\tilde{\mathbf{M}}_x(\tilde{r}_1,\tilde{r}_2)}{\tilde{r}_1\tilde{r}_2\sin\theta}\left(\delta^{3/2}\frac{r_m}{\sqrt{2}}\left(\sin\chi\frac{\partial}{\partial q_3} + \cos\chi\frac{\partial}{\partial q_2}\right) - \frac{\delta}{2}\frac{1-2\delta}{\tan\theta}\right). \qquad (2.36)$$

$$\begin{aligned}\tilde{\mathbf{U}} &= \frac{1}{4}\left[\left(\frac{(1-2\delta)(1-4\delta)}{\sin^2\theta} - \delta^2\right)\mathbf{I}_x + \delta^2\mathbf{L}_x^2\right]G^+(q_1,q_2,q_3) \\ &\quad +\frac{\delta}{2}\frac{1-2\delta}{\sin^2\theta}G^-(q_1,q_2,q_3)\,\mathbf{L}_x. \qquad (2.37)\end{aligned}$$

and

$$\tilde{\Gamma} = -\frac{1}{\tilde{r}_1} - \frac{1}{\tilde{r}_2} + \lambda\left[\tilde{r}_1^2 + \tilde{r}_2^2 - 2\tilde{r}_1\tilde{r}_2\cos\theta\right]^{-1/2}. \qquad (2.38)$$

where $\tilde{r}_1$ and $\tilde{r}_2$ are given by Eq. (1.48). With the matrix $\tilde{\mathbf{M}}_x$ given by Eq. (2.26), we can write the term $\delta\tilde{\mathbf{W}}$ as a matrix by defining

$$A = \frac{\mathbf{1}}{\tilde{r}_2^2\sin\theta}\left(\delta^{3/2}\frac{r_m}{\sqrt{2}}\left(\sin\chi\frac{\partial}{\partial q_3} + \cos\chi\frac{\partial}{\partial q_2}\right) - \frac{\delta}{2}\frac{1-2\delta}{\tan\theta}\right). \qquad (2.39)$$

and

$$B = \frac{\mathbf{1}}{\tilde{r}_1^2\sin\theta}\left(\delta^{3/2}\frac{r_m}{\sqrt{2}}\left(\sin\chi\frac{\partial}{\partial q_3} + \cos\chi\frac{\partial}{\partial q_2}\right) - \frac{\delta}{2}\frac{1-2\delta}{\tan\theta}\right). \qquad (2.40)$$

and absorbing these terms into the matrix $\tilde{\mathbf{M}}_x$. We have

$$\delta\tilde{\mathbf{W}}_x = \begin{bmatrix} 0 & A & 0 & 0 & \cdots & 0 \\ xB & 0 & 2A & 0 & \cdots & 0 \\ 0 & (x-1)B & 0 & 3A & \cdots & 0 \\ 0 & 0 & (x-2)B & 0 & \ddots & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & xA \\ 0 & 0 & 0 & 0 & B & 0 \end{bmatrix}. \tag{2.41}$$

This term is the only non-diagonal term in the Hamiltonian, coming in at order δ, and it thus serves to couple the $x+1$ differential equations. At δ order $A = B = -1/(2r_m^2 s_m t_m)$ and the δ order Hamiltonian (also known as the harmonic order Hamiltonian) becomes

$$\tilde{\mathbf{H}}_2(q_1, q_2, q_3) = \left[-\frac{1}{2}\left(\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2} + \frac{\partial^2}{\partial q_3^2} \right) + \frac{1}{2}\omega_1^2 q_1^2 + \frac{1}{2}\omega_2^2 q_2^2 + \frac{1}{2}\omega_3^2 q_3^2 - \frac{3}{2r_m^2 s_m^2} \right] \mathbf{I}_x - \frac{\mathbf{S}_x}{2r_m^2 s_m t_m}. \tag{2.42}$$

Notice that the terms in square brackets are identical to the S-wave harmonic order terms. The harmonic order Schrödinger equation is still a set of $x+1$ coupled differential equations, coupled by the matrix $\mathbf{S}_x$. This matrix can be diagonalized by a equivalence transformation which takes $\mathbf{S}_x \rightarrow \mathbf{L}_x$.

$$\mathbf{L}_x = \mathbf{Q}_x \mathbf{R}_x \mathbf{S}_x \left[\mathbf{Q}_x \mathbf{R}_x\right]^{-1}.$$

This transformation works as follows. The transformation $\bar{\mathbf{S}}_x = \mathbf{R}_x \mathbf{S}_x \mathbf{R}_x^{-1}$, where

$$\mathbf{R}_x = \begin{pmatrix} \sqrt{1} & 0 & 0 & 0 & \cdots & 0 & 0 \\ 0 & \sqrt{\frac{1}{x}} & 0 & 0 & \cdots & 0 & 0 \\ 0 & 0 & \sqrt{\frac{1\times 2}{x(x-1)}} & 0 & \cdots & 0 & 0 \\ 0 & 0 & 0 & \sqrt{\frac{1\times 2\times 3}{x(x-1)(x-2)}} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & 0 & \cdots & \sqrt{\frac{1}{x}} & 0 \\ 0 & 0 & 0 & 0 & \cdots & 0 & \sqrt{1} \end{pmatrix}.$$

changes $\mathbf{S}_x$ to the symmetric matrix

$$\bar{\mathbf{S}}_x = \begin{pmatrix} 0 & \sqrt{x} & 0 & \cdots & \cdots & \cdots & 0 & 0 & 0 \\ \sqrt{x} & 0 & \sqrt{2(x-1)} & \cdots & \cdots & \cdots & 0 & 0 & 0 \\ 0 & \sqrt{2(x-1)} & 0 & \ddots & \cdots & \cdots & 0 & 0 & 0 \\ 0 & 0 & \sqrt{3(x-2)} & \ddots & \ddots & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & \ddots & \ddots & \sqrt{(x-2)3} & 0 & 0 \\ 0 & 0 & 0 & \cdots & \cdots & \ddots & 0 & \sqrt{(x-1)2} & 0 \\ 0 & 0 & 0 & \cdots & \cdots & \cdots & \sqrt{(x-1)2} & 0 & \sqrt{x} \\ 0 & 0 & 0 & \cdots & \cdots & \cdots & 0 & \sqrt{x} & 0 \end{pmatrix}$$

Now if we consider the example of $x = 1$ (corresponding to P^o states) we find

$$\mathbf{L}_1 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{and} \quad \bar{\mathbf{S}}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

and it is clear that $\frac{1}{2}\mathbf{L}_1$ and $\frac{1}{2}\bar{\mathbf{S}}_1$ are the $J = 1/2$ angular momentum matrix representations for J_z and J_x respectively. In general, $\frac{1}{2}\mathbf{L}_x$ and $\frac{1}{2}\bar{\mathbf{S}}_x$ are matrix representations of J_z and J_x, respectively, with $J = x/2$. To transform $\bar{\mathbf{S}}_x$ to $\mathbf{L}_x$ we simply operate with the appropriate real orthogonal rotation matrix that would take J_x to J_z. This would be a clockwise rotation of $\pi/2$ about the y-axis. This transformation would

also take $\mathbf{L}_x \rightarrow -\bar{\mathbf{S}}_x$. The appropriate rotation matrix is the inverse of the Wigner rotation matrix, $\mathbf{d}^J(\theta)$, for rotations about the y-axis. Thus we have

$$\mathbf{Q}_x = \left[\mathbf{d}^{x/2}\left(\frac{\pi}{2}\right)\right]^\dagger .$$

When we apply the transformation

$$\mathbf{H}' = \mathbf{Q}_x\mathbf{R}_x\tilde{\mathbf{H}}\left[\mathbf{Q}_x\mathbf{R}_x\right]^{-1} . \tag{2.43}$$

to the Hamiltonian we simply change Eqs. (2.35) and (2.37) by letting $\mathbf{L}_x \rightarrow -\bar{\mathbf{S}}_x$, while the term $\delta\bar{\mathbf{W}}_x$ becomes $\delta\mathbf{W}'_x = \mathbf{Q}_x\mathbf{R}_x\delta\bar{\mathbf{W}}_x\left[\mathbf{Q}_x\mathbf{R}_x\right]^{-1}$. Explicitly,

$$\delta\mathbf{W}'_x = \begin{bmatrix} \frac{x}{2}(A+B) & \frac{\sqrt{x}}{2}(A-B) & 0 & 0 & \\ -\frac{\sqrt{x}}{2}(A-B) & \left(\frac{x}{2}-1\right)(A+B) & \frac{\sqrt{2(x-1)}}{2}(A-B) & 0 & \\ 0 & -\frac{\sqrt{2(x-1)}}{2}(A-B) & \left(\frac{x}{2}-2\right)(A+B) & \ddots & \\ 0 & 0 & \ddots & \ddots & \frac{\sqrt{x}}{2}(A-B) \\ & & & -\frac{\sqrt{x}}{2}(A-B) & -\frac{x}{2}(A+B) \end{bmatrix} . \tag{2.44}$$

The wavefunction $\mathbf{\Phi}_{L,\pi}$ is transformed as

$$\mathbf{G}_{L,\pi} = \mathbf{Q}_x\mathbf{R}_x\mathbf{\Phi}_{L,\pi} .$$

Finally, for the δ order Schrödinger equation we have

$$\mathbf{H}'_2\mathbf{G}_0^{L,\pi} = \varepsilon_0\mathbf{G}_0^{L,\pi} . \tag{2.45}$$

$$\begin{aligned} \mathbf{H}'_2 \;=\; & \left[-\frac{1}{2}\left(\frac{\partial^2}{\partial q_1^2} - \frac{\partial^2}{\partial q_2^2} - \frac{\partial^2}{\partial q_3^2}\right) + \frac{1}{2}\omega_1^2 q_1^2 + \frac{1}{2}\omega_2^2 q_2^2 + \frac{1}{2}\omega_3^2 q_3^2 \right. \\ & \left. - \frac{3}{2r_m^2 s_m^2}\right]\mathbf{I}_x - \frac{\mathbf{L}_x}{2r_m^2 s_m t_m} , \end{aligned} \tag{2.46}$$

where

$$\mathbf{G}_0^{L,\pi}(q_1,q_2,q_3) = \mathbf{Q}_x\mathbf{R}_x\mathbf{\Phi}_0^{L,\pi}(q_1,q_2,q_3)\,. \tag{2.47}$$

Equation (2.45) consists of $x+1$ uncoupled and separable simple harmonic oscillator differential equations, one for each of the $x+1$ components $[\mathbf{G}_0^{L,\pi}(q_1,q_2,q_3)]_\alpha$ of the vector $\mathbf{G}_0^{L,\pi}(q_1,q_2,q_3)$. Thus, all components, $[\mathbf{G}_0]_\alpha$, of the zeroth order wavefunction are identical and equal to a product of three Hermite polynomials as in the S-wave case. The only difference is that their energy depends on the index α because of the diagonal matrix $\mathbf{L}_x$ in last term in the harmonic order Hamiltonian, Eq. (2.46). Thus, by diagonalizing the harmonic order Hamiltonian we have made the zeroth order energy multivalued. We simply pick one of these energies as our zeroth order energy by picking a value for α, say $\alpha=\gamma$, where $\gamma = 1,2,\ldots,x+1$. The zeroth order wavefunction then consists not of $x+1$ identical components but rather a single non-zero component, the γ^{th} component, with all other components equal to zero. By choosing a specific component of the zeroth order wavefunction to start with we are in effect choosing a fourth quantum number, n_4. Choosing a different component of the zeroth order wavefunction gives us the zeroth order energy for a different state. For example, as will be discussed later, choosing $n_a=0$, $n_s=0$, $n_\theta=0$, and $\gamma=1$, denoted by the ket $|0001\rangle$, we will calculate the energy series for the $1s2p\ ^1P^o$ state, while choosing $\gamma=2$ will give us the $1s2p\ ^3P^o$ state.

The zeroth order wavefunction is now given by

$$[\mathbf{G}_0]_\alpha = \begin{cases} \omega_1^{1/4}h_{n_a}\left(\omega_1^{1/2}q_1\right)\omega_2^{1/4}h_{n_s}\left(\omega_2^{1/2}q_2\right)\omega_3^{1/4}h_{n_\theta}\left(\omega_3^{1/2}q_3\right) & \alpha=\gamma \\ 0 & \alpha\neq\gamma \end{cases} \qquad \alpha = 1,2,\ldots,x+1. \tag{2.48}$$

and the zeroth order energy is

$$\varepsilon_0 = \left(n_a+\frac{1}{2}\right)\omega_1 + \left(n_s+\frac{1}{2}\right)\omega_2 + \left(n_\theta+\frac{1}{2}\right)\omega_3 + \left(n_4+\frac{1}{2}\right)\omega_4 - \frac{3}{2r_m^2s_m^2}. \tag{2.49}$$

where

$$\omega_4 = -\frac{1}{r_m^2 s_m t_m}, \qquad \text{and} \qquad n_4 = \frac{L+1-\gamma_2-2\gamma}{2}, \tag{2.50}$$

and α and γ range from 1 to $x+1$. Or we can write

$$\begin{aligned} &1 \leq \gamma \leq L+1 \text{ for the } \pi = (-1)^L \text{ states and} \\ &1 \leq \gamma \leq L \text{ for the } \pi = (-1)^{L+1} \text{ states.} \end{aligned} \tag{2.51}$$

The scaled energy $\tilde{E}$ to first order is given by

$$\begin{aligned} \tilde{E} &= -\frac{1}{4r_m^2 s_m^2} + \delta\left[-\frac{3}{2r_m^2 s_m^2} + \omega_1\left(n_a + \frac{1}{2}\right) + \omega_2\left(n_s + \frac{1}{2}\right)\right. \\ &\left. + \omega_3\left(n_\theta + \frac{1}{2}\right) + \omega_4\left(n_4 + \frac{1}{2}\right)\right]. \end{aligned} \tag{2.52}$$

Also n_a, n_s and n_θ are the number of quanta in the antisymmetric stretch, symmetric stretch and bending vibration modes respectively. Finally, in order to satisfy the Pauli principle, the total spin S must satisfy [5]

$$\begin{aligned} &S = 1 \text{ when } n_a + \gamma_2 + \gamma - 1 \text{ is odd and} \\ &S = 0 \text{ when } n_a + \gamma_2 + \gamma - 1 \text{ is even.} \end{aligned} \tag{2.53}$$

2.3 The Full Schrödinger Equation and Its Solution

Up to this point we have found the zeroth order wavefunction and the zeroth and first order (harmonic order) energies. We have also defined four quantum numbers in the large D limit which we can choose according to which state we would like to calculate in 3 dimensions. For example we would like to find the energies and wavefunctions for the $1s2p\ ^1P^o$ and $1s2p\ ^3P^o$ states. We know that these are the lowest lying states with P^o symmetry so we choose the smallest possible values for $\{n_a, n_s, n_\theta\}$ which would be $\{0,0,0\}$. Also we know that for P^o we have $L=1$, and

$\pi = -1$ thus $\gamma_2 = 0$ and $x = 1$. Thus the wavefunction $\mathbf{G}^{L,\pi}$ will be a column vector with two elements so that γ will take the values $\gamma = 1$ and $\gamma = 2$ (see Eq. (2.51)). Finally, from Eq. (2.53), we have that $\gamma = 2$ for the $1s2p\ ^3P^o$ state and $\gamma = 1$ for the $1s2p\ ^1P^o$ state. Selecting one of these states forces us to set all elements of the column vector $\mathbf{G}_0^{L,\pi}$ to zero except the γ^{th} element which becomes a product of three harmonic oscillator functions with quantum numbers n_a, n_s and n_θ . To obtain higher order corrections to the energy and wavefunction we need to consider the expansion of the full Hamiltonian.

After the equivalence transformation of Eq. (2.43) the full Schrödinger equation becomes

$$\mathbf{H}'_{L,\pi}(q_1, q_2, q_3)\,\mathbf{G}^{L,\pi}(q_1, q_2, q_3) = \tilde{E}\,\mathbf{G}^{L,\pi}(q_1, q_2, q_3) \tag{2.54}$$

where

$$\mathbf{H}'_{L,\pi} = \delta^2\mathbf{T}' + \delta\,\mathbf{W}'_x + \mathbf{U}' + V''\mathbf{I}_x$$

and

$$\begin{aligned}
\delta^2\mathbf{T}' &= \delta\left[-\frac{1}{2}\left(\cos^2\chi\frac{\partial^2}{\partial q_3^2} - 2\sin\chi\cos\chi\frac{\partial^2}{\partial q_2\partial q_3} + \sin^2\chi\frac{\partial^2}{\partial q_2^2} + \frac{\partial^2}{\partial q_1^2}\right)\right. \\
&\quad \left. -G^+(q_1, q_2, q_3)\,\frac{r_m^2}{2}\left(\cos^2\chi\frac{\partial^2}{\partial q_2^2} + 2\sin\chi\cos\chi\frac{\partial^2}{\partial q_2\partial q_3} + \sin^2\chi\frac{\partial^2}{\partial q_3^2}\right)\right]\mathbf{I}_x \\
&\quad +\delta^{3/2}G^-(q_1, q_2, q_3)\cot\theta\frac{r_m}{\sqrt{2}}\left(\sin\chi\frac{\partial}{\partial q_3} + \cos\chi\frac{\partial}{\partial q_2}\right)\bar{\mathbf{S}}_x.
\end{aligned} \tag{2.55}$$

$$\begin{aligned}
\mathbf{U}' &= \frac{1}{4}\left[\left(\frac{(1-2\delta)(1-4\delta)}{\sin^2\theta} - \delta^2\right)\mathbf{I}_x + \delta^2\bar{\mathbf{S}}_x^2\right]G^+(q_1, q_2, q_3) \\
&\quad -\frac{\delta}{2}\frac{1-2\delta}{\sin^2\theta}G^-(q_1, q_2, q_3)\,\bar{\mathbf{S}}_x.
\end{aligned} \tag{2.56}$$

The terms $\delta\,\mathbf{W}'_x$ and V'' are given by Eqs. (2.44) and (2.38) respectively.

The Hamiltonian, wavefunction and energy are expanded in powers of $\delta^{1/2}$ as before

$$\mathbf{H}'_{L,\pi} = \sum_{j=0}^{\infty}\delta^{\frac{j}{2}}\mathbf{H}'_j, \qquad \mathbf{G}^{L,\pi} = \sum_{p=0}^{\infty}\delta^{\frac{p}{2}}\mathbf{G}_p^{L,\pi}. \tag{2.57}$$

and

$$\tilde{E} = V_{\rm eff}(r_m, r_m, \theta_m) + \delta \sum_{j=0}^{\infty} \delta^j \varepsilon_{2j}. \tag{2.58}$$

When we expand the Hamiltonian we collect all terms that multiply the same power of q_1, q_2, q_3, as well as $\delta^{1/2}$. There are also other terms that multiply derivatives of the $q's$ as well as powers of the $q's$. These terms are collected separately. The final expanded Hamiltonian is given by

$$\begin{aligned}
\mathbf{H}'_{L.\pi} \;=\; & \left[-\frac{\delta}{2}\left(\frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_2^2} + \frac{\partial^2}{\partial q_3^2}\right)\right. \\
& + \sum_{j=3}^{\infty} \delta^{j/2} \sum_{k=0}^{(j-2)/2} \sum_{l=0}^{j-2-2k} T1(j,k,l)\, q_1^{2k}\, q_2^{l}\, q_3^{j-2-2k-l} \\
& \left. \times \left(\cos^2\chi \frac{\partial^2}{\partial q_2^2} + 2\sin\chi\cos\chi \frac{\partial^2}{\partial q_2 \partial q_3} + \sin^2\chi \frac{\partial^2}{\partial q_3^2}\right)\right] \mathbf{I}_x \\
& + \sum_{j=4}^{\infty} \delta^{j/2} \sum_{k=0}^{(j-4)/2} \sum_{l=0}^{j-4-2k} T2(j,k,l)\, q_1^{2k+1}\, q_2^{l}\, q_3^{j-4-2k-l} \\
& \times \left(\sin\chi \frac{\partial}{\partial q_3} + \cos\chi \frac{\partial}{\partial q_2}\right) \bar{\mathbf{S}}_x \\
& + \left[\sum_{j=0}^{\infty} \delta^{j/2} \sum_{k=0}^{j/2} \sum_{l=0}^{j-2k} U1(j,k,l)\, q_1^{2k}\, q_2^{l}\, q_3^{j-2k-l} \right. \\
& + \sum_{j=2}^{\infty} \delta^{j/2} \sum_{k=0}^{(j-2)/2} \sum_{l=0}^{j-2-2k} U2(j,k,l)\, q_1^{2k}\, q_2^{l}\, q_3^{j-2-2k-l} \\
& \left. + \sum_{j=4}^{\infty} \delta^{j/2} \sum_{k=0}^{(j-4)/2} \sum_{l=0}^{j-4-2k} U3(j,k,l)\, q_1^{2k}\, q_2^{l}\, q_3^{j-4-2k-l} \right] \mathbf{I}_x \\
& + \left[\sum_{j=3}^{\infty} \delta^{j/2} \sum_{k=0}^{(j-3)/2} \sum_{l=0}^{j-3-2k} U4(j,k,l)\, q_1^{2k+1}\, q_2^{l}\, q_3^{j-3-2k-l} \right. \\
& \left. + \sum_{j=5}^{\infty} \delta^{j/2} \sum_{k=0}^{(j-5)/2} \sum_{l=0}^{j-5-2k} U5(j,k,l)\, q_1^{2k+1}\, q_2^{l}\, q_3^{j-5-2k-l} \right] \bar{\mathbf{S}}_x \\
& + \left[\sum_{j=4}^{\infty} \delta^{j/2} \sum_{k=0}^{(j-4)/2} \sum_{l=0}^{j-4-2k} U6(j,k,l)\, q_1^{2k}\, q_2^{l}\, q_3^{j-4-2k-l} \right] \bar{\mathbf{S}}_x^2 \\
& + \delta\, \mathbf{W}'_x.
\end{aligned} \tag{2.59}$$

The term $\delta \mathbf{W}'_x$ is still given by Eq. (2.44) but now A and B become

$$\begin{aligned} A &= \sum_{j=2}^{\infty} \delta^{j/2} \sum_{k=0}^{j-2} \sum_{l=0}^{j-2-k} A1(j,k,l)\; q_1^k\; q_2^l\; q_3^{j-2-k-l} \\ &+ \sum_{j=3}^{\infty} \delta^{j/2} \sum_{k=0}^{j-3} \sum_{l=0}^{j-3-k} A2(j,k,l)\; q_1^k\; q_2^l\; q_3^{j-3-k-l} \left(\sin\chi \frac{\partial}{\partial q_3} + \cos\chi \frac{\partial}{\partial q_2} \right) \\ &+ \sum_{j=4}^{\infty} \delta^{j/2} \sum_{k=0}^{j-4} \sum_{l=0}^{j-4-k} A3(j,k,l)\; q_1^k\; q_2^l\; q_3^{j-4-k-l}, \end{aligned}$$

with B equaling the same expansion with the exception that the coefficients $Bi(j,k,l) = (-1)^k Ai(j,k,l)$.[57]

These expansions of the Hamiltonian, wavefunction and scaled energy are then substituted into the Schrödinger equation. We obtain equations that look exactly like the S-wave case except that the Hamiltonian and wavefunction coefficients are matrices or column vectors respectively. Substitution into Eq. (2.54) gives

$$\sum_{j=0}^{\infty} \mathbf{H}'_j \delta^{j/2} \sum_{p=0}^{\infty} \mathbf{G}_p \delta^{p/2} = \sum_{p=0}^{\infty} \mathbf{G}_p \delta^{p/2} \left(V_{\rm eff}(r_m, r_m, \theta_m) + \delta \sum_{j=0}^{\infty} \varepsilon_{2j} \delta^j \right). \qquad (2.60)$$

As before, the δ^o term gives $\mathbf{H}'_0 \mathbf{\Phi}_0 = V_{\rm eff}(r_m, r_m, \theta_m)\mathbf{\Phi}_0$ which simply says that $\mathbf{H}'_0 = V_{\rm eff}(r_m, r_m, \theta_m)\mathbf{I}_x$. Thus, $\mathbf{H}'_0$ is a diagonal matrix with each diagonal element being equal to $V_{\rm eff}(r_m, r_m, \theta_m)$, the energy as $D \to \infty$. The $\delta^{1/2}$ term gives $(\mathbf{H}'_0\mathbf{\Phi}_1 + \mathbf{H}'_1\mathbf{\Phi}_0) = V_{\rm eff}(r_m, r_m, \theta_m)\mathbf{\Phi}_1$, but $\mathbf{H}'_1$ contains only effective potential terms and is the derivative of the effective potential evaluated at its minimum. Thus, $\mathbf{H}'_1 = \mathbf{0}$, and we are left with $\mathbf{H}'_0\mathbf{\Phi}_1 = V_{\rm eff}(r_m, r_m, \theta_m)\mathbf{\Phi}_1$ which gives us no new information. Eq. (2.60) can now be written as

$$\sum_{j=2}^{\infty} \mathbf{H}'_j \delta^{j/2} \sum_{p=0}^{\infty} \mathbf{G}_p \delta^{p/2} = \delta \sum_{p=0}^{\infty} \mathbf{G}_p \delta^{p/2} \sum_{j=0}^{\infty} \varepsilon_j \delta^{j/2} \qquad (2.61)$$

with $\varepsilon_{2j+1} = 0$. After a change of variables and some rearranging we can write

$$\sum_{p=0}^{\infty} \delta^{j/2} \sum_{l=0}^{p} (\mathbf{H}_l - \varepsilon_l \mathbf{I}_x)\, \mathbf{G}_{p-l} = \mathbf{0}.$$

where $\mathbf{H}_l = \mathbf{H}'_{l+2}$. This then leads us to an infinite set of coupled inhomogeneous differential matrix equations

$$\sum_{l=0}^{p} (\mathbf{H}_l - \varepsilon_l \mathbf{I}_x)\, \mathbf{G}_{p-l} = \mathbf{0} \qquad p = 0, 1, 2, \ldots \tag{2.62}$$

For $p = 0$ this equation gives the zeroth order Schrödinger equation. $\mathbf{H}_0\mathbf{G}_0 = \varepsilon_0\mathbf{G}_0$. Identifying $\mathbf{H}_0$ with $\mathbf{H}'_2$ we find that $\mathbf{H}_0$ is given by Eq. (2.46) and thus $\mathbf{G}_0$ is given by Eq. (2.48).

For $p > 0$ we obtain equations that can be solved recursively once the $p = 0$ solution is known. The method we use is called the matrix method and is discussed in the next chapter.

Chapter 3

Computational Strategies

3.1 The Matrix Method for States With $L = 0$

Previously the matrix method has been discussed for one degree of freedom and briefly for three degrees of freedom [8, 9]. Here we consider the three degree of freedom case in detail so as to better understand how to implement it for states with $L \neq 0$.

Since the harmonic oscillator eigenfunctions given by Eq. (1.56) form a complete orthonormal basis set we can write each of the wavefunction expansion coefficients, Φ_p, introduced in Eq. (1.52), as a linear combination of products of the h_ν .

$$\Phi_p = (\omega_1\omega_2\omega_3)^{1/4} \sum_{i=0}^{m_{p_1}} \sum_{j=0}^{m_{p_2}} \sum_{k=0}^{m_{p_3}} {}^{i,j,k}a_p \; h_i\left(\omega_1^{1/2}q_1\right) h_j\left(\omega_2^{1/2}q_2\right) h_k\left(\omega_3^{1/2}q_3\right). \qquad (3.1)$$

The upper limits in the summations are finite numbers which will be discussed below. We can use the rank-3 tensor, or cube, $\mathbf{a}_p$ with elements ${}^{i,j,k}a_p$ to represent the function Φ_p in a basis of triple products of harmonic oscillator eigenfunctions. We can also write the value of the overlap integral of two expansion coefficients Φ_p and Φ_q as inner products of the tensors $\mathbf{a}_p$ and $\mathbf{a}_q$,

$$\begin{aligned} &\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Phi_p^*\Phi_q \; dq_1dq_2dq_3 \\ = \; &(\omega_1\omega_2\omega_3)^{1/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \sum_{i,j,k} {}^{i,j,k}a_p \; h_i^* \; h_j^* \; h_k^* \sum_{l,m,n} {}^{l,m,n}a_q \; h_l \; h_m \; h_n \; dq_1dq_2dq_3 \end{aligned}$$

$$
\begin{aligned}
&= \sum_{i,j,k}\sum_{l,m,n} {}^{i,j,k}a_p \; {}^{l,m,n}a_q \left(\omega_1^{1/2}\int_{-\infty}^{\infty} h_i^* h_l \; dq_1\right)\left(\omega_2^{1/2}\int_{-\infty}^{\infty} h_j^* h_m \; dq_2\right) \\
&\quad \times \left(\omega_3^{1/2}\int_{-\infty}^{\infty} h_k^* h_n \; dq_3\right) \\
&= \sum_{i,j,k}\sum_{l,m,n} {}^{i,j,k}a_p \; {}^{l,m,n}a_q \; \delta_{i,l} \; \delta_{j,m} \; \delta_{k,n} = \sum_{i,j,k} {}^{i,j,k}a_p \; {}^{i,j,k}a_q \\
&= \mathbf{a}_p^T \cdot \mathbf{a}_q.
\end{aligned}
$$

We are now working in a three-dimensional space spanned by products of the form

$$h_i\left(\omega_1^{1/2}q_1\right) h_j\left(\omega_2^{1/2}q_2\right) h_k\left(\omega_3^{1/2}q_3\right).$$

A single product of this form may be represented by a rank-3 tensor with a 1 in the i,j,k position and zeros everywhere else. Since the three-dimensional basis functions are products of three one-dimensional basis functions, h_ν, the rank-3 tensors can be thought of as a direct product of three rank-1 tensors. In other words, the basis function h_1 can be represented by a column with a 1 in position 1 (the position indices of these tensors start at zero since the basis functions h_ν can take $\nu = 0, 1, 2, \ldots$. Recall that ν is a simple harmonic oscillator quantum number.). h_2 is represented by a column with a 1 in position 2 and h_3 becomes a column with a 1 in position 3. Thus the product $h_1 h_3 h_2$ can be represented by a direct product of the corresponding column vectors yielding a rank-3 tensor with a 1 in position 1, 3, 2.

The h_ν satisfy the following recursion relations

$$
\begin{aligned}
q_i h_\nu\left(\omega_i^{1/2}q_i\right) &= (2\omega_i)^{-1/2}\left[\nu^{1/2}h_{\nu-1}\left(\omega_i^{1/2}q_i\right) + (\nu+1)^{1/2}h_{\nu+1}\left(\omega_i^{1/2}q_i\right)\right]. \\
\frac{d}{dq_i}h_\nu\left(\omega_i^{1/2}q_i\right) &= \left(\frac{\omega_i}{2}\right)^{1/2}\left[\nu^{1/2}h_{\nu-1}\left(\omega_i^{1/2}q_i\right) - (\nu+1)^{1/2}h_{\nu+1}\left(\omega_i^{1/2}q_i\right)\right].
\end{aligned}
$$

We see that the effect of operating on $h_\nu(\omega_i^{1/2}q_i)$ with the operator q_i can be represented by multiplication of the column representation of h_ν by the matrix $\mathbf{q}_i$

$$\mathbf{q}_i = \frac{1}{\sqrt{2\omega_i}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \\ \sqrt{1} & 0 & \sqrt{2} & 0 & \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \\ & & \vdots & & \ddots \end{pmatrix},$$

and similarly the effect of operating on $h_\nu(\omega_i^{1/2}q_i)$ by the operator d/dq_i can be represented by multiplication of the column representation of h_ν by the matrix $\mathbf{d}/\mathbf{dq}_i$

$$\frac{\mathbf{d}}{\mathbf{dq}_i} = \sqrt{\frac{\omega_i}{2}} \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \\ -\sqrt{1} & 0 & \sqrt{2} & 0 & \\ 0 & -\sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & -\sqrt{3} & 0 & \\ & & \vdots & & \ddots \end{pmatrix}.$$

The wavefunction consists of products of three h_ν and is represented by rank-3 tensors which are direct products of the columns which represent the h_ν. Therefore, the operator, say q_1, operating on the wavefunction would be represented by the operator $\mathbf{q}_1 \otimes \mathbf{I} \otimes \mathbf{I}$ where $\mathbf{I}$ is a unit matrix operator. In other words, the Hamiltonian contains terms which have factors of the form $q_1^l q_2^m q_3^n$. These factors become operators which operate on the wavefunction and are represented by a direct product of the matrices of each individual operator q_i^j. The Hamiltonian then becomes a rank-6 tensor which operates on, or is contracted with, a rank-3 tensor wavefunction giving a rank-3 tensor wavefunction multiplied by the energy.

As another example, the kinetic term, T, of the Hamiltonian contains terms of the form [Eq. (1.49)]

$$q_1^{2k}\, q_2^l\, q_3^{j-2-2k-l} \frac{\partial^2}{\partial q_2 \partial q_3}.$$

which can be written as

$$q_1^{2k} q_2^l \frac{\partial}{\partial q_2} q_3^{j-2-2k-l} \frac{\partial}{\partial q_3},$$

since q_i commutes with d/dq_j but does not commute with d/dq_i for $i \neq j$. Writing these as matrix operators gives

$$\mathbf{q}_1^{2k} \otimes \left[\mathbf{q}_2^l \frac{\mathbf{d}}{\mathbf{dq}_2}\right] \otimes \left[\mathbf{q}_3^{j-2-2k-l} \frac{\mathbf{d}}{\mathbf{dq}_3}\right],$$

where we would do the respective matrix multiplication first and then perform the direct product. In particular, the harmonic order Hamiltonian, H_0, becomes

$$\begin{aligned} \mathbf{H}_0 \;=\; & -\frac{1}{2}\left(\left(\frac{\mathbf{d}}{\mathbf{dq}_1}\right)^2 \otimes \mathbf{I} \otimes \mathbf{I} + \mathbf{I} \otimes \left(\frac{\mathbf{d}}{\mathbf{dq}_2}\right)^2 \otimes \mathbf{I} + \mathbf{I} \otimes \mathbf{I} \otimes \left(\frac{\mathbf{d}}{\mathbf{dq}_3}\right)^2\right) \\ & + \frac{1}{2}\omega_1^2 \left(\mathbf{q}_1^2 \otimes \mathbf{I} \otimes \mathbf{I}\right) + \frac{1}{2}\omega_2^2 \left(\mathbf{I} \otimes \mathbf{q}_2^2 \otimes \mathbf{I}\right) + \frac{1}{2}\omega_3^2 \left(\mathbf{I} \otimes \mathbf{I} \otimes \mathbf{q}_3^2\right) \\ & - \frac{3}{2r_m^2 s_m^2}\mathbf{I}, \end{aligned} \tag{3.2}$$

where $\mathbf{I}$ is a rank-2 unit tensor everywhere except in the last term where it is a rank-6 unit tensor.

The perturbation equations, Eq. (1.55), can now be written as

$$\sum_{l=0}^{p} \left(\mathbf{H}_l - \varepsilon_l \mathbf{I}\right) \mathbf{a}_{p-l} = \mathbf{0} \qquad p = 0, 1, 2, \ldots, \tag{3.3}$$

where $\mathbf{I}$ is the rank-6 unit tensor and $\mathbf{0}$ is the rank-3 zero tensor. Now rather than having to solve an infinite set of differential equations we simply have to contract a bunch of tensors and then extract the energy and wavefunctions.

The case $p = 0$ in Eq. (3.3) has already been solved. The energy ε_0 is given by Eq. (1.44) and the wavefunction Φ_0 is given by Eq. (1.45). Φ_0 consists of a single product of three h_i and so by Eq. (3.1) the tensor, $\mathbf{a}_0$, which represents Φ_0, contains a 1 at the location $(i, j, k) = (n_a, n_s, n_\theta)$ and zeros everywhere else.

For $p = 1$ we have

$$\left(\mathbf{H}_0 - \varepsilon_0 \mathbf{I}\right) \mathbf{a}_1 + \mathbf{H}_1 \mathbf{a}_0 = \mathbf{0}, \tag{3.4}$$

where we have remembered that $\varepsilon_1 = 0$. The only unknown in Eq. (3.4) is $\mathbf{a}_1$ which can be found in the usual manner as long as the tensor $\mathbf{K} \equiv (\mathbf{H}_0 - \varepsilon_0 \mathbf{I})$ has an inverse.

$\mathbf{H}_0$ is a diagonal rank six tensor since it is written in terms of its eigenfunctions, the $h_\nu(\omega_i^{1/2} q_i)$. Since $\mathbf{I}$ is also a diagonal rank six tensor, $\mathbf{K}$ is a diagonal rank six tensor. The question is, does $\mathbf{K}$ have an inverse? We can construct the elements of $\mathbf{K}$ by calculating the elements of $\mathbf{H}_0$, $(\mathbf{H}_0)_{i,j,k,l,m,n}$, with the indices being integers greater than or equal to zero. Recalling that the i, j, k, l, m, n element of the tensor product of three rank two tensors, $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$, is given by $\mathbf{A}_{i,j}\mathbf{B}_{k,l}\mathbf{C}_{m,n}$, we can find $(\mathbf{H}_0)_{i,j,k,l,m,n}$ from Eq. (3.2).

$$
\begin{aligned}
(\mathbf{H}_0)_{i,j,k,l,m,n} &= -\frac{1}{2}\left[\left(\left(\frac{\mathbf{d}}{\mathbf{dq}_1}\right)^2\right)_{i,j}\delta_{k,l}\delta_{m,n} + \delta_{i,j}\left(\left(\frac{\mathbf{d}}{\mathbf{dq}_2}\right)^2\right)_{k,l}\delta_{m,n}\right. \\
&\quad \left. + \delta_{i,j}\delta_{k,l}\left(\left(\frac{\mathbf{d}}{\mathbf{dq}_3}\right)^2\right)_{m,n}\right] \\
&\quad + \frac{1}{2}\omega_1^2\left(\mathbf{q}_1^2\right)_{i,j}\delta_{k,l}\delta_{m,n} + \frac{1}{2}\omega_2^2\delta_{i,j}\left(\mathbf{q}_2^2\right)_{k,l}\delta_{m,n} + \frac{1}{2}\omega_3^2\delta_{i,j}\delta_{k,l}\left(\mathbf{q}_3^2\right)_{m,n} \\
&\quad - \frac{3}{2r_m^2\sin^2\theta_m}\delta_{i,j}\delta_{k,l}\delta_{m,n} \\
&= \frac{1}{2}\left(\omega_1^2\left(\mathbf{q}_1^2\right)_{i,j} - \left(\left(\frac{\mathbf{d}}{\mathbf{dq}_1}\right)^2\right)_{i,j}\right)\delta_{k,l}\delta_{m,n} \\
&\quad + \frac{1}{2}\left(\omega_2^2\left(\mathbf{q}_2^2\right)_{k,l} - \left(\left(\frac{\mathbf{d}}{\mathbf{dq}_2}\right)^2\right)_{k,l}\right)\delta_{i,j}\delta_{m,n} \\
&\quad + \frac{1}{2}\left(\omega_3^2\left(\mathbf{q}_3^2\right)_{m,n} - \left(\left(\frac{\mathbf{d}}{\mathbf{dq}_3}\right)^2\right)_{m,n}\right)\delta_{i,j}\delta_{k,l} \\
&\quad - \frac{3}{2r_m^2 s_m^2}\delta_{i,j}\delta_{k,l}\delta_{m,n}
\end{aligned}
\tag{3.5}
$$

where,

$$\mathbf{q}_i^2 = \frac{1}{2\omega_i} \begin{pmatrix} 1 & 0 & \sqrt{2} & 0 & 0 & \\ 0 & 3 & 0 & \sqrt{6} & 0 & \\ \sqrt{2} & 0 & 5 & 0 & \sqrt{12} & \\ 0 & \sqrt{6} & 0 & 7 & 0 & \ddots \\ 0 & 0 & \sqrt{12} & 0 & 2j+1 & \\ & & & \ddots & & \ddots \end{pmatrix}.$$

and

$$\left(\frac{\mathbf{d}}{\mathbf{dq}_i}\right)^2 = \frac{\omega_i}{2} \begin{pmatrix} -1 & 0 & \sqrt{2} & 0 & 0 & \\ 0 & -3 & 0 & \sqrt{6} & 0 & \\ \sqrt{2} & 0 & -5 & 0 & \sqrt{12} & \\ 0 & \sqrt{6} & 0 & -7 & 0 & \ddots \\ 0 & 0 & \sqrt{12} & 0 & -(2j+1) & \\ & & & \ddots & & \ddots \end{pmatrix}.$$

Clearly, the terms in parentheses in Eq. (3.5) are non-zero only along the diagonal. We then have:

$$\begin{aligned} (\mathbf{H}_0)_{i,j,k,l,m,n} &= \frac{1}{2}\omega_1 (2j+1)\,\delta_{i,j}\delta_{k,l}\delta_{m,n} + \frac{1}{2}\omega_2 (2l+1)\,\delta_{i,j}\delta_{k,l}\delta_{m,n} \\ &\quad + \frac{1}{2}\omega_3 (2n+1)\,\delta_{i,j}\delta_{k,l}\delta_{m,n} - \frac{3}{2r_m^2 \sin^2\theta_m}\delta_{i,j}\delta_{k,l}\delta_{m,n} \\ &= \left(\omega_1\left(j+\frac{1}{2}\right) + \omega_2\left(l+\frac{1}{2}\right) + \omega_3\left(n+\frac{1}{2}\right) - \frac{3}{2r_m^2 s_m^2}\right)\delta_{i,j}\delta_{k,l}\delta_{m,n}. \end{aligned}$$

$\mathbf{H}_0$ is thus a diagonal rank six tensor, i.e. a rank six tensor with non-zero elements only when $i = j$, and $k = l$, and $m = n$. To finish constructing $\mathbf{K}_{i,j,k,l,m,n}$ we simply subtract $\varepsilon_0\delta_{i,j}\delta_{k,l}\delta_{m,n}$ from $(\mathbf{H}_0)_{i,j,k,l,m,n}$ with ε_0 given by Eq. (1.44).

$$\mathbf{K}_{i,j,k,l,m,n} = \left(\omega_1 (j - n_a) + \omega_2 (l - n_s) + \omega_3 (n - n_\theta)\right)\delta_{i,j}\delta_{k,l}\delta_{m,n}$$

Clearly $\mathbf{K}$ is diagonal and has a zero on the diagonal when $j = n_a$ and $l = n_s$ and $n = n_\theta$. Thus $\mathbf{K}$ has no inverse and we cannot use it to solve Eq. (3.4). What we can do, however, is define a tensor $\tilde{\mathbf{K}}$ whose elements are the reciprocal of the elements of $\mathbf{K}$ except that we place a 0 in the location where $\mathbf{K}$ had a zero on the diagonal. In other words,

$$\tilde{\mathbf{K}}_{i,j,k,l,m,n} = \left(\omega_1 (j - n_a) + \omega_2 (l - n_s) + \omega_3 (n - n_\theta)\right)^{-1}$$

for $i = j$, $k = l$, $m = n$ and ($j \neq n_a$ or $l \neq n_s$ or $n \neq n_\theta$); and

$$\tilde{\mathbf{K}}_{i,j,k,l,m,n} = 0 \qquad \text{elsewhere.}$$

Then the product $\tilde{\mathbf{K}}\mathbf{K}$ will then be a unit tensor of rank six but with a zero when $i = j = n_a$ and $k = l = n_s$ and $m = n = n_\theta$.

With the normalization

$$\begin{aligned} \langle \phi_0 | \phi_p \rangle &= \mathbf{a}_0^T \cdot \mathbf{a}_p = \delta_{0,p} \\ \langle \phi_p | \phi_q \rangle &= \mathbf{a}_p^T \cdot \mathbf{a}_q = \delta_{p,q} \end{aligned} \tag{3.6}$$

we see that since the $\{n_a, n_s, n_\theta\}$ element of $\mathbf{a}_0^T$ is a 1 and all other elements are zero then the $\{n_a, n_s, n_\theta\}$ element of $\mathbf{a}_p$ is zero when $p > 0$. Thus $(\tilde{\mathbf{K}}\mathbf{K})\mathbf{a}_p = \mathbf{a}_p$ for $p > 0$ since $\tilde{\mathbf{K}}\mathbf{K}$ would make the $\{n_a, n_s, n_\theta\}$ element zero if it was not zero to begin with. Finally, if we now multiply Eq. (3.4) by $\tilde{\mathbf{K}}$ we are able to solve for $\mathbf{a}_1$.

$$\begin{aligned} & \tilde{\mathbf{K}} (\mathbf{H}_0 - \varepsilon_0 \mathbf{I}) \mathbf{a}_1 + \tilde{\mathbf{K}} \mathbf{H}_1 \mathbf{a}_0 = \mathbf{0} \\ \Rightarrow \quad & \tilde{\mathbf{K}}\mathbf{K}\mathbf{a}_1 + \tilde{\mathbf{K}} \mathbf{H}_1 \mathbf{a}_0 = \mathbf{0} \\ \Rightarrow \quad & \mathbf{a}_1 + \tilde{\mathbf{K}} \mathbf{H}_1 \mathbf{a}_0 = \mathbf{0} \end{aligned}$$

which implies $\mathbf{a}_1 = -\tilde{\mathbf{K}}\mathbf{H}_1\mathbf{a}_0$. In general if we multiply Eq. (3.3) on the left by $\tilde{\mathbf{K}}$ we obtain an equation for $\mathbf{a}_p$.

$$\begin{aligned}\tilde{\mathbf{K}}\sum_{l=0}^{p}(\mathbf{H}_l - \varepsilon_l\mathbf{I})\,\mathbf{a}_{p-l} &= \tilde{\mathbf{K}}(\mathbf{H}_0 - \varepsilon_0\mathbf{I})\,\mathbf{a}_p + \tilde{\mathbf{K}}\sum_{l=1}^{p}(\mathbf{H}_l - \varepsilon_l\mathbf{I})\,\mathbf{a}_{p-l} \\ &= \tilde{\mathbf{K}}\mathbf{K}\mathbf{a}_p + \tilde{\mathbf{K}}\sum_{l=1}^{p}(\mathbf{H}_l - \varepsilon_l\mathbf{I})\,\mathbf{a}_{p-l} = \mathbf{0}\end{aligned}$$

which implies

$$\mathbf{a}_p = \tilde{\mathbf{K}}\sum_{l=1}^{p}(\varepsilon_l\mathbf{I} - \mathbf{H}_l)\,\mathbf{a}_{p-l} \qquad \text{for } p > 0. \tag{3.7}$$

In addition we can find an equation for the energy coefficient ε_p by contracting $\mathbf{a}_0^T$ with Eq. (3.3) on the left,

$$\begin{aligned}\mathbf{a}_0^T \cdot \sum_{l=0}^{p}(\mathbf{H}_l - \varepsilon_l\mathbf{I})\,\mathbf{a}_{p-l} &= \mathbf{a}_0^T \cdot \sum_{l=0}^{p}\mathbf{H}_l\mathbf{a}_{p-l} - \mathbf{a}_0^T \cdot \sum_{l=0}^{p}\varepsilon_l\mathbf{I}\mathbf{a}_{p-l} \\ &= \mathbf{a}_0^T \cdot \mathbf{H}_0\mathbf{a}_p + \mathbf{a}_0^T \cdot \sum_{l=1}^{p}\mathbf{H}_l\mathbf{a}_{p-l} - \sum_{l=0}^{p}\varepsilon_l\mathbf{a}_0^T \cdot \mathbf{I}\mathbf{a}_{p-l} \\ &= \mathbf{a}_0^T \cdot \sum_{l=1}^{p}\mathbf{H}_l\mathbf{a}_{p-l} - \sum_{l=0}^{p}\varepsilon_l\delta_{0,p-l} = \mathbf{0}.\end{aligned}$$

The first term in the second row is zero because $\mathbf{a}_p$ has a zero in the $\{n_a, n_s, n_\theta\}$ position and $\mathbf{H}_0$ is diagonal so that the product $\mathbf{H}_0\mathbf{a}_p$ also has a zero in the $\{n_a, n_s, n_\theta\}$ position. Contracting this with $\mathbf{a}_0^T$, which is non-zero only at the $\{n_a, n_s, n_\theta\}$ position, then gives zero. We then obtain

$$\varepsilon_p = \mathbf{a}_0^T \cdot \sum_{l=1}^{p}\mathbf{H}_l \quad \mathbf{a}_{p-l} \qquad \text{for } p > 0. \tag{3.8}$$

3.1.1 The wavefunction arrays have finite size.

Looking back at Eq. (3.1) we see that the wavefunction expansion coefficients are finite sums of products of the h_i. Now we can explain why the sums are finite and not infinite. First consider the zeroth order wavefunction for a state with large dimension quantum numbers $\{n_a, n_s, n_\theta\}$. There is only one product of three h_i as is seen in

Eq. (1.45). Thus the tensor $\mathbf{a}_0$, which represents the zeroth order coefficient of the wavefunction, has a 1 in position (n_a, n_s, n_θ) and zeros everywhere else. The rank-3 tensor, $\mathbf{a}_0$, is a direct product of three rank-1 tensors, or column vectors, $\mathbf{a}_0 = \mathbf{a}_{01} \otimes \mathbf{a}_{02} \otimes \mathbf{a}_{03}$. The column $\mathbf{a}_{01}$ has a 1 in the n_a position, similarly for the other two column vectors. Thus the upper limits of the sums in Eq. (3.1) are $m_{0_1} = n_a$, $m_{0_2} = n_s$, and $m_{0_3} = n_\theta$.

Now that we know the zeroth order energy, ε_0, and the zeroth order wavefunction, $\mathbf{a}_0$, we can proceed to $p = 1$ in Eq. (3.7). This yields $\mathbf{a}_1 = \tilde{\mathbf{K}}(\varepsilon_1 \mathbf{I} - \mathbf{H}_1)\mathbf{a}_0$. We need to calculate the tensor product $-\mathbf{H}_1\mathbf{a}_0$, multiply this by $\tilde{\mathbf{K}}$, which is diagonal and simply multiplies each element by some numerical factor, and finally add the tensor $\tilde{\mathbf{K}}\varepsilon_1\mathbf{I}$ which, in this case, is zero since $\varepsilon_1 = 0$. The structure of $\mathbf{a}_1$ will be identical to the structure of $\mathbf{H}_1\mathbf{a}_0$ since $\tilde{\mathbf{K}}$ is diagonal. The only difference might be that one element of $\mathbf{H}_1\mathbf{a}_0$ that is non-zero might become zero when $\mathbf{H}_1\mathbf{a}_0$ is multiplied by $\tilde{\mathbf{K}}$.

The terms in $\mathbf{H}_1$ correspond to H_3' and, as can be seen by examination of Eqs. (1.49)-(1.51), contains powers of q_1 up to q_1^2, powers of q_2 up to q_2^3 and q_3 up to q_3^3. The kinetic term, T contains derivatives with respect to q_2 and q_3 which, when written as a matrix, have the same structure as the matrices for q_2 and q_3. Thus the structure of the matrix $\mathbf{q}_2^3$ is identical to the structure of say $\mathbf{q}_2^1(\mathbf{d}/\mathbf{dq}_2)^2$. So for now we are only concerned with the structure of $\mathbf{H}_1$ and so to simplify the discussion we will ignore the matrices corresponding to the derivative terms and instead focus on the matrices for the $q's$.

Any order of the Hamiltonian can be written as $\mathbf{H}_n = \mathbf{H}_{n1} \otimes \mathbf{H}_{n2} \otimes \mathbf{H}_{n3}$ where $\mathbf{H}_{n1}$ contains only $\mathbf{q}_1$ and its derivatives. $\mathbf{H}_{n2}$ contains only $\mathbf{q}_2$ and its derivatives and similarly for $\mathbf{H}_{n3}$. Similarly, any order of the wavefunction can be written as $\mathbf{a}_p = \mathbf{a}_{p1} \otimes \mathbf{a}_{p2} \otimes \mathbf{a}_{p3}$. The product of $\mathbf{H}_{n3}$ with the wavefunction tensor, $\mathbf{a}_p$, is written as $\mathbf{H}_{n3}\mathbf{a}_p = \mathbf{H}_{n1}\mathbf{a}_{p1} \otimes \mathbf{H}_{n2}\mathbf{a}_{p2} \otimes \mathbf{H}_{n3}\mathbf{a}_{p3}$. Let us define $\mathbf{a}_1' = \mathbf{H}_1\mathbf{a}_0 = \mathbf{H}_{11}\mathbf{a}_{01} \otimes \mathbf{H}_{12}\mathbf{a}_{02} \otimes \mathbf{H}_{13}\mathbf{a}_{03} = \mathbf{a}_{11}' \otimes \mathbf{a}_{12}' \otimes \mathbf{a}_{13}'$.

The construction of $\mathbf{a}'_{11}$ will involve only powers of $\mathbf{q}_1$ the highest power being 2. The structure of $\mathbf{q}_i^2$ looks like

$$\mathbf{q}_i^2 \propto \begin{pmatrix} x & 0 & x & 0 & 0 & \\ 0 & x & 0 & x & 0 & \\ x & 0 & x & 0 & x & \\ 0 & x & 0 & x & 0 & \ddots \\ 0 & 0 & x & 0 & x & \\ & & & \ddots & & \ddots \end{pmatrix}$$

where an x represents a non-zero element. Since the column $\mathbf{a}_{01}$ has a 1 in the n_a position, when it is multiplied by $\mathbf{q}_1^2$ we get a column with non-zero elements only up to the $n_a + 2$ element because of the presence of the lower diagonal in $\mathbf{q}_1^2$ which is two elements down from the main diagonal. Thus the upper summation index in Eq. (3.1), m_{1_1}, need only be as high as $n_a + 2$.

Similarly, the construction of $\mathbf{a}'_{12}$ and $\mathbf{a}'_{13}$ involve only powers of $\mathbf{q}_2$ and $\mathbf{q}_3$, respectively, with the highest power of either being 3. The structure of $\mathbf{q}_i^3$ looks like

$$\mathbf{q}_i^3 \propto \begin{pmatrix} 0 & x & 0 & x & 0 & \\ x & 0 & x & 0 & x & \\ 0 & x & 0 & x & 0 & \ddots \\ x & 0 & x & 0 & x & \\ 0 & x & 0 & x & 0 & \ddots \\ & & \ddots & & \ddots & \end{pmatrix}.$$

Thus, the last non-zero element of either $\mathbf{a}'_{12}$ or $\mathbf{a}'_{13}$ will be at the $n_s + 3$ or $n_\theta + 3$ position, respectively, allowing us to write $m_{1_2} = n_s + 3$ and $m_{1_3} = n_\theta + 3$ for the upper summation indices of Eq. (3.1).

From the preceding analysis we see that since the first column of the matrix $\mathbf{q}_i^n$ will have its last non-zero element in row n (we consider the first row to have index zero), $\mathbf{q}_i^n \mathbf{a}_{0i}$ will be a column with its last non-zero element in row $n_i + n$. ($n_i = n_a, n_s,$

or n_θ when $i = 1, 2,$ or 3, respectively) Also, any column vector, $\mathbf{a}_{pi}$, when multiplied by $\mathbf{q}_i^n$ will have the index of its last non-zero element increased by at most n.

Consider the construction of $\mathbf{a}_2$. From Eq. (3.7) we have

$$\mathbf{a}_2 = \bar{\mathbf{K}}\left[(\varepsilon_1\mathbf{I} - \mathbf{H}_1)\,\mathbf{a}_1 + (\varepsilon_2\mathbf{I} - \mathbf{H}_2)\,\mathbf{a}_0\right]$$

and we see that the structure is determined by the products $\mathbf{H}_1\mathbf{a}_1$ and $\mathbf{H}_2\mathbf{a}_0$. Let $\mathbf{a}_2' = \mathbf{H}_1\mathbf{a}_1 = \mathbf{H}_{11}\mathbf{a}_{11} \otimes \mathbf{H}_{12}\mathbf{a}_{12} \otimes \mathbf{H}_{13}\mathbf{a}_{13} = \mathbf{a}_{21}' \otimes \mathbf{a}_{22}' \otimes \mathbf{a}_{23}'$. Since $\mathbf{a}_{11}$ has its last non-zero element at position $n_a + 2$ and $\mathbf{H}_{11}$ contains powers of $\mathbf{q}_1$ up to $\mathbf{q}_1^2$, then $\mathbf{a}_{21}'$ will have its last non-zero element at position $n_a + 4$. Similarly, $\mathbf{a}_{12}$ and $\mathbf{a}_{13}$ have their last non-zero elements at position $n_s + 3$ and $n_\theta + 3$ respectively, and since $\mathbf{H}_{12}$ and $\mathbf{H}_{13}$ have powers of $\mathbf{q}_2$ and $\mathbf{q}_3$, respectively, with the highest power of either being 3, then $\mathbf{a}_{22}'$ and $\mathbf{a}_{23}'$ will have their last non-zero elements at $n_s + 6$ and $n_\theta + 6$ respectively.

Finally, we can also define $\mathbf{a}_2'' = \mathbf{H}_2\mathbf{a}_0 = \mathbf{H}_{21}\mathbf{a}_{01} \otimes \mathbf{H}_{22}\mathbf{a}_{02} \otimes \mathbf{H}_{23}\mathbf{a}_{03} = \mathbf{a}_{21}'' \otimes \mathbf{a}_{22}'' \otimes \mathbf{a}_{23}''$. $\mathbf{H}_2$ corresponds to H_4' and, as can be seen by examination of Eqs. (1.49)-(1.51), contains powers of q_1 up to q_1^4, powers of q_2 up to q_2^4 and q_3 up to q_3^4. Since $\mathbf{a}_{01}$, $\mathbf{a}_{02}$ and $\mathbf{a}_{03}$ have their last non-zero elements at positions n_a, n_s, and n_θ, respectively, then $\mathbf{a}_{21}''$, $\mathbf{a}_{22}''$, and $\mathbf{a}_{23}''$ will have their last non-zero elements at positions $n_a + 4$, $n_s + 4$, and $n_\theta + 4$, respectively. Thus to accommodate all of the non-zero terms that arise from the products $\mathbf{H}_1\mathbf{a}_1$ and $\mathbf{H}_2\mathbf{a}_0$ we must let the upper summation indices of Eq. (3.1) for $p = 2$ be $m_{2_1} = n_a + 4$, $m_{2_2} = n_s + 6$, and $m_{2_3} = n_\theta + 6$.

As one more check we can consider $\mathbf{a}_3 = \bar{\mathbf{K}}\left[(\varepsilon_1\mathbf{I} - \mathbf{H}_1)\,\mathbf{a}_2 + (\varepsilon_2\mathbf{I} - \mathbf{H}_2)\,\mathbf{a}_1 + (\varepsilon_3\mathbf{I} - \mathbf{H}_3)\,\mathbf{a}_0\right]$. A little analysis shows that from the $\mathbf{H}_1\mathbf{a}_2$ term we find the maximum indices for any non-zero terms to be $m_{3_1} = n_a + 6$, $m_{3_2} = n_s + 9$, and $m_{3_3} = n_\theta + 9$. The other two terms require indices equal to or less than these.

In general, $\mathbf{a}_p$ contains the term $\mathbf{H}_1\mathbf{a}_{p-1}$ and it is the structure of this term that determines the structure of $\mathbf{a}_p$. Moreover, we can write $m_{p_1} = n_a + 2p$, $m_{p_2} = n_s + 3p$, and $m_{p_3} = n_\theta + 3p$ showing that each order of the wavefunction can be written as a finite sum of products of three harmonic oscillator eigenfunctions.

3.2 The Matrix Method for States With $L \neq 0$

Now we can apply the matrix method to the set of perturbation equations, Eq. (2.62). $\mathbf{H}_l$ is the coefficient of $\delta^{(l+2)/2}$ in the Hamiltonian and is an $x+1$ by $x+1$ matrix whose elements are products of the q_i and their derivatives. $\mathbf{H}_l$ is already a rank-2 tensor and when we apply the matrix method it becomes a rank-8 tensor. The elements of $\mathbf{H}_l$ can now be labeled by eight indices $[\mathbf{H}_l]_{i,j,k,l,m,n,\alpha,\beta}$ the first six indices take values from zero to infinity and the last two take values from one to $x+1$. The matrix $\mathbf{I}_x$ now becomes a rank-8 unit tensor, $\mathbf{I}$, with index ranges identical to those for $\mathbf{H}_l$. Finally, $\mathbf{G}_{p-l}$ becomes a rank-4 tensor which we write as $\mathbf{a}_{p-l}$ as we did for the S-wave case. The elements of $\mathbf{a}_{p-l}$, i.e. ${}^{j,l,n,\beta}\mathbf{a}_{p-l}$, have four indices with the first three taking values from zero to infinity and the last taking values from one to $x+1$. The wavefunction $\mathbf{a}_0$ now consists of a 1 in the $\{n_a, n_s, n_\theta, \gamma\}$ position and zeros everywhere else. The perturbation equations now look like

$$\sum_{l=0}^{p} (\mathbf{H}_l - \varepsilon_l \mathbf{I})\, \mathbf{a}_{p-l} = \mathbf{0} \qquad p = 0, 1, 2, \ldots \tag{3.9}$$

We again consider the tensor $\mathbf{K} \equiv (\mathbf{H}_0 - \varepsilon_0 \mathbf{I})$, which is now a rank-8 tensor, and as before we can show that it is diagonal with one diagonal element equal to zero.

$$\mathbf{K}_{i,j,k,l,m,n,\alpha,\beta} = (\omega_1 (j - n_a) + \omega_2 (l - n_s) + \omega_3 (n - n_\theta) + \omega_4(\gamma - \beta))\, \delta_{i,j}\delta_{k,l}\delta_{m,n}\delta_{\alpha,\beta}.$$

Thus $\mathbf{K}$ has no inverse and so we define a new rank-8 tensor $\tilde{\mathbf{K}}$ as

$$\tilde{\mathbf{K}}_{i,j,k,l,m,n,\alpha,\beta} = (\omega_1 (j - n_a) + \omega_2 (l - n_s) + \omega_3 (n - n_\theta) + \omega_4(\gamma - \beta))^{-1}$$

for $i = j$ and $k = l$ and $m = n$ and $\alpha = \beta$ and ($j \neq n_a$ or $l \neq n_s$ or $n \neq n_\theta$ or $\beta \neq \gamma$); and

$$\tilde{\mathbf{K}}_{i,j,k,l,m,n,\alpha,\beta} = 0 \qquad \text{elsewhere.}$$

The product $\tilde{\mathbf{K}}\mathbf{K}$ will be a rank-8 unit tensor with a zero when $i = j = n_a$ and $k = l = n_s$ and $m = n = n_\theta$ and $\alpha = \beta = \gamma$.

Equation (3.6) for the normalization of the $\mathbf{a}_p$ still applies, and we see that since the $\{n_a, n_s, n_\theta, \gamma\}$ element of $\mathbf{a}_0^T$ is a 1 and all other elements are zero then the $\{n_a, n_s, n_\theta, \gamma\}$ element of $\mathbf{a}_p$ is zero when $p > 0$. Thus $(\tilde{\mathbf{K}}\mathbf{K})\mathbf{a}_p = \mathbf{a}_p$ for $p > 0$ since $\tilde{\mathbf{K}}\mathbf{K}$ would make the $\{n_a, n_s, n_\theta, \gamma\}$ element zero if it was not zero to begin with. Finally, as in the S-wave case, we multiply Eq. (3.9) on the left by $\tilde{\mathbf{K}}$ obtaining an equation for $\mathbf{a}_p$,

$$\mathbf{a}_p = \tilde{\mathbf{K}} \sum_{l=1}^{p} (\varepsilon_l \mathbf{I} - \mathbf{H}_l)\, \mathbf{a}_{p-l} \qquad \text{for } p > 0. \tag{3.10}$$

and we find an equation for the energy coefficient ε_p by contracting $\mathbf{a}_0^T$ with Eq. (3.9) on the left,

$$\varepsilon_p = \mathbf{a}_0^T \cdot \sum_{l=1}^{p} \mathbf{H}_l \quad \mathbf{a}_{p-l} \qquad \text{for } p > 0. \tag{3.11}$$

These equations are identical to those for the S-wave case except for the fact that the wavefunctions are rank-4 tensors and the Hamiltonian coefficients are rank-8 tensors. Also, the tensor indices are not symmetric. In other words, all the indices in the S-wave case range from zero to infinity but in the higher angular momentum case the last index of the wavefunction coefficients (and the last two in the Hamiltonian coefficients) range from one to $x + 1$. These last indices, α and β may be thought of as angular momentum indices since as angular momentum increases so too does $x + 1$.

3.3 The Computer Code

3.3.1 Introduction

To solve the perturbation equations of Eqs. (3.10) and (3.11), I started with FORTRAN code developed by Tim Germann [9] which dealt specifically with S-wave states. The extension to higher angular momentum states seemed, at first, straight forward but upon further analysis and subsequent trials it proved to be rather complex and at times frustrating. It *seemed* simple because the perturbation equations for S-wave [Eq. (3.7)] are identical in form to those for higher angular momentum.

The Hamiltonian coefficients are simply rank-8 tensors rather than rank-6, and the wavefunctions are rank-4 tensors rather than rank-3. The first difficulty was in understanding the original S-wave code.

The code can be broken down into two programs: one program calculates all the Hamiltonian expansion coefficients and writes them to files, and the other program actually solves the perturbation equations. The original code was written quite efficiently which made it hard to decipher especially since there were very few comments in the code itself. Understanding the S-wave code resulted in about one hundred pages of notes that I, very briefly, summarize below in terms of higher angular momentum.

Next, was the problem of how to calculate all the new terms in the Hamiltonian (compare Eq. (1.49) and (1.50) with Eq. (2.59).) The calculation of one specific term in the higher angular momentum Hamiltonian will be discussed in the next section. The resulting code, consisting of several subroutines, for the expansion of the Hamiltonian is listed in Appendix A. The ability to do λ variation, i.e. allow λ to be a function of δ up to order δ^2, was also added to the code. This allows one to study the H^- ion as well as the case $\lambda = 0$ which proved indispensable while the code was being debugged. The $\lambda = 0$ case is simply a case of non-interacting electrons resulting in energies that are sums of hydrogenic energies with $Z = 2$. The energy coefficients are easily calculated analytically and compared to code output.

Finally, the second program had to be rewritten to include all the new Hamiltonian terms and take into account the fact that the Hamiltonian is a rank-8 tensor and the wavefunction is a rank-4 tensor. In Tim's original code he applied memory saving techniques referred to as wavefunction truncation and axis contraction. The axis contraction technique depended on the fact that the coordinate q_1 appeared only in even powers. It was not immediately clear how this techniques would be coded for higher angular momentum since the Hamiltonian contains both even and odd powers of q_1.

The first attempt was to write the code without the two memory saving techniques mentioned above. After many attempts the code finally compiled and was run but,

as is usually the case, the numbers for $\lambda = 0$ were not correct. Many Mathematica notebooks were created to solve the first few orders of the perturbation equations from which the correct values for $\lambda = 0$ appeared. Then by comparing the wavefunction coefficients, element by element, the bug was found. The bug was in a section of the code that hadn't been touched. The matrices that represent q and $\partial/\partial q$ were multiplied in the wrong order. For some reason this didn't affect the S-wave results, but it certainly affected higher angular momentum. Now there was a code that would give beautiful results for $\lambda = 0$ but it wrote and read the wavefunction tensors to and from disk and thus was very slow. The memory saving techniques could then be implemented so the wavefunctions could be stored in memory. The final code resulted in over three hundred pages of notes mostly detailing the memory saving techniques. The resulting code is listed in Appendix B.

Currently the code is run in quadruple precision on the IBM SP2 at the University of Oklahoma Department of Physics and Astronomy. The SP2 is a machine with six RS6000 processors enabling one to run parallel or serial code. Currently the code is a serial code and thus runs on a single node of the SP2. Each node has at most 512MB available which allows calculation of the energy series up to twenty-seventh order in δ for the states with the lowest angular momentum and quantum numbers. I have run a calculation for $L = 20$, but I can only get fifteen coefficients.

Future goals include writing the code in parallel. I am currently teaching at Oakton Community College in Des Plaines Illinois and I am working with a faculty member to develop a four or five node parallel processor from pentium III's. The plan is to develop my code on this machine as part of a student project: writing it in such a way that it could then be run on larger parallel machines. This would allow us to obtain many more energy coefficients, while reducing round-off error by using more efficient and precise algorithms.

3.3.2 Expansion of the Hamiltonian

I will illustrate the expansion of the Hamiltonian with an example. Consider the third line in the Hamiltonian, Eq. (2.59) which corresponds to the term

$$\mathbf{T}2 = \delta^{3/2} G^{-}(q_1, q_2, q_3) \cot\theta \frac{r_m}{\sqrt{2}} \left(\sin\chi \frac{\partial}{\partial q_3} + \cos\chi \frac{\partial}{\partial q_2} \right) \bar{\mathbf{S}}_x$$

in the third line of Eq. (2.55). The term in parentheses multiplied by the matrix $\bar{\mathbf{S}}_x$ becomes a rank-8 tensor when the matrix method is applied. In the notation of Sec. 3.1 it becomes

$$\left(\sin\chi \mathbf{I} \otimes \mathbf{I} \otimes \frac{\mathbf{d}}{\mathbf{dq_3}} \otimes \bar{\mathbf{S}}_x + \cos\chi \mathbf{I} \otimes \frac{\mathbf{d}}{\mathbf{dq_2}} \otimes \mathbf{I} \otimes \bar{\mathbf{S}}_x \right).$$

The fact that this is a tensor and it is contracted with the wavefunction is addressed in the second part of the code which will be discussed in the next section. For now we will ignore this part and focus on the expansion of

$$\delta^{3/2} G^{-}(q_1, q_2, q_3) \cot\theta \frac{r_m}{\sqrt{2}}. \tag{3.12}$$

The term G^{-} is almost the same as the term G^{+}. G^{+} is expanded as a power series in $\delta^{1/2}$

$$\begin{aligned} G^{+} &= \sum_{n=0}^{\infty} \delta^{n/2} G_n^{+}. \\ G_n^{+} &= \frac{(-1)^n (n+1)}{2^{n/2} r_m^{n+2}} \sum_{k=0}^{n/2} \sum_{l=0}^{n-2k} C(n,k,l) q_1^{2k} q_2^{l} q_3^{n-2k-l}. \end{aligned}$$

where

$$C(n,k,l) = (-1)^l \binom{n}{2k} \binom{n-2k}{l} (\cos\chi)^l (\sin\chi)^{n-2k-l}.$$

The coefficients $C(n,k,l)$ are calculated in the subroutine setup_C.f listed in appendix A. G^- is then expanded as

$$\begin{aligned} G^- &= \sum_{n=0}^{\infty} \delta^{n/2} G_n^-, \\ G_n^- &= \frac{(-1)^n (n+1)}{2^{n/2} r_m^{n+2}} \sum_{k=0}^{(n-1)/2} \sum_{l=0}^{n-2k-1} B(n,k,l) q_1^{2k+1} q_2^l q_3^{n-2k-l} - 1. \end{aligned}$$

where

$$B(n,k,l) = \frac{1}{\cos\chi} \frac{n-2k-l}{2k+1} C(n,k,l).$$

The coefficients $B(n,k,l)$ are calculated in the subroutine setup_B.f in appendix A.

Next we expand the term $\cot\theta$ in Eq. (3.12). Leaving out a lot of details we have

$$\cot\theta = \sum_{j=0}^{\infty} \sum_{n=0}^{j} \cot(j,n) \delta^{j/2} q_2^n q_3^{j-n}.$$

where

$$\cot(j,n) = \cot\theta_m \, S(j,n) \left(\frac{\sqrt{2}}{r_m}\right)^j \sum_{m=0}^{j} \sum_{i=m}^{j} a2(j-i,1) \, a1(i,m).$$

The coefficients S, $a2$, and $a1$ are involved in the expansion of $\sin\theta$ and $\cos\theta$ and are calculated in the subroutines sin_derivs.f and gtoy.f. The coefficient $\cot(j,n)$ is then calculated in the subroutine cotan.f.

Finally, to complete the expansion of Eq. (3.12) we multiply the expansions for $\cot\theta$ and G^- together and obtain

$$\begin{aligned} &\delta^{3/2} G^-(q_1,q_2,q_3) \cot\theta \frac{r_m}{\sqrt{2}} \\ &= \sum_{j=4}^{\infty} \sum_{k=0}^{(j-4)/2} \sum_{l=0}^{j-4-2k} \delta^{j/2} T2(j,k,l) q_1^{2k+1} q_2^l q_3^{j-2k-l-4}. \end{aligned}$$

which is calculated in the subroutine setup_T.f and is given by

$$T2(j,k,l) = \sum_{m=0}^{j-4} \frac{(-2)(j-m-2)}{j-m-1} C(j-m) \sum_{n=0}^{\min(l,m)} B(j-m-3,k,l-n) \cot(m,n).$$

The coefficients $C(j-m)$ are calculated previously and given by

$$C(j) = \frac{(-1)^{j+1}(j-1)}{2^{j/2}\Gamma_m^{j-2}}.$$

The term $\mathbf{T2}$ is then given by

$$\mathbf{T2} = \sum_{j=4}^{\infty} \sum_{k=0}^{(j-4)/2} \sum_{l=0}^{j-4-2k} \delta^{j/2} T2(j,k,l)\, q_1^{2k+1} q_2^l q_3^{j-2k-l-4} \left(\sin\chi \frac{\partial}{\partial q_3} + \cos\chi \frac{\partial}{\partial q_2} \right) \bar{\mathbf{S}}_x.$$

When the matrix method is applied it is convenient to write this term as two separate terms

$$\begin{aligned} \mathbf{T2} \;=\; & \sum_{j=4}^{\infty} \sum_{k=0}^{(j-4)/2} \sum_{l=0}^{j-4-2k} \delta^{j/2} T2(j,k,l) \left[\sin\chi\, \mathbf{q}_1^{2k+1} \otimes \mathbf{q}_2^l \otimes \mathbf{q}_3^{j-2k-l-4} \frac{\mathbf{d}}{\mathbf{dq_3}} \otimes \bar{\mathbf{S}}_x \right. \\ & \left. + \cos\chi\, \mathbf{q}_1^{2k+1} \otimes \mathbf{q}_2^l \frac{\mathbf{d}}{\mathbf{dq_2}} \otimes \mathbf{q}_3^{j-2k-l-4} \otimes \bar{\mathbf{S}}_x \right]. \end{aligned}$$

Because of the way that the matrix method is implemented it is convenient to introduce the identity

$$q^m \frac{\partial}{\partial q} = \frac{\partial}{\partial q} q^m - m q^{m-1}.$$

Substituting this identity into the equation for $\mathbf{T2}$ gives four terms which are referred to as T2_1, T2_2, T2_3 and T2_4 in the comments of the subroutine comp_H_A.f in appendix B.

All of the other terms in the Hamiltonian are expanded in a similar way. T1 gives rise to ten different terms. U1, U2, U3 are each one term. These thirteen terms are identical to the S-wave terms. For higher angular momentum we have the additional four terms of T2, a single term from each of U4, U5, and U6; one term each from A1, A3, B1, and B3; and four terms each from A2 and B2 for a total of nineteen additional terms. These nineteen additional terms are non-diagonal in the sense that they either multiply the matrix $\bar{\mathbf{S}}_x$ or its square, or they are involved in the non-diagonal term $\delta \mathbf{W}_x'$.

3.3.3 Implementation of the matrix method

Suppose we wanted the energy $\tilde{E}$ to third order in δ or sixth order in $\delta^{1/2}$. $\tilde{E}$ would be written as (see Eq. (2.58))

$$\tilde{E} = V_{\rm eff}(r_m, r_m, \theta_m) + \delta\varepsilon_0 + \delta^2\varepsilon_2 + \delta^3\varepsilon_4.$$

We already know the terms $V_{\rm eff}(r_m, r_m, \theta_m)$ and ε_0 so that we must calculate the terms ε_2 and ε_4 using Eq. (3.11). From this equation we see that we need only calculate the wavefunction coefficients up to $\mathbf{a}_3$. Writing out Eqs. (3.10) and (3.11) gives

$$\begin{aligned}
\mathbf{a}_1 &= \tilde{\mathbf{K}}(\varepsilon_1\mathbf{I} - \mathbf{H}_1)\mathbf{a}_0 = -\tilde{\mathbf{K}}\mathbf{H}_1\mathbf{a}_0, \\
\mathbf{a}_2 &= \tilde{\mathbf{K}}\left[(\varepsilon_1\mathbf{I} - \mathbf{H}_1)\mathbf{a}_1 + (\varepsilon_2\mathbf{I} - \mathbf{H}_2)\mathbf{a}_0\right] \\
&= \tilde{\mathbf{K}}\left[-\mathbf{H}_1\mathbf{a}_1 - \mathbf{H}_2\mathbf{a}_0 + \varepsilon_2\mathbf{I}\,\mathbf{a}_0\right], \\
\mathbf{a}_3 &= \tilde{\mathbf{K}}\left[(\varepsilon_1\mathbf{I} - \mathbf{H}_1)\mathbf{a}_2 + (\varepsilon_2\mathbf{I} - \mathbf{H}_2)\mathbf{a}_1 + (\varepsilon_3\mathbf{I} - \mathbf{H}_3)\mathbf{a}_0\right] \\
&= \tilde{\mathbf{K}}\left[-\mathbf{H}_1\mathbf{a}_2 - \mathbf{H}_2\mathbf{a}_1 - \mathbf{H}_3\mathbf{a}_0 + \varepsilon_2\mathbf{I}\,\mathbf{a}_1\right]
\end{aligned} \tag{3.13}$$

and

$$\begin{aligned}
\varepsilon_1 &= 0, \\
\varepsilon_2 &= \mathbf{a}_0^T\left[\mathbf{H}_1\mathbf{a}_1 + \mathbf{H}_2\mathbf{a}_0\right], \\
\varepsilon_3 &= 0, \\
\varepsilon_4 &= \mathbf{a}_0^T\left[\mathbf{H}_1\mathbf{a}_3 + \mathbf{H}_2\mathbf{a}_2 + \mathbf{H}_3\mathbf{a}_1 + \mathbf{H}_4\mathbf{a}_0\right].
\end{aligned} \tag{3.14}$$

In general, for n^{th} order in $\delta^{1/2}$ we need energy coefficients up to ε_{n-2} and wavefunction coefficients up to $\mathbf{a}_{n-3}$. Also, the highest order Hamiltonian coefficient is $\mathbf{H}_{n-2}$ which is $\mathbf{H}'_n$ and is the $\delta^{n/2}$ order term in Eq. (2.59).

The second program, listed in Appendix B, calculates the energy and wavefunction coefficients using Eqs. (3.13) and (3.14). In the main program, qhelium.f, we start by calling the subroutine qinput.f which inputs the Hamiltonian expansion coefficients

that were calculated in the first program. Along with the expansion coefficients we input various other constants such as λ, ω_1 through ω_4, ε_∞, etc. We then calculate the harmonic order energy, ε_0, and store the harmonic order wavefunction coefficient, $\mathbf{a}_0$, as a four dimensional array with a one in location $\{n_a,\ n_s,\ n_\theta,\ \gamma\}$ and zeros everywhere else. Actually, the indices for the arrays in the FORTRAN code start at 1 and thus we put a one in location $\{n_a + 1,\ n_s + 1,\ n_\theta + 1,\ \gamma\}$ since the first three quantum numbers start at zero but the fourth, γ , starts at 1. Arrays are also created for the other wavefunction coefficients $\mathbf{a}_1$ through $\mathbf{a}_4$. Since the terms in square brackets for ε_4 are exactly those we would calculate for $\mathbf{a}_4$ we need an array for $\mathbf{a}_4$ even though we do not calculate it completely.

The next step is to call the subroutine comp_H_A.f. The first pass through this subroutine calculates the contribution of $\mathbf{a}_0$ to all higher order wavefunction coefficients. In other words, we calculate $\mathbf{H}_1\mathbf{a}_0$ and store the result in the array for $\mathbf{a}_1$: then we calculate $\mathbf{H}_2\mathbf{a}_0$ and store the result in the array for $\mathbf{a}_2$: etc. When we come out of comp_H_A.f for the first time we have the array for $\mathbf{a}_j = \mathbf{H}_j\mathbf{a}_0$ for $j > 0$. $\mathbf{a}_1$ is not yet complete and before we complete it we multiply the array for $\mathbf{a}_1$ by $\mathbf{a}_0^T$ on the left. This operation basically extracts the $\{n_a + 1,\ n_s + 1,\ n_\theta + 1,\ \gamma\}$ element of $\mathbf{H}_1\mathbf{a}_0$ which gives us $\varepsilon_1 = 0$. Next, we complete $\mathbf{a}_1$ by multiplying $\mathbf{H}_1\mathbf{a}_0$ by $-\tilde{\mathbf{K}}$ on the left. This amounts to multiplying each element of $\mathbf{H}_1\mathbf{a}_0$ by one of the elements of $\tilde{\mathbf{K}}$ but does not combine elements of $\mathbf{H}_1\mathbf{a}_0$ since $\tilde{\mathbf{K}}$ is diagonal. This completes the wavefunction $\mathbf{a}_1$.

We then pass through comp_H_A.f again and this time we calculate the contribution that $\mathbf{a}_1$ gives to every higher order wavefunction coefficient. We calculate $\mathbf{H}_1\mathbf{a}_1$ and store this in the array for $\mathbf{a}_2$ so that the array for $\mathbf{a}_2$ contains $\mathbf{H}_1\mathbf{a}_1 + \mathbf{H}_2\mathbf{a}_0$: we calculate $\mathbf{H}_2\mathbf{a}_1$ and store it in the array for $\mathbf{a}_3$: etc. Coming out of comp_H_A.f the second time we have $\mathbf{a}_j = \mathbf{H}_j\mathbf{a}_0 + \mathbf{H}_{j-1}\mathbf{a}_1$ for $j > 1$. The $\{n_a + 1,\ n_s + 1,\ n_\theta + 1,\ \gamma\}$ element of the array for $\mathbf{a}_2$ is equal to ε_2 and we complete $\mathbf{a}_2$ by first subtracting $\varepsilon_2\mathbf{I}\,\mathbf{a}_0$, which essentially sets the $\{n_a + 1,\ n_s + 1,\ n_\theta + 1,\ \gamma\}$ element equal to zero, and then multiplying the array by $-\tilde{\mathbf{K}}$. We continue this process until we calculate the final energy coefficient.

Finally, as each wavefunction is completed it is stored in memory as well as written to the hard drive, and the energy coefficients are written to a file as well. We write only the non-zero elements of the wavefunctions to disk along with the four indices that give the location of the element in the array.

One note of caution! Both FORTRAN codes are written so that the first quantum number is the anti-symmetric stretch, the second quantum number is the bend, not the symmetric stretch, and the third is the symmetric stretch. Every non-zero element of each wavefunction array corresponds to a triple product of harmonic oscillator eigenfunctions. The first index gives the quantum number for the anti-symmetric stretch, q_1, the second index gives the quantum number for the bend q_3, and the third index is for the symmetric stretch, q_2. So care must be taken when using these wavefunction files. Wavefunction summation will be discussed in the next chapter.

3.3.3.1 Wavefunction truncation and axis contraction

We now briefly discuss the memory saving techniques mentioned above. As was mentioned in Sec. (3.1.1) the wavefunction arrays have finite size. The arrays are used to construct the wavefunction coefficients from Eq. (3.1) with the upper limits of the sums being finite. The upper limits were seen to equal $m_{p_1} = n_a + 2p$, $m_{p_2} = n_s + 3p$, and $m_{p_3} = n_\theta + 3p$, where p is the order of the wavefunction coefficient. In order to be able to use a single code for several states we set $m_{p_1} = m_{p_2} = m_{p_3} = n_{\max} + 3p$, where $n_{\max}$ is perhaps 6 so that we can calculate states with quanta from zero to five without having to recompile the code. This gives array indices that range from one to $n_{\max} + 3p$ for the first three indices and from one to two for the fourth index for P^o states. For a 40^{th} order calculation, giving twenty energy coefficients, we have $p = 1, 2, \ldots, 38$. Rather than dimensioning every wavefunction array separately we dimension a single main array with dimensions $n_{\max} + 3p_{\max}$ by $n_{\max} + 3p_{\max}$ by $n_{\max} + 3p_{\max}$ by 2 by 39 to hold all wavefunction arrays (for P^o states). In the case of $p_{\max} = 38$ and quadruple precision this array takes 2156 MB of memory! Well, this is not good.

The first remedy is to take a close look at which wavefunction elements are actually required to calculate the energy coefficients. After a bit of analysis it was found that we need all wavefunction elements up to $\mathbf{a}_{p_{\max}/2}$ thereafter the required elements have maximum indices that decrease by three for each wavefunction beyond $\mathbf{a}_{p_{\max}/2}$. This only applies to the first three indices of the wavefunctions, and we are also assuming that $p_{\max}$ is even. Thus, since the maximum index for $\mathbf{a}_{p_{\max}/2}$ is $n_{\max} + 3p_{\max}/2$ and this is the largest wavefunction array then we dimension our main array as $n_{\max} + 3p_{\max}/2$ by $n_{\max} + 3p_{\max}/2$ by $n_{\max} + 3p_{\max}/2$ by 2 by 39. For $p_{\max} = 38$ and quadruple precision this array needs 312 MB of memory. That is much better.

The final memory saving technique is called axis contraction and is possible because if one holds all wavefunction indices fixed except the first, one finds that every other element is zero. This can be seen by a few examples. Appendix C contains the results of a Mathematica notebook that looks at the first few wavefunction arrays for three different states. The states are labeled by their large dimension quantum numbers for example "podd0001" is a P^o state with $n_a = n_s = n_\theta = 0$ and $\gamma = 1$.

Since the first index has every other element zero, with a little accounting we can contract this axis and reduce its dimension by a factor of 2. Then our main wavefunction array is dimensioned as above except the first dimension is $(n_{\max} + 3p_{\max}/2)/2$. For $p_{\max} = 38$ this array now needs 159 MB of memory.

The wavefunction array is the largest array in the code. By including the memory requirements of the other arrays and with the limitation of about 500 MB of usable memory in the SP2 we are able to calculate up to 56^{th} order in $\delta^{1/2}$ which gives us 27 energy coefficients for P^o states with a maximum large order quantum number $n_{\max} = 5$. For any other higher angular momentum states, due to memory restrictions, we will always get fewer energy coefficients.

This concludes the discussion of the matrix method and its implementation. In the next chapter we will discuss various results of calculations on a few P^o states and their interdimensionally degenerate D^o counterparts.

Chapter 4

Results

4.1 Introduction

In this chapter we will discuss the results of three states in particular. They are P^o states with large dimension quantum numbers $|0,0,0,1\rangle$, $|0,0,0,2\rangle$, and $|1,0,0,2\rangle$. We start with these states because the $|0,0,0,\gamma\rangle$ states are the lowest states with P^o symmetry and the state $|1,0,0,2\rangle$ will be shown to have some interesting connections to the $|0,0,0,1\rangle$ state. Specifically, in Sec. 2.3 we determined that the $|0,0,0,1\rangle$ state is a $1s2p\ ^1P^o$ state while the $|0,0,0,2\rangle$ state is a $1s2p\ ^3P^o$ state. In a similar fashion we find that the $|1,0,0,2\rangle$ state is a $2s2p\ ^1P^o$ state.

We performed a 56^{th} order perturbation calculation for each of these states yielding 27 energy coefficients (or 28 if you count ε_∞) resulting in a power series in δ to 27^{th} order. The energy coefficients are listed in tables 4.1 through 4.1.

4.1.1 Hydrogenic Energies

As a zeroth order approximation we can consider the helium atom in the independent particle model by letting $\lambda = 0$ ($Z \to \infty$). This results in the energy consisting of a sum of two hydrogenic energies. The hydrogen atom was studied by Herschbach where he found the D-dimensional energies to be given by

$$E_{N,D} = -\frac{1}{2}\frac{Z^2}{\left(k+l+1+\frac{1}{2}(D-3)\right)^2}$$

Order in δ	Coefficient in a.u.
0	-2.737769141127724147455168711194991O(0)
1	-5.551756945600749213060138000908886O(0)
2	-4.038619049752687138719675487898376 4(1)
3	9.375629652475850773343320212285813 8(1)
4	-2.509429502890261130146290248889694 2(3)
5	4.552459917578108967442554774499151 2(4)
6	-1.021964722688194384928040652652350 6(6)
7	2.430297997876153526356248391389009 3(7)
8	-6.045517523367570886045737636500889 7(8)
9	1.552512873064601672540844703841835 0(10)
10	-4.085551103299783904815506155971233 6(11)
11	1.096109342777412863197326252428354 5(13)
12	-2.987189049203979530530789789036609 5(14)
13	8.246902784029669798737498291637260 1(15)
14	-2.301292155408245805395484244599302 3(17)
15	6.477210269090682449780670588396333 2(18)
16	-1.834149312742619290279802735858720 6(20)
17	5.204617297646448491299563890109537 2(21)
18	-1.468938610305914841468312083129361 3(23)
19	4.058590893951909087749138142232418 1(24)
20	-1.056771101160697098369852573786010 7(26)
21	2.314027493299966535142700353105468 8(27)
22	-2.071502204177096942044905057500000 0(28)
23	-2.177244281601510036920390786912000 0(30)
24	2.210761385998432463571716159242240 0(32)
25	-0.145847811477777753012469425196236 80(35)
26	0.762473054954300088026787055340093 44(36)
27	-0.266102662456729260304025048925287 22(38)

Table 4.1: Energy coefficients for the $|0.0.0.1\rangle$ $1s2p\ ^1P^o$ state. The number in parentheses is the power of ten.

Order in δ	Coefficient in a.u.
0	-2.737769141127724147455168711194991O(0)
1	-6.563426951126544121662671274507256 6(0)
2	-2.711105446897587469088980936574519 2(1)
3	-6.588070221187058054327217645675779 0(1)
4	-9.341394486917727177280460175890130 7(1)
5	-9.818938351197119410573583819711434 9(2)
6	4.938511012781323584712064526978876 7(3)
7	-7.425596529367217053842379274225410 9(4)
8	9.997771806070218610921622129649564 0(5)
9	-1.345703459347029994750248174499598 8(7)
10	1.148168817772229757002206820325599 1(8)
11	2.676564105809271776948549713052413 8(9)
12	-2.429460205262787195757846590015187 0(11)
13	1.255161983524194136508126561125459 1(13)
14	-5.706854064903904301258803375338502 0(14)
15	2.475877236670642842061614220709486 7(16)
16	-1.046841660674619674430906907256030 5(18)
17	4.302439708210670882601665006531402 5(19)
18	-1.678121137615581588320189515292644 5(21)
19	5.800372145231620384776462147402763 4(22)
20	-1.360148492842765964358881472328186 0(24)
21	-3.015483521609390021037156999902343 8(25)
22	8.072102121214861197537416729031250 0(27)
23	-8.543365515381879413931165688080000 0(29)
24	7.391162445029876936339435904921600 0(31)
25	-5.835091422919272842333396616871936 0(33)
26	0.434320885584985662985022290324881 41(36)
27	-0.306582195299271774592966270860048 47(38)

Table 4.2: Energy coefficients for the $|0,0,0,2\rangle$ $1s2p\ ^3P^o$ state. The number in parentheses is the power of ten.

Order in δ	Coefficient in a.u.
0	-2.737769141127724147455168711194991O(0)
1	-3.014399084571209349544620308815147 4(0)
2	-7.311916308847629210291760198563658 4(0)
3	-6.310561218839201954144472432469474 3(2)
4	-5.610782448769765375829695028790949 1(3)
5	-7.497874538142108510662374620343997 0(4)
6	3.980941802277006734538398941015552 2(6)
7	7.408466693059015478956201643829514 5(7)
8	1.592375893542991533200902067283862 4(9)
9	-5.579664677675381640765223349980987 8(10)
10	-1.563947343955095177045099746483637 5(12)
11	-4.188617395322184635399705882668596 6(13)
12	9.236900607754739134656678851209715 7(14)
13	3.789345837865535774487246602456380 6(16)
14	1.202257226515496952451695501881459 9(18)
15	-1.468132491587706021833729113974709 4(19)
16	-9.735076292415638449285289108958386 4(20)
17	-3.576895101714428636907241457953118 (22)
18	1.434139045474030739067363160312473 8(23)
19	2.596609604071374537425720203279876 7(25)
20	1.064000327057750392811921788429687 5(27)
21	3.939784979033370232503669503750000 0(27)
22	-6.778069555171963069645934882160000 0(29)
23	-3.580387399829398520589283190323200 0(31)
24	9.842518697447061873185787899084800 0(31)
25	-0.242283803645775238840478154820157 44(35)
26	0.456945076479993356132746674336012 70(37)
27	-0.262917534158677768643341397760116 00(39)

Table 4.3: Energy coefficients for the $|1,0,0,2\rangle$ $2s2p\ ^1P^o$ state. The number in parentheses is the power of ten.

$$= -\frac{2Z^2}{(2k+2l-1+D)^2} \tag{4.1}$$

where k is the number of radial nodes, l is the angular momentum, D is the spatial dimension, Z is the nuclear charge, and $N = k + l + 1$ is the principle quantum number. At zeroth order in λ the energy of the helium atom becomes

$$E_o = -2Z^2 \left[\frac{1}{(2k_1 + 2l_1 - 1 + D)^2} + \frac{1}{(2k_2 + 2l_2 - 1 + D)^2} \right]. \tag{4.2}$$

where the subscripts denote electron 1 or 2.

Consider a $1s2p$ state. The $1s$ gives us $k = 0$ and $l = 0$ while the $2p$ gives us $k = 0$ and $l = 1$. The total energy then becomes

$$E_o = -2Z^2 \left[\frac{1}{(D-1)^2} + \frac{1}{(D+1)^2} \right].$$

We can see that there will be second order poles in the energy function when $D = +1$ and $D = -1$. The energy calculated through the matrix method gives a scaled energy, $\tilde{E}$, where

$$\tilde{E} = \frac{E}{Z^2 \delta^2},$$

and $\delta = 1/(D + \gamma_2 + 1)$. For P^o states we have $\delta = 1/(D+1)$ since $\gamma_2 = 0$ and we can write the scaled hydrogenic energy as

$$\tilde{E}_o = -2 \left[\frac{(D+1)^2}{(D-1)^2} + 1 \right];$$

where we have, in effect, factored off the second order pole at $D = -1$. Writing this in terms of δ gives

$$\tilde{E}_o = -2 \left[\frac{1}{4\left(\delta - \frac{1}{2}\right)^2} + 1 \right].$$

The energy $\tilde{E}_o$, as a function of δ, has a second order pole at $\delta = 1/2$ with a residue of $-1/2$.

As another example consider a $2s2p$ state. The $2s$ gives us $k = 1$ and $l = 0$ while the $2p$ gives us $k = 0$ and $l = 1$. The total unscaled energy then becomes

$$E_o = -4Z^2 \left[\frac{1}{(D+1)^2}\right].$$

In this case there will be a second order pole in the energy function when $D = -1$ but there is no pole for $D = +1$. Again, for P^o states we have $\delta = 1/(D+1)$ and we can write the scaled hydrogenic energy as

$$\tilde{E}_o = -4 \left[\frac{(D+1)^2}{(D+1)^2}\right] = -4.$$

By factoring off the second order pole at $D = -1$ we eliminate all "hydrogenic" poles, at zeroth order for $2s2p$ states, that might arise from treating λ as a perturbation parameter. However, other poles may arise due to singularities in the wavefunction.

Considering λ to be a perturbation parameter gives $\tilde{E}_o$, Eq. (4.2), as a zeroth order approximation to the energy. For $1s2p$ states this zeroth order approximation has a second order pole at $D = 1$ ($\delta = 1/2$) and thus we would expect the energy for helium with $\lambda \neq 0$ to have this pole structure as well since it can be "built" from this zeroth order result. This is indeed what we find, as discussed below. All of the $1s2p$ states we will discuss have poles at $D = 1$ ($\delta = 1/2$) with a residue of $-1/2$. Likewise, all of the $2s2p$ states we will discuss do not show the existence of a second order pole at $D = 1$. Table 4.1.1 lists several states along with their hydrogenic poles.

From this table it is clear that all states will have second order poles at $D = 3-2N$ and at $D = 3-2n$. For states with N or n equal to 2 the second order pole at $D = -1$ is factored out by scaling the energy by $1/\delta^2$.

Any helium wavefunction can be written as a linear combination of products of hydrogenic wavefunctions since they form a complete set. To exactly construct a helium wavefunction, an infinite number of hydrogenic wavefunctions are needed, including arbitrarily large values of the principal quantum number [58]. Thus one might expect the helium energy function to have second order poles at all negative

State	Possible Terms	Second Order Poles
$1s^2$	$^1S^e$	$D = +1$
$1s2s$	$^{1,3}S^e$	$D = +1, -1$
$1s2p$	$^{1,3}P^o$	$D = +1, -1$
$1s3s$	$^{1,3}S^e$	$D = +1, -3$
$1s3p$	$^{1,3}P^o$	$D = +1, -3$
$1s3d$	$^{1,3}D^e$	$D = +1, -3$
$\vdots$		$\vdots$
$1snl$	$^{1,3}l,\ \pi = (-1)^l$	$D = +1, 3 - 2n$
$\vdots$		$\vdots$
$2s^2$	$^1S^e$	$D = -1$
$2s2p$	$^{1,3}P^o$	$D = -1$
$2s3s$	$^{1,3}S^e$	$D = -1, -3$
$2s3p$	$^{1,3}P^o$	$D = -1, -3$
$\vdots$		$\vdots$
$2p^2$	$^1S^e, ^3P^e, ^1D^e$	$D = -1$
$2p3s$	$^{1,3}P^o$	$D = -1, -3$
$2p3p$	$^{1,3}S^e, ^{1,3}P^e, ^{1,3}D^e$	$D = -1, -3$
$2p3d$	$^{1,3}P^o, ^{1,3}D^o, ^{1,3}F^o$	$D = -1, -3$
$\vdots$		$\vdots$
Nl_1nl_2	$\cdots$	$D = 3 - 2N, 3 - 2n$
$\vdots$		$\vdots$

Table 4.4: Various hydrogenic states and their second order poles.

odd integers of D except $D = -1$. For P^o states this corresponds to second order poles at $\delta = -1/2, -1/4, -1/6, \ldots$.

4.1.2 Large Order Quantum Numbers

The energy to harmonic order is given by

$$\begin{aligned}\tilde{E} &= \varepsilon_\infty + \delta\varepsilon_0 = -\frac{1}{4r_m^2 s_m^2} + \delta\left[-\frac{3}{2r_m^2 s_m^2} + \omega_1\left(n_a + \frac{1}{2}\right)\right. \\ &\left. + \omega_2\left(n_s + \frac{1}{2}\right) + \omega_3\left(n_\theta + \frac{1}{2}\right) + \omega_4\left(n_4 + \frac{1}{2}\right)\right], \end{aligned} \tag{4.3}$$

where

$$n_4 = \frac{L + 1 - \gamma_2 - 2\gamma}{2}. \tag{4.4}$$

We have been labeling states with the three quantum numbers n_a, n_s, and n_θ along with a fourth quantum number, γ, where γ takes values given by Eq. (2.51). There is another quantum number that is useful, the T quantum number, which is given by

$$T = L + 1 - \gamma. \tag{4.5}$$

As discussed in Ref. [5] and above on page 20, this quantum number is identified as the same T quantum number as in the work of Herrick, Stillinger, Kellman, and others (see Refs. [37, 48, 59, 60]). It is identified as the modulus of the projection of the angular momentum about the inter-electron axis. The internal state of the atom is determined more explicitly when we introduce this quantum number along with the number of quanta in the antisymmetric stretch, symmetric stretch and bend normal modes. For $D = 3$, singly excited states are identified by $T = 0$ (see Eq. (1.16)) and for doubly excited states T can take values given by

$$\begin{aligned} 0 \;&\leq\; T \leq L \text{ when } \pi = (-1)^L \text{ and} \\ 1 \;&\leq\; T \leq L \text{ when } \pi = (-1)^{L+1}. \end{aligned} \tag{4.6}$$

From Eq. (2.51) we had that γ ranges from 1 to $L + 1$ for states with $\pi = (-1)^L$ and from 1 to L for states with $\pi = (-1)^L$; thus, as we move down the column vector $\mathbf{G}_0$ for the harmonic order wavefunction, γ increases from 1 to $L + 1$ or L while T decreases from L to 0 or 1 respectively. For P^o states γ equals 1 or 2 while T equals 1 or 0 respectively. Hence, the state $|0, 0, 0, 1\rangle$ is a $T = 1$ state while the states $|0, 0, 0, 2\rangle$ and $|1, 0, 0, 2\rangle$ are $T = 0$ states. This seems to suggest that the $|0, 0, 0, 1\rangle$ state is doubly excited, but we identified it with the $1s2p\ ^1P^o$ state simply summing the expansion for its energy and evaluating it at $D = 3$. We must remember that the quantum numbers $\{n_a, n_s, n_\theta, \gamma\}$ are large D quantum numbers. Thus when $D = 3$, the state's character may change if it is somehow connected or mixed with

some other state. Also, it seems that the state $|1.0.0.2\rangle$ could be singly excited but by comparing its energy with that of the $2s2p\ ^1P^o$ we find that it is definitely a doubly excited state. It turns out that there is a connection between the $|0.0.0.1\rangle$ state and the $|1.0.0.2\rangle$ state. Before we discuss this connection we describe how the energy series are summed and how we deal with the pole structure mentioned above.

4.2 Energy Summation

The energy series obtained are divergent so we can not simply sum them in the usual way. Instead we use linear Padé approximants to sum the energy series. Padé approximants are ratios of polynomials in the expansion parameter δ. The "diagonal sequence" consists of the Padé approximants whose numerator and denominator are polynomials up to order n in δ, denoted $[n/n]$. Similarly, off-diagonal sequences are labeled $[n/n+1]$, $[n+1/n]$, etc. Due to the presence of the polynomial in the denominator the Padé approximants can model poles of the energy function, poles that may be plotted on the complex δ plane. Also, by arranging poles and zeros in a particular way in the complex δ plane, Padé approximants can even model more complicated singularities such as square-root branch points and essential singularities [61].

More specifically, the $[L/M]$ Padé approximant, $S_{[L/M]}$, is given by the rational function

$$S_{[L/M]}(\delta) = \frac{\sum_{n=0}^{L} A_n\, \delta^n}{\sum_{n=0}^{M} B_n\, \delta^n}. \tag{4.7}$$

with the choice of $B_0 = 1$. The remaining $L + M + 1$ coefficients are determined so that the first $L + M + 1$ terms in the Taylor series expansion of the Padé approximant match the first $L + M + 1$ terms of the series we are trying to sum. Equivalently, Padé approximants are constructed with the requirement that

$$Q\,E - P \sim 0.$$

where E is the energy series, P is the numerator in Eq. (4.7) and Q is the denominator. The "~ 0" means asymptotic to 0 up to and including order $L + M$ so that the energy series E is asymptotic to the Padé approximate $S_{[L/M]}$.

In addition, a quadratic Padé approximant may be constructed by introducing a third polynomial, R, of order N with the requirement

$$Q\,E^2 - P\,E + R \sim 0.$$

where "~ 0" means asymptotic to zero up to and including order $L + M + N + 1$. The energy is then asymptotic to the quadratic Padé approximant $S_{[L/M/N]}$ given by

$$S_{[L/M/N]} = \frac{1}{2}\left(\frac{P}{Q} + \frac{(P^2 - 4Q\,R)^{1/2}}{Q}\right). \tag{4.8}$$

The square root term in the quadratic approximant means that $S_{[L/M/N]}$ is a multivalued function with two branches. Summing the energy series with a quadratic approximant will give energy values on only one branch corresponding to the energy of a particular state while the other branch might correspond to a different state. We will not use the quadratic approximants to actually sum the energy series but rather to locate possible square root branch points that may result from Fermi Resonances as discussed in Sec. 1.6.6 and below.

Initial summation of the energy series gives somewhat poor results with slow, or even no, convergence. We can accelerate and improve the convergence of the Padé approximants by analyzing the singularity structure of the energy series as modeled by the approximants. Poles are modeled by the roots of the polynomial Q. A pole that we can consider to be real is one that is present in a series of Padé approximants and remains stable, i.e. in the same location in the complex δ plane, as L and M are varied in a smooth manner.

For the $|0.0.0.1\rangle$ and $|0.0.0.2\rangle$ states it was found that the Padé approximants were placing a second order pole at $\delta = 1/2$ ($D = 1$). The placement of this pole agrees with the discussion of poles in the hydrogenic energy function as discussed

above. If we multiply the energy series by the factor $(\delta - 1/2)^2$ and sum the resulting series at $\delta = 1/2$ we determine that the residue of the second order pole at $\delta = 1/2$ is equal to $-1/2$. Finally we subtract, from the original energy series, the term $-\frac{1}{2}\frac{1}{(\delta-1/2)^2}$, essentially subtracting off the pole at $\delta = 1/2$ ($D = 1$). This new series sums much better agreeing with other results to four decimal places (five significant figures) for both P^o states under consideration.

We can do better by again looking at the singularity structure of the Padé approximants after having subtracted off the pole at $\delta = 1/2$ ($D = 1$). For both the $|0.0.0.1\rangle$ and $|0.0.0.2\rangle$ states the Padés place a first order pole at $\delta = -1/2$ ($D = -3$). Previous work by Doren and Herschbach[43], and the discussion in Sec. 4.1.1, has shown that we should expect a second order pole at $D = -3$ but rather we find a first order pole! In a similar manner we determine the residue (from the $[n + 1/n]$ Padé) of this pole and subtract it. The numbers we obtain give us one additional decimal place of agreement. The results for the $1s2p\ ^{1,3}P^o$ states and their interdimensionally degenerate counterparts, the $2p3d\ ^{3,1}D^o$ states respectively, are shown in Table 4.2.

State		Energy (au)	Reference
1s2p $^3P^o$		-2.133 162 4	
		-2.133 164 19	[62]
1s2p $^1P^o$		-2.123 843 0	
		-2.123 843 08	[62]
2p3d $^1D^o$	${}_n(K,T)^A_N = {}_2(0.1)^0_3$	-0.563 800 39	
		-0.563 800 40	[63]
2p3d $^3D^o$	${}_n(K,T)^A_N = {}_2(0.1)^0_3$	-0.559 328 260	
		-0.559 328 25	[63]
2s2p $^1P^o$		-0.696 3	
		-0.694 17	[64]
		-0.693 13	[65]
$N = 3\ ^3D^o$		-0.294 13	

Table 4.5: Energies of the $^{1,3}P^o$ and $^{1,3}D^o$ states calculated from 27^{th} order Padé summation along with energies calculated elsewhere.

Summing the series for the $|1,0.0.2\rangle$ state proved to be a bit more problematic. As discussed in Sec. 4.1.1 there was no evidence of a pole at $\delta = 1/2$ ($D = 1$). After

some analysis there seemed to be a fairly stable first order pole at $\delta = 1/10$ and the residue seemed to converge at about 0.0121. After subtracting this pole we found no remaining stable poles on the positive real δ axis, however there did seem to be a somewhat stable first order pole near $\delta = -0.15$ with a residue of 0.0309. After subtracting these two poles there remained no lone stable poles but many stable pole-zero pairs and the energy was still not converging well. The energy seemed to want to converge to about -0.7354 or so. This energy is midway between the $2s2p\ ^1P^o$ and $2s2p\ ^3P^o$ states [64, 65] and we expect the $|1,0,0,2\rangle$ state to be a singlet (see Eq. (2.53)).

The presence of stable pole-zero pairs in the Padé approximants is a sign of a possible branch cut connecting two branch points of the energy function. Recall that for S-wave states, branch points arose from the presence of Fermi Resonances where two states were degenerate at zeroth order for some value of λ. Let's look at possible Fermi Resonances that might connect the $|1,0,0,2\rangle$ state with some other state.

4.3 Fermi Resonances

As we did for S-wave states in Sec. 1.6.6 we again consider the harmonic order energy coefficient

$$\varepsilon_0 = -\frac{3}{2r_m^2 s_m^2} + \omega_1\left(n_a + \frac{1}{2}\right) + \omega_2\left(n_s + \frac{1}{2}\right) + \omega_3\left(n_\theta + \frac{1}{2}\right) + \omega_4\left(n_4 + \frac{1}{2}\right).$$

where

$$n_4 = \frac{L + 1 - \gamma_2 - 2\gamma}{2} = 1 - \gamma \qquad \text{for } P^o \text{ states.} \tag{4.9}$$

The harmonic frequencies ω_1, ω_2, and ω_3 are identical to the S-wave frequencies but now we have an additional frequency ω_4 that may bring about a more complex spectrum of Fermi resonances when it is commensurate with the original frequencies. Figure 4.1 is a plot of these frequencies as functions of λ. We see very clearly that for a particular value of λ, $\lambda = \lambda^* = 0.755929$, $\omega_1 = \omega_4$. We will find $\varepsilon_0 = \varepsilon_0'$ for states with quantum numbers $\{n_a, n_s, n_\theta, n_4\}$ and $\{n_a', n_s', n_\theta', n_4'\}$ when $n_s = n_s'$

and $n_\theta = n'_\theta$ (since the ratio of ω_2 and ω_3 is not a rational number in this case) and $n_a + n_4 = n'_a + n'_4$. From Eq. (4.9) we must have

$$n_a - \gamma = n'_a - \gamma'$$

for a $\omega_1 : \omega_4 = 1 : 1$ Fermi Resonance. Thus, in general, the harmonic order energies will be degenerate when $\lambda = 0.755929$ for the states $|n_a, n_s, n_\theta, \gamma\rangle$ and $|n_a \pm 1, n_s, n_\theta, \gamma \pm 1\rangle$ remembering that, for P^o states, the quantum number $\gamma = 1$ or 2 which implies that only pairs of states will be degenerate.

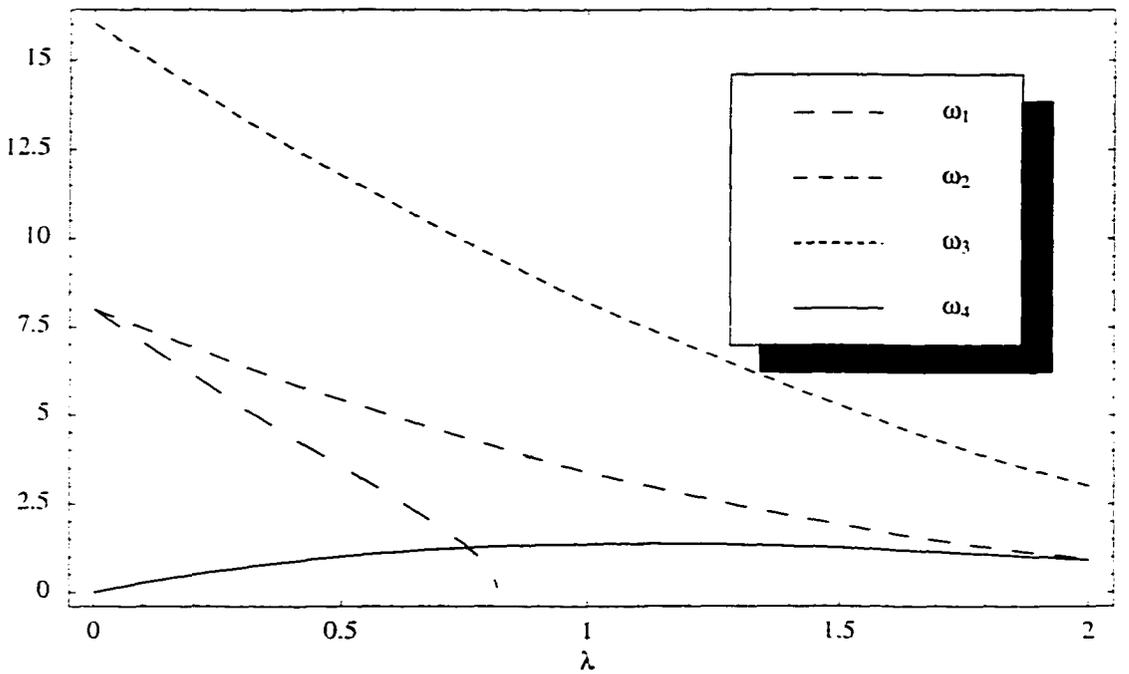


Figure 4.1: ω_1, ω_2, ω_3, and ω_4 as functions of λ.

The states $|0, 0, 0, 1\rangle$ and $|1, 0, 0, 2\rangle$ are such that they are degenerate at the $1 : 1$ Fermi Resonance. Figure 4.2 is a plot of the harmonic order energies for ${}^1P^o$ states verses λ. As can be seen from the figure there are several other Fermi Resonances corresponding to the many possible combinations of commensurate harmonic frequencies. We also plot the harmonic order energies for ${}^3P^o$ states in Fig. 4.3.

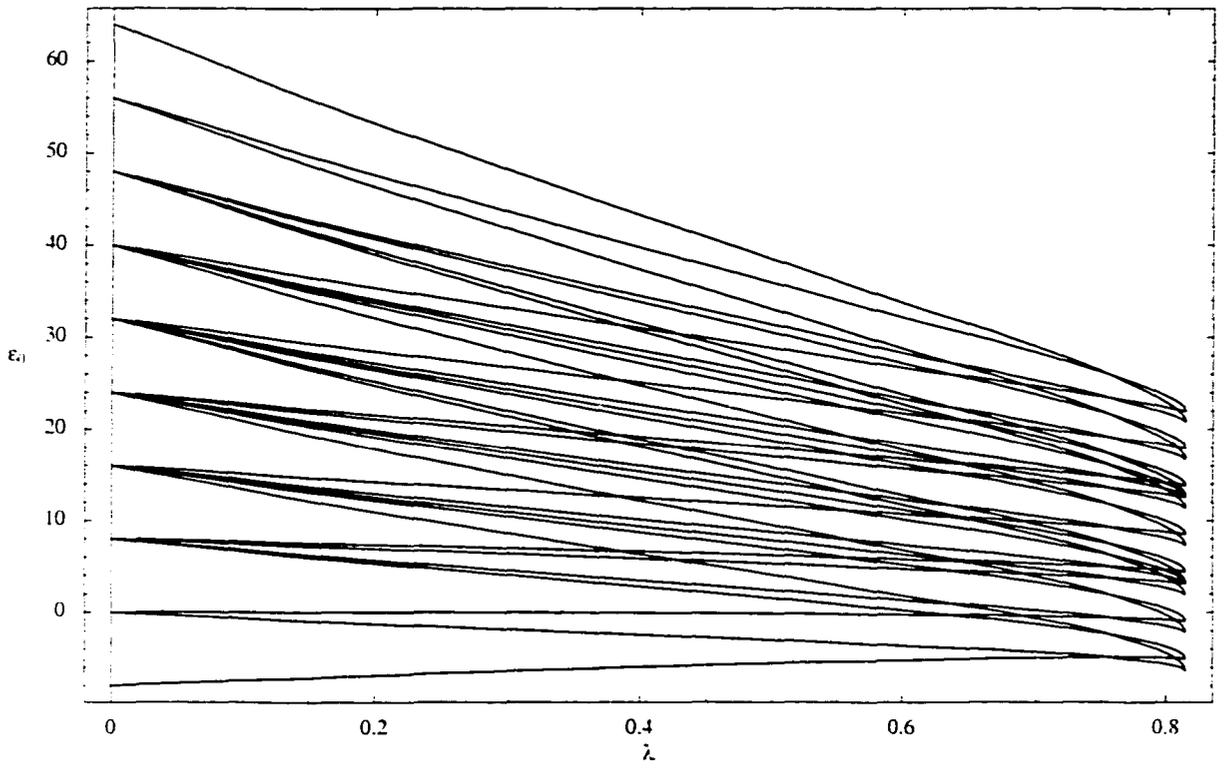


Figure 4.2: Harmonic order energies as functions of λ for ${}^1P^o$ states. The order of the states from lowest to highest is $|0001\rangle$, $|1002\rangle$, $|0101\rangle$, $|2001\rangle$, $|1102\rangle$, etc. at $\lambda = 0.2$. Notice the degeneracy at $\lambda = 0.755929$ for the $|0001\rangle$ and $|1002\rangle$ states.

With the knowledge of a Fermi Resonance between the $|0,0,0,1\rangle$ and $|1,0,0,2\rangle$ states we would expect to find one or two square-root branch points at the same location(s) in the complex δ plane for both states. Furthermore, as $\lambda \rightarrow 0.755929$ the branch-point(s) should move toward the origin. The branch points can be found by calculating the quadratic Padé approximants, $S_{[L/M/N]}$, of each energy series and plotting the discriminant polynomial, $P^2 - 4QR$. As we vary L, M, and N in a regular way we look for branch points that remain stable.

Analysis of the $|1,0,0,2\rangle$ state gives a single branch point on the negative real δ-axis at $\delta_c = -0.032$ for $\lambda = 0.5$. As λ is increased toward 0.75 this branch point moves toward the origin. There is also a complex conjugate pair of branch points at $+0.0165 \pm 0.0249I$ that also converge toward the origin as λ increases. Analysis of

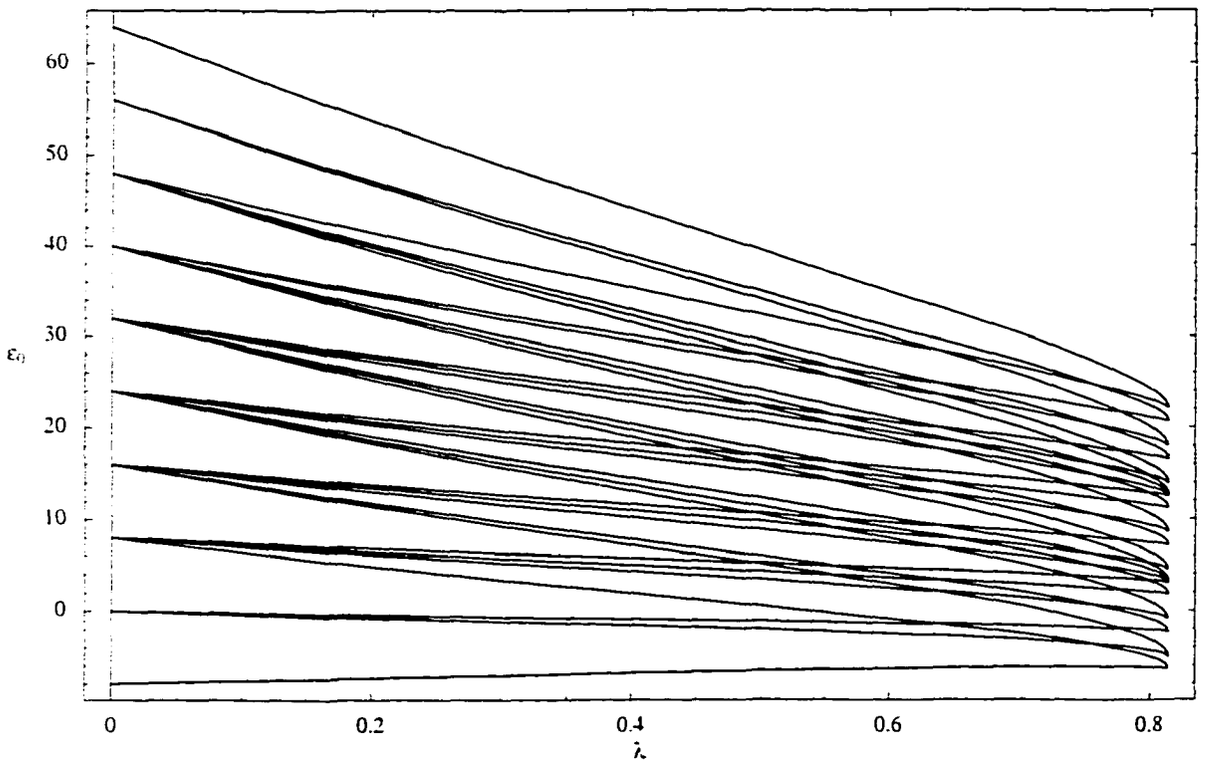


Figure 4.3: Harmonic order energies as functions of λ for ${}^3P^o$ states. The order of the states from lowest to highest is $|0002\rangle$, $|1001\rangle$, $|0102\rangle$, $|2002\rangle$, $|1101\rangle$, etc. at $\lambda = 0.2$. Notice there are no states degenerate with the $|0002\rangle$ state.

the $|0,0,0,1\rangle$ state also shows a stable single branch point at $\delta_c = -0.032$ but no other stable complex conjugate pairs.

It would seem that these two states are connected, due to a Fermi-type Resonance, by the branch point at $\delta_c = -0.032$. Thus, the energy function for each state is actually part of a single two-valued function evaluated on one of its Riemann sheets. Usually one finds a pair of branch points with a branch cut connecting them. There were no other stable branch points common to these two states but perhaps the second branch point is too far from the origin for the Padés to model accurately.

As was discussed in Sec. 1.6.6, the presence of branch points being shared by two energy functions suggests that the corresponding states will exchange character as one goes from large D to $D = 3$. This exchange of character usually comes about by the presence of an avoided crossing. Thus, one can relate the presence of stable

square root branch points to the presence of avoided crossings and therefore to the conclusion that the state will change character as one varies D from large D to the physical $D = 3$.

Another verification that each energy function is a single branch of a two-valued function is by adding the two energy series and seeing if the branch point is still present. As mentioned previously, when two energy functions are each a single branch of a two-valued function they can be written as

$$E_{0001}(\delta) = f(\delta) + g(\delta)\sqrt{\delta - \delta_c}$$

and

$$E_{1002}(\delta) = f(\delta) - g(\delta)\sqrt{\delta - \delta_c}.$$

If we add these two functions

$$E(\delta) = E_{0001}(\delta) + E_{1002}(\delta)$$

and analyze the branch point structure we should no longer see the branch point at δ_c. This is exactly what is found when we add the energy series of the $|0.0.0.1\rangle$ and $|1.0.0.2\rangle$ states. The branch point at $\delta_c = -0.032$ is removed thus validating the assumption that these two states are single, separate branches of a two-valued function.

Furthermore, with the function $E(\delta)$ no longer having a branch point on the negative real axis perhaps it will sum better than the $|1.0.0.2\rangle$ state did alone. We first looked at the pole structure of $E(\delta)$ and found a second order pole at $\delta = 1/2$ with a residue of approximately $-1/2$ as well as a first order pole at $\delta = 0.1$ with a residue of about 0.0131. When these poles were subtracted the remaining series summed much better and converged to $E(\delta = 1/4) = -2.8201$ a.u. (We evaluated the energy at $\delta = 1/4$ because for P^o states $\delta = 1/(D+1)$). Now by subtracting the energy of the $|0.0.0.1\rangle$ state, $E_{0001}(1/4) = -2.123843$ a.u. we find an energy for the $|1.0.0.2\rangle$ state of $E_{1002}(1/4) = -0.6963$ a.u. This energy is in much better

agreement with the $2s2p\ ^1P^o$ state found in the literature. Also, we can sum $E(\delta)$ at $D = 5$ ($\delta = 1/6$) to find an energy for the interdimensionally degenerate $^3D^o$ state. We find $E(1/6) = -0.85346$ a.u. and after subtracting off the energy of the $^3D^o$ state that is interdimensionally degenerate with the $|0,0,0,1\rangle$ state we find $E_{1002}(1/6) = -0.294132$. I have not yet found a state in the literature to compare this to but it seems to lie below the $N = 3$ threshold. The energies discussed above are listed in Table 4.2.

Finally, we mentioned in Sec. 4.1.2 that, for large D, the $|0,0,0,1\rangle$ state is a $T = 1$ state, while the $|1,0,0,2\rangle$ state is a $T = 0$ state. We also mentioned that all singly excited states are $T = 0$ states. Therefore, since the $|0,0,0,1\rangle$ state sums to a singly excited state at $D = 3$ either our designation for the T quantum number is wrong or the $|0,0,0,1\rangle$ state must change character from a $T = 1$ state at large D to a $T = 0$ state at small D. From the above branch point analysis it is clear that the $|0,0,0,1\rangle$ state exchanges character with the $|1,0,0,2\rangle$ state becoming a $T = 0$ state while the $|1,0,0,2\rangle$ state becomes a $T = 1$ state. The exchange of character can also be seen through wavefunction analysis which will be considered in the next section.

4.4 Wavefunction Summation

In this final section we will consider only wavefunctions of P^o states. As discussed in Sec. 2.2.1 the wavefunction can be written as

$$\Psi^{L,\pi} = \left[\mathbf{W}^{L,\pi}\right]^T \mathbf{F}^{L,\pi}$$

where

$$\mathbf{F}^{L,\pi} = \begin{pmatrix} F_1 \\ \pm F_2 \end{pmatrix} \qquad \text{and} \qquad \mathbf{W}^{L,\pi} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \end{pmatrix}.$$

We then substituted this wavefunction into the Schrödinger equation to obtain a matrix differential equation for the function $\mathbf{F}^\Gamma$ whose components are functions only

of the internal coordinates. After a few coordinate transformations and the equivalence transformation of Eq. (2.43) we obtained the wavefunction $\mathbf{G}^{L,\pi}$. perturbation equations

$$\sum_{l=0}^{p} (\mathbf{H}_l - \varepsilon_l \mathbf{I}_x)\, \mathbf{G}_{p-l} = \mathbf{0} \qquad p = 0.1, 2. \ldots$$

Like $\mathbf{F}^{\Gamma}$. $\mathbf{G}^{L,\pi}$ is a column vector whose components are functions only of the internal coordinates. The components of $\mathbf{G}^{L,\pi}$ are then expanded in a power series in $\delta^{1/2}$ which can be written as

$$\mathbf{G}^{L,\pi} = \sum_{p=0}^{\infty} \delta^{\frac{p}{2}} \mathbf{G}_p^{L,\pi},$$

where $\mathbf{G}_p^{L,\pi}$ is also a column vector. Expanding the Hamiltonian in powers of $\delta^{1/2}$ allowed us to derive a set of perturbation equations with which to solve the components of $\mathbf{G}^{L,\pi}$. Implementation of the matrix method results in each component. $\mathbf{G}_p^{L,\pi}$. being a sum of triple products of harmonic oscillator eigenfunctions. Each triple product can be designated as$|\nu_1, \nu_2, \nu_3\rangle$

$$|\nu_1, \nu_2, \nu_3\rangle = h_{\nu_1}\left(\omega_1^{1/2} q_1\right) h_{\nu_2}\left(\omega_2^{1/2} q_2\right) h_{\nu_3}\left(\omega_3^{1/2} q_3\right).$$

Consider the following example. For all P^o states. $\mathbf{G}^{L,\pi}$ has two components labeled by either $\gamma = 1$ for the top component or $\gamma = 2$ for the bottom component. The zeroth order component, $\mathbf{G}_0^{L,\pi}$, tor the state $|0.0.0.1\rangle$ starts out with the triple product $|0.0.0\rangle$ in the top component and nothing in the bottom component. When the first order wavefunction is calculated we find that the top component contains

$$0.697\,|210\rangle - 0.477\,|010\rangle + 0.287\,|030\rangle + 0.163\,|201\rangle + \text{ smaller terms.} \qquad (4.10)$$

while the bottom component contains

$$-3.425\,|100\rangle.$$

Higher order corrections contain more terms but result in a similar sum.

We sum these terms by doing a point-by-point summation. We first choose a value for $\{r_1, r_2, \theta\}$, then transform to normal coordinates $\{q_1, q_2, q_3\}$. We then evaluate all the relevant triple products that come in at all orders that we are concerned with. For a given order we add the triple products multiplied by their coefficients (Eq. (4.10)). At this point we have a power series expansion in δ for a single point in $\{r_1, r_2, \theta\}$ space. We then either do a Padé summation, or a straight summation, and evaluate the result at $D = 3$ or whatever dimension we are interested in.

For the $|0,0,0,1\rangle\ ^1P^o$ state we plot, in Figs. 4.4, the top component of the wavefunction for various values of dimension using straight summation through third order in $\delta^{1/2}$. At large dimension the top component has large electron density on the $r_1 = r_2$ potential ridge, indicative of a doubly excited state. But, as dimension is reduced toward $D = 3$ the single lobe splits into two lobes. They fall off the potential ridge much like singly excited states. Thus the $|0,0,0,1\rangle\ ^1P^o$ state changes character from doubly excited to singly excited as D goes from infinity to 3.

The bottom component of the $|0,0,0,1\rangle\ ^1P^o$ state is shown in Fig. 4.5. These plots are also straight summations through third order in $\delta^{1/2}$. Notice how, even at large D, the bottom component shows singly excited character. In fact, the bottom component is the $T = 0$ component and singly excited states are $T = 0$ states.

Similarly, Fig. 4.6 shows the evolution of the top component of the $|1,0,0,2\rangle\ ^1P^o$ state. These plots are straight summations through third order in $\delta^{1/2}$. For large D this state starts out looking doubly excited and remains looking doubly excited as $D \to 3$. But, if we look at Fig. 4.7, we see that the bottom component looks like a singly excited state for all D! With a little care we can compare the relative sizes of the top and bottom components and we find that as $D \to 3$ the top component becomes larger than the bottom component. This suggests that the $|1,0,0,2\rangle$ state has more $T = 1$ character at $D = 3$ than it had for large D. This is further evidence that the $|0,0,0,1\rangle$ and $|1,0,0,2\rangle$ states exchange character as we go from large D to $D = 3$.

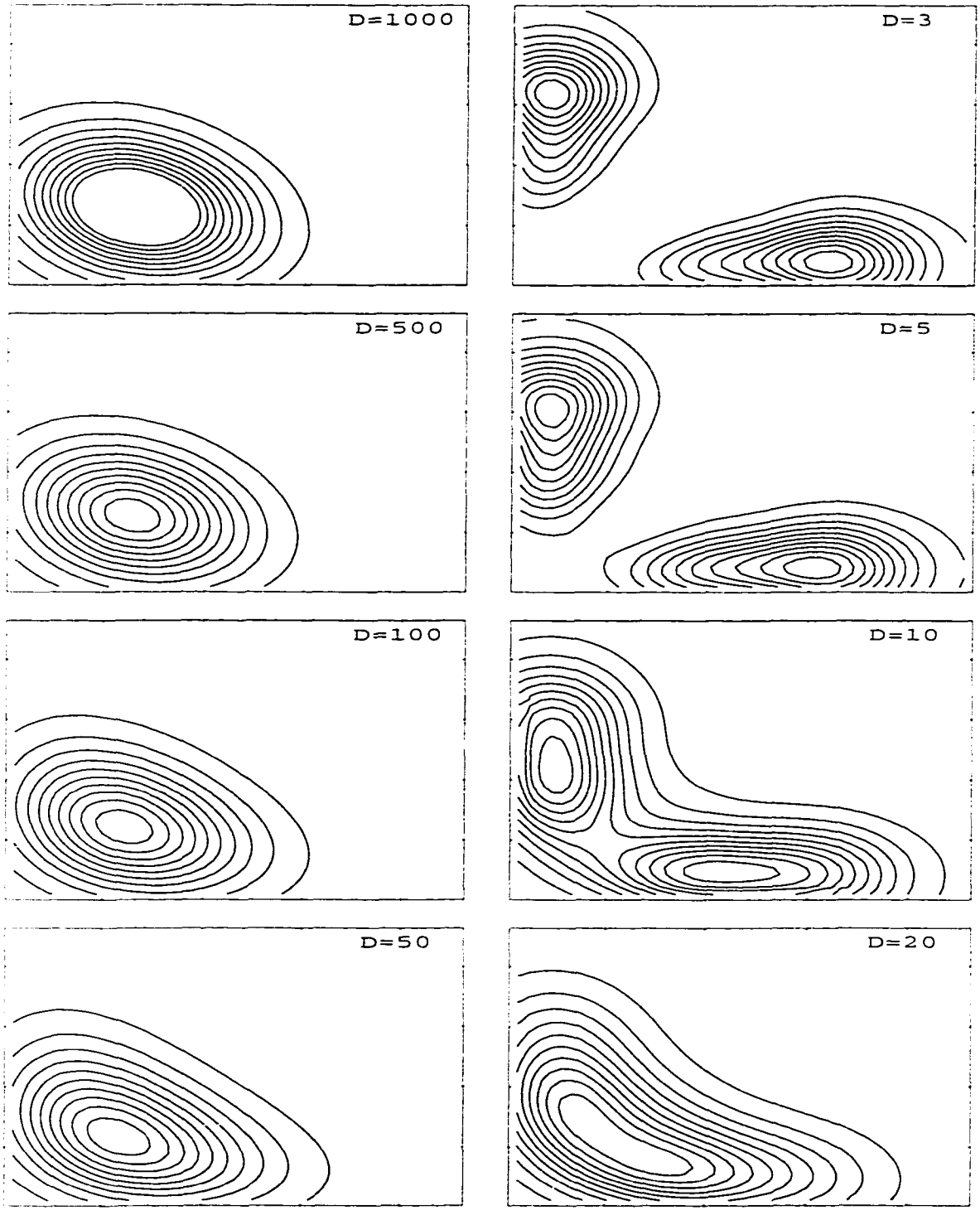


Figure 4.4: The top component for the state $|0,0,0,1\rangle$. The horizontal axis is $\tilde{r}_1$ and the vertical axis is $\tilde{r}_2$, ranging from 0 to 10/9.

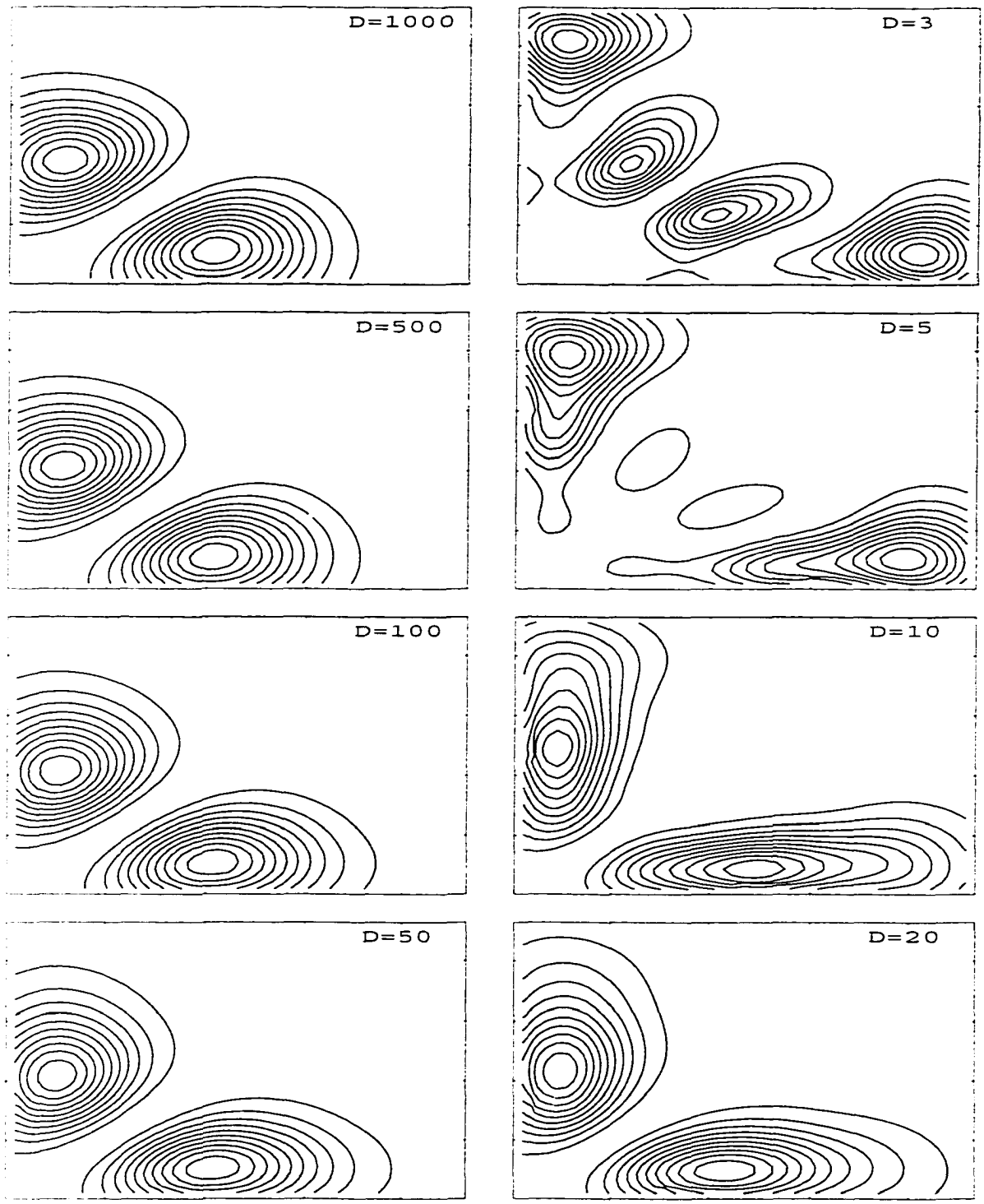


Figure 4.5: The bottom component for the state $|0, 0, 0.1\rangle$. The horizontal axis is $\tilde{r}_1$ and the vertical axis is $\tilde{r}_2$, ranging from 0 to 10/9.

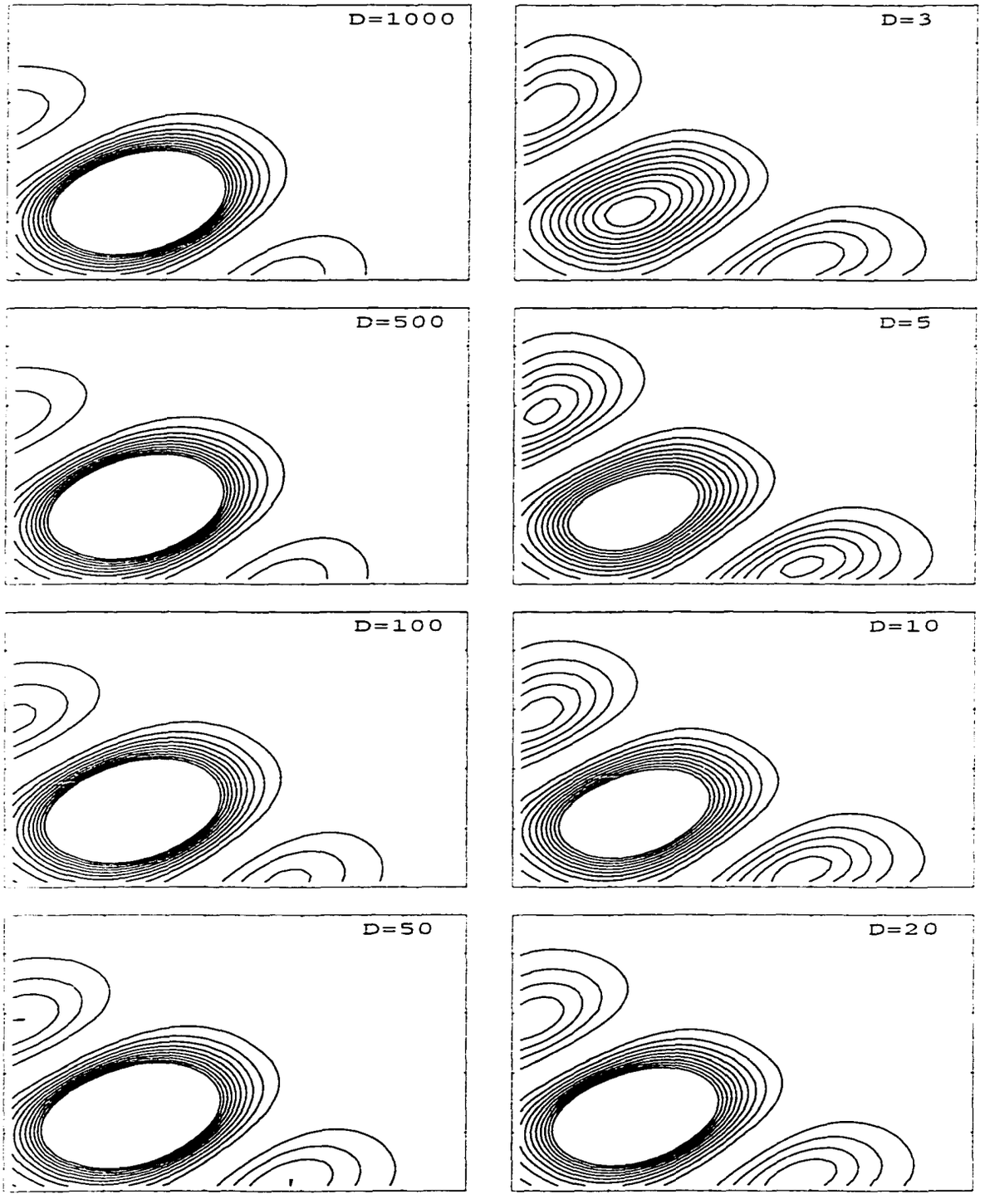


Figure 4.6: The top component for the state $|1,0,0,2\rangle$. The horizontal axis is $\tilde{r}_1$ and the vertical axis is $\tilde{r}_2$, ranging from 0 to 10/9.

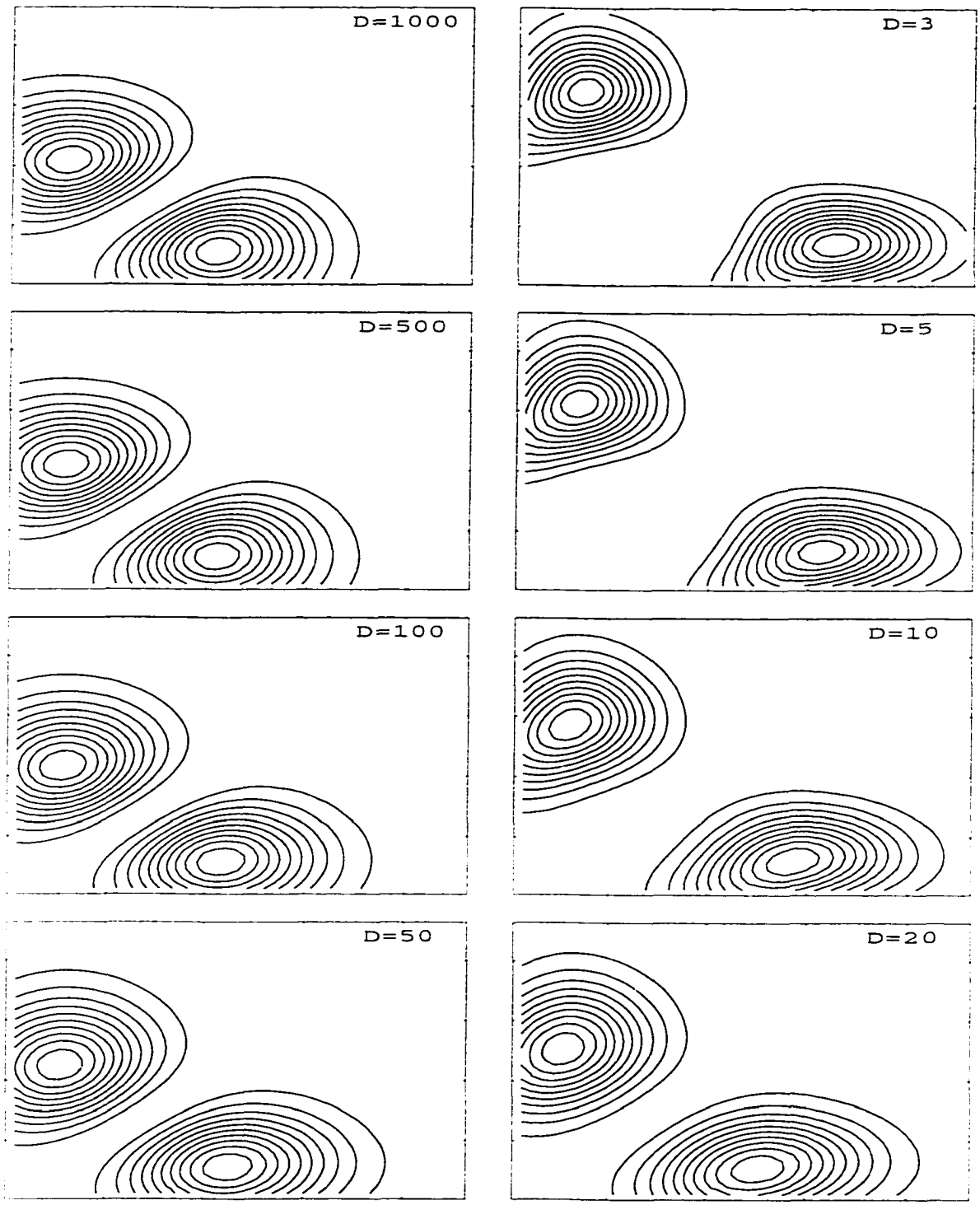


Figure 4.7: The bottom component for the state $|1,0,0,2\rangle$. The horizontal axis is $\tilde{r}_1$ and the vertical axis is $\tilde{r}_2$, ranging from 0 to 10/9.

Chapter 5

Conclusions

This work has extended previous work on the helium atom by enabling one to calculate not only S-wave states but in addition, any state with any total orbital angular momentum. Thus we can now calculate the entire spectrum of the helium atom including bound states as well as resonances. Advantages of dimensional perturbation theory over other methods include having electron correlation present at lowest order, being able to calculate wavefunctions without any additional work than that required to calculate energy coefficients, and there is no need to truncate a wavefunction expansion since, at each order in $\delta^{1/2}$, the wavefunction expansion is exact. The wavefunction expansion at each order in $\delta^{1/2}$ is a finite sum of triple products of Hermite polynomials.

Calculating the wavefunctions via the matrix method makes it relatively easy to calculate expectation values. An operator would be expressed in terms of the normal coordinates q_i, and possibly their derivatives, which would then be expressed as matrices. Like the Hamiltonian, the operator would become a rank-8 tensor and the expectation value would be a contraction of this operator with a wavefunction on the right followed by contraction of the wavefunction's transpose on the left.

This research has demonstrated the validity of the higher angular momentum methods developed by Watson and Dunn. The results obtained for the lowest lying states of P^o symmetry are quite satisfying in light of the complexity of the formalism. This gives one hope for the success of future calculations of yet higher angular

momentum states. Not only does this research validate the formalism for the two-electron atom, but gives us confidence that the formalism is correct for N-electron atomic states with arbitrary angular momentum as well.

Work that can now easily be accomplished is the calculation of any state of the helium atom with the only limitation being computer memory and round-off error. To help with this problem it is the author's intention to eventually write the code in parallel. Other projects that can now be considered are the following. Develop a better understanding of the K, T, and A quantum numbers since our DPT approach starts with an inherently molecular-like atom which is known to describe doubly excited states well. We hope to better understand the presence of the rotor series which is obtained when one keeps all quantum numbers fixed but increases L. And finally one can also expand about a different point in the potential to be able to calculate resonance widths.

There are many more possibilities for further study using DPT on the helium atom. One can also try to apply this formalism to completely different systems such as Bose-Einstein condensates or quantum dots. In fact, this work has begun and hopefully DPT as applied to these systems will be as fruitful as it was for the helium atom.

Reference List

[1] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 516 (1963).

[2] M. Dunn and D. K. Watson, Ann. Phys. (N.Y.) **251**, 266 (1996).

[3] M. Dunn and D. K. Watson, Ann. Phys. (N.Y.) **251**, 319 (1996).

[4] M. Dunn and D. K. Watson, Few Body Syst. **21**, 187 (1996).

[5] M. Dunn and D. K. Watson, Phys. Rev. A **59**, 1109 (1999).

[6] C. Schwartz, Phys. Rev. **123**, 1700 (1961).

[7] G. Breit, Phys. Rev. **35**, 1930 (569).

[8] M. Dunn *et al.*, J. Chem. Phys. **101**, 5987 (1994).

[9] T. C. Germann, Ph.D. thesis, Harvard University, 1995.

[10] N. Bohr, Philos. Mag. **26**, 476 (1913).

[11] J. Mehra and H. Rechenberg, *The Historical Development of Quantum Theory* (Springer-Verlag, Heidelberg, 1982).

[12] W. Heisenberg, Z. Phys. **39**, 499 (1926).

[13] A. Unsold, Ann. Phys. **82**, 355 (1927).

[14] J. C. Slater, Proc. Natl. Acad. Sci. **13**, 423 (1927).

[15] G. W. Kellner, Z. Phys. **44**, 91 (1927).

[16] E. A. Hylleraas, Z. Phys. **48**, 469 (1928), ; Hylleraas, E. A., *ibid.* **54**, 347 (1929).

[17] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).

[18] J. G. Leopold and I. C. Percival, J. Phys. B **13**, 1037 (1980).

[19] J. G. Leopold, I. C. Percival, and A. S. Tworkowski, J. Phys. B **13**, 1025 (1980).

[20] G. Tanner, K. Richter, and J. M. Rost, Rev. Mod. Phys. **72**, 497 (2000).

[21] G. W. F. Drake, in *Atomic, Molecular, and Optical Physics Handbook* (AIP Press, ADDRESS, 1996), Chap. 11.

[22] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).

[23] K. Frankowski and C. L. Pekeris, Phys. Rev. **146**, 46 (1966). : **150**, 366(E) (1966).

[24] D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).

[25] J. M. Feagin and J. S. Briggs, Phys. Rev. Lett. **57**, 984 (1986).

[26] G. D. Doolen, J. Nuttall, and R. W. Stagat, Phys. Rev. A **10**, 1612 (1974).

[27] Y. K. Ho, Phys. Rev. A **34**, 4402 (1986).

[28] Y. K. Ho, Z. Phys. D: At. Mol. Clusters **11**, 277 (1989).

[29] K. Richter and D. Wintgen, J. Phys. B **24**, L565 (1991).

[30] K. Richter, J. S. Briggs, D. Wintgen, and E. A. Solov'ev, J. Phys. B **25**, 3929 (1992).

[31] A. Burgers, D. Wintgen, and J.-M. Rost, J. Phys. B **28**, 3163 (1995).

[32] J. M. Rost, K. Schulz, M. Domke, and G. Kaindl, J. Phys. B **30**, 4663 (1997).

[33] D. L. Knirk, J. Chem. Phys. **60**, 66 (1974). ;**60**, 760 (1974).

[34] H. Klar, J. Phys. A **18**, 1561 (1985).

[35] J. Macek, J. Phys. B **1**, 831 (1968).

[36] C. D. Lin, Physics Reports **257**, 1 (1995).

[37] C. D. Lin, Phys. Rev. A **29**, 1019 (1984).

[38] D. R. Herrick and Sinanoglu, Phys. Rev. A **11**, 97 (1975).

[39] *Dimensional Scaling in Chemical Physics*, edited by D. R. Herschbach, J. Avery, and O. Goscinski (Kluwer Academic, Dordrecht, 1993).

[40] M. Dunn and D. K. Watson, J. Phys. Chem. **97**, 2457 (1993).

[41] D. R. Herschbach, J. G. Loeser, and D. K. Watson, Z. Phys. D **10**, 195 (1988).

[42] D. J. Doren and D. R. Herschbach, Phys. Rev. A **34**, 2665 (1986).

[43] D. J. Doren and D. R. Herschbach, Phys. Rev. A **34**, 2654 (1986).

[44] D. R. Herschbach, in *Dimensional Scaling in Chemical Physics* (Kluwer Academic, Dordrecht, 1993), Chap. 2.

[45] M. J. M. Hill, Trans. Cambridge Philos. Soc. **13**, 36 (1883).

[46] D. K. Watson and D. Z. Goodson, Phys. Rev. A **51**, R5 (1995).

[47] J. G. Loeser and D. R. Herschbach, J. Chem. Phys. **84**, 3882 (1986).

[48] D. R. Herrick, Adv. Chem. Phys. **52**, 1 (1983).

[49] D. R. Herrick, J. Math. Phys. **16**, 281 (1975).

[50] D. R. Herrick and F. H. Stillinger, Phys. Rev. A **11**, 42 (1975).

[51] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods For Scientists and Engineers* (McGraw-Hill, New York, 1978).

[52] M. Dunn, D. K. Watson, J. R. Walkup, and T. C. Germann, J. Chem. Phys. **104**, 9870 (1996).

[53] See also C. Bottcher, D. R. Schultz, and D. H. Madison, Phys. Rev. A **49**, 1714 (1994); D. R. Schultz, C. Bottcher, D. H. Madison, *et. al.*, *ibid.* **50**, 1348 (1994).

[54] D. Z. Goodson, D. K. Watson, J. G. Loeser, and D. R. Herschbach, Phys. Rev. A **44**, 97 (1991).

[55] A. A. Suvernev and D. Z. Goodson, Chem. Phys. Lett. **269**, 177 (1997).

[56] More precisely the indicies $\{L, \pi\}$ are replaced by the index Γ which labels the irreducible representation of the D-dimensional orthogonal group $O(D)$, the group of rotations and reflections in D-dimensions. We concern ourselves only with those irreducible representations that survive down to $D = 3$. These representations may be denoted by a Young diagram with γ_i boxes in the i^{th} row, $1 \leq i \leq 2$, and γ_2 is restricted to be 0 or 1. Γ is then taken to be the partition $\Gamma = [\gamma_1, \gamma_2]$. In three dimensions the $\Gamma = [\gamma_1]$ states are the $L = \gamma_1$, $\pi = (-1)^L$ states and the $\Gamma = [\gamma_1, 1]$ states are the $L = \gamma_1$, $\pi = (-1)^{L+1}$ states. Also $r = \gamma_1 - \gamma_2$. For example, the P^o states would have $L = \gamma_1 = 1$ and $\pi = -1$. This would imply that the P^o states would transform under the irreducible representation denoted by $\Gamma = [1]$, (i.e. $\gamma_1 = 1$, $\gamma_2 = 0$.) Similarly, D^o states would be represented by $\Gamma = [2, 1]$.

[57] In the computer code the array Ai is stored as $R12IIi$ and the array Bi is stored as $R21IIi$, but since the two arrays are related we store only the $R12IIi$.

[58] D. Z. Goodson, M. Lopez-Cabrera, D. R. Herschbach, and J. D. Morgan III, J. Chem. Phys. **97**, 8481 (1992).

[59] M. Dunn, Z. Chen, and L. C. D., J. Phys. B **23**, 2435 (1990).

[60] M. E. Kellman, Phys. Rev. Lett. **55**, 1738 (1985).

[61] G. A. Baker, Jr., and P. Graves-Morris, *Encyclopedia of Mathematics and its Applications* (Addison-Wesley, Reading, MA., 1981), Vol. 13.

[62] A. Kono and S. Hattori, Phys. Rev. A **34**, 1727 (1986).

[63] A. K. Bhatia, Phys. Rev. A **6**, 2498 (1972).

[64] W. C. Martin, J. Phys. Chem. Ref. Data **2**, 257 (1973).

[65] Y. K. Ho, Phys. Rev. A **23**, 2137 (1981).

Appendix A

The Hamiltonian Expansion Code

A.1 main.h

```
C     Header file to declare arrays and variables common to all
C     routines.
      real*16 R12W(3,0:60,0:60,0:60)
      real*16 U(6,0:60,0:30,0:60),T(2,0:60,0:30,0:60)
      real*16 B(0:60,0:30,0:60),bnom(0:60,0:60),a1(0:60,0:60)
      real*16 a2(0:60,0:60),cot(0:60,0:60),s(0:60,0:60)
      real*16 coschi(0:60), sinchi(0:60)
      real*16 ZERO, ONE, sqrt2
      integer maxj
      common /all/ R12W,U,T,B,bnom,a1,a2,cot,s,coschi,sinchi,
     . ZERO,ONE,sqrt2,maxj
c  This code uses about 45 MB for SIZE=60
```

A.2 main.f

```
      PROGRAM SETUP_HELIUM
      IMPLICIT NONE
c     Modified for higher L 8/96
c     Modified for lambda = zero 11/96
      integer SIZE, lamvar
c      integer i,j,k,l,iarr(3)
      real*16 lam, lambar, c_m, r_m, Vxx, Vyy, Vxy, V0, E0, E2
      real*16 omega(4), tanchi, chi, cm1, s_m, rm3, cmfact
```

```
      real*16 lam1,lam2,lam3, lambda, delta
      include 'main.h'
      ZERO=0.0q0
      ONE=1.0q0
      SIZE=60
      sqrt2 = sqrt(2*ONE)
C  Input various parameters
      write(*,*) 'Do you want lambda variation? 1=YES, 2=NO.'
      read(5,*) lamvar
      if (lamvar .eq. 1) then
       write(*,*) 'Quadratic lambda variation'
       write(*,*)
       write(*,*) 'Enter lambda for delta = 1/3; (D=3): '
       read(*,*) lam3
       write(*,*)
       write(*,*) 'Enter lambda for delta=0; (D = Infinity):'
       read(5,*) lam
       write(*,*)
       write(*,*) 'Now enter a lambda for some other delta=1/D:'
       write(*,*) 'Enter D: '
       read(5,*) delta
       delta = 1/delta
       write(*,*)
       write(*,*) 'Enter lambda for delta = ',delta, ':'
       read(5,*) lambda
       lam2 = (9.q0*lam3 + lam*(3.q0/delta - 9.q0) -
     .  3.q0*lambda/delta)/(ONE - 3.q0*delta)
       lam1 = (lambda - lam  - lam2*delta*delta)/delta
       write(*,*) 'lambda = lam + lam1*delta + lam2*delta^2'
       write(*,*)
      else
       write(*,*) 'Enter lambda for delta = 1/3; (D = 3):'
       read(5,*) lam
       write(*,*)
       lam1 = ZERO
       lam2 = ZERO
```

```
      endif
      write(*,*) 'lam = ', lam
      write(*,*) 'lam1 = ', lam1
      write(*,*) 'lam2 = ', lam2
      write(*,*)
      write(*,*) 'Enter maximum order in sqrt(1/D) (max.',SIZE,'):'
      read(5,*) maxj
      write(*,*) 'maxj = ',maxj
      write(*,*)
C  Analytic expressions
C   ---temporary variables for convenience: cm1, rm3, cmfact
      lambar = sqrt2 * lam / 16.q0
      c_m = -2.q0*lambar*(lambar + sqrt(lambar*lambar + ONE))
      write(*,*) 'cos(theta_m) =', c_m
      cm1 = ONE + c_m
      r_m = ONE / (4.q0*cm1*cm1)
      write(*,*) 'r_m =', r_m
      E0 = -4.q0*cm1*cm1*cm1/(ONE-c_m)
      write(*,*) 'E(0) =', E0
      s_m = sin(acos(c_m))
      write(*,*) 'sin(theta_m) =', s_m
      rm3 = r_m*r_m*r_m
      cmfact = 2.q0*(ONE-c_m)
      Vxx = (0.375q0/(r_m*s_m*s_m)-ONE+lam/(2.q0*sqrt(cmfact))) / rm3
      write(*,*) 'Vxx =', Vxx
      cmfact = lam / (cmfact*sqrt(cmfact))
      omega(1) = sqrt((0.75q0/(r_m*s_m*s_m) - 2.q0 - cm1*cmfact)/rm3)
      Vyy = (3.q0*(c_m*c_m)/(s_m*s_m) + ONE) / (2.q0*r_m*s_m*s_m)
      Vyy = (Vyy + (3.q0+c_m)*cmfact/2.q0) / rm3
      Vxy = (c_m/(s_m*r_m*s_m*s_m) + cmfact*s_m)/rm3
      V0  = -1.5q0/(r_m*r_m*s_m*s_m) + lam1/(sqrt2*r_m*sqrt(ONE-c_m))
      write(*,*) 'Vyy =', Vyy
      write(*,*) 'Vxy =', Vxy
      write(*,*) 'V0 =', V0
      omega(2) = sqrt((Vxx-Vyy)*(Vxx-Vyy) + Vxy*Vxy)
      omega(3) = sqrt(Vxx + Vyy - omega(2))
```

```
      omega(2) = sqrt(Vxx + Vyy + omega(2))
      omega(4) = -c_m/(r_m*r_m*s_m*s_m)
      write(*,*) 'omega(1) =', omega(1)
      write(*,*) 'omega(2) =', omega(2)
      write(*,*) 'omega(3) =', omega(3)
      write(*,*) 'omega(4) =', omega(4)
      if (lam .eq. ZERO) then
c      there is no transformation to normal coordinates;
c      x and y are already normal coordinates. This implies that
c      chi = pi/2. See helium higher L potential expansion notes
c      page 4A.
       chi = asin(ONE)
       coschi(1) = ZERO
       sinchi(1) = ONE
       tanchi = ZERO  !we won't actually use tanchi since it is actually singular
      else
       chi = Vxy / (Vyy - Vxx)
       tanchi = (Vyy-Vxx)*(ONE + sqrt(ONE + chi * chi))/Vxy
       chi = atan(tanchi)
       coschi(1) = cos(chi)
       sinchi(1) = sin(chi)
       write(*,*) 'tan(chi) =', tanchi
      endif
      write(*,*) 'chi =', chi
      write(*,*) 'sinchi =', sinchi(1)
      write(*,*) 'coschi =', coschi(1)
      E2 = V0
C  Preliminary initialization
      call binom
      call chifact
      write(*,*) 'setup_C --'
      CALL setup_C
      write(*,*) 'setup_B --'
      CALL setup_B
      call sin_derivs(s_m,c_m)
      call gtoy(s_m,c_m)
```

```
C  Centrifugal potential
      write(*,*) 'setup_U --'
      CALL setup_U(r_m, s_m)
      call cotan(r_m, s_m, c_m)
C  Potential term
      write(*,*) 'setup_V --'
      CALL setup_V(r_m, lam,lam1,lam2, c_m)
      write(*,*) 'setup_W --'
      call setup_W(r_m,s_m)
C  Kinetic term
      write(*,*) 'setup_T --'
      CALL setup_T(r_m)
C   Save parameters for iterative loop to compute E(j), j = 3,4,..., maxj
      write(*,*) 'save --'
      CALL save_params(omega, E0, E2)
c 20   format(a10,i2,':',i2,':',i2)
      end
```

A.3 binom.f

```
C     Calculates binomial coefficients recursively
      subroutine binom
      implicit none
      integer n, m
      include 'main.h'
      do n=0,maxj
       do m=0,maxj
        bnom(n,m) = ZERO
       enddo
      enddo
      do n = 0, maxj
         bnom(n,0) = ONE
         do m = 1, n/2
            bnom(n,m) = bnom(n,m-1) * (n+ONE-m)/(ONE*m)
         end do
         do m = 0, n/2
```

```
            bnom(n,n-m) = bnom(n,m)
          end do
        end do
        end
```

A.4 chifact.f

```
        subroutine chifact
        implicit none
        integer j
        include 'main.h'
        coschi(0) = ONE
        sinchi(0) = ONE
        do j=2,maxj
         coschi(j) = coschi(j-1)*coschi(1)
         sinchi(j) = sinchi(j-1)*sinchi(1)
        enddo
        end
```

A.5 cotan.f

```
         subroutine cotan(r_m, s_m, c_m)
        implicit none
        integer i,j,m,n
        real*16 r_m, s_m, c_m, jfact,prefact
        include 'main.h'
c S(j,n) is calculated in setup_U.f
        if (c_m .eq. ZERO) then
         prefact=1/s_m
        else
         prefact=c_m/s_m
         a2(0,1) = ONE
        endif
        jfact = ONE
        do j=0, maxj
          do n=0, j
```

```
      cot(j,n) = ZERO
      do m=0,j
        do i=m,j
          cot(j,n) = cot(j,n) + a2(j-i,1)*a1(i,m)
        enddo
      enddo
      cot(j,n) = cot(j,n)*prefact*s(j,n)*jfact
    enddo
    jfact = jfact*sqrt2/r_m
  enddo
  a2(0,1) = ZERO
  end
```

A.6 gtoy.f

```
  subroutine gtoy(s_m,c_m)
  implicit none
  integer j,p,i
  real*16 s_m,c_m, tan_m, fact
  include 'main.h'
  do j=0,maxj
   do p=0,maxj
    a2(j,p) = ZERO
   enddo
  enddo
  a2(0,0) = ONE
  do j = 1, maxj
     a2(j,0) = ZERO
  end do
  if (c_m .eq. ZERO) then
   fact = - ONE
   a2(0,1) = ZERO
   do j = 0, maxj-2, 2
     a2(j+1,1) = fact
     a2(j+2,1) = ZERO
     fact = -fact / ((j+2)*(j+3)*ONE)
```

```
        end do
        if ((maxj/2)*2 .ne. maxj) a2(maxj,1) = fact
       else
        tan_m = s_m / c_m
        fact = ONE
        do j = 0, maxj-1, 2
          a2(j,1) = fact
          fact = -fact / ((j+1)*ONE)
          a2(j+1,1) = tan_m * fact
          fact = fact / ((j+2)*ONE)
        end do
        if ((maxj/2)*2 .eq. maxj) a2(maxj,1) = fact
        a2(0,1) = ZERO
       endif
C  and fill in remaining a2_j^{(p)} elements
       do p = 2, maxj
          do j = p, maxj
             a2(j,p) = ZERO
             do i = 1, j-p+1
                a2(j,p) = a2(j,p) + a2(j-i,p-1) * a2(i,1)
             end do
          end do
       end do
       end
```

A.7 sin_derivs.f

```
       subroutine sin_derivs(s_m,c_m)
       implicit none
       real*16 s_m, c_m, cot_m, fact
       integer j,p,i
       include 'main.h'
       do j=0,maxj
        do p=0,maxj
         a1(j,p) = ZERO
        enddo
```

```
      enddo
      cot_m = c_m / s_m
      fact = -ONE
      a1(0,0) = ONE
      do j = 1, maxj
         a1(j,0) = ZERO
      end do
C  initialize a1_j^{(1)} elements
      do j = 0, maxj-1, 2
         a1(j,1) = fact
         fact = fact / ((j+1)*ONE)
         a1(j+1,1) = cot_m * fact
         fact = -fact / ((j+2)*ONE)
      end do
      if (((maxj/2)*2) .eq. maxj ) a1(maxj,1) = fact
      a1(0,1) = ZERO
C  and fill in remaining a1_j^{(p)} elements
      do p = 2, maxj
         do j = p, maxj
            a1(j,p) = ZERO
            do i = 1, j-p+1
               a1(j,p) = a1(j,p) + a1(j-i,p-1) * a1(i,1)
            end do
         end do
      end do
      end
```

A.8 setup_B.f

```
      subroutine setup_B
      implicit none
      real*16 lfact
      integer j,k,l, twok
      include 'main.h'
      do j=0,maxj
       do k=0,maxj/2
```

```
   do l=0,maxj
    B(j,k,l) = ZERO
   enddo
  enddo
 enddo
 do j = 1, maxj
  do k = 0, (j-1)/2
   twok = 2*k
   lfact = ONE
   do l = 0, j-twok-1
     B(j,k,l) = lfact*bnom(j,twok+1)*bnom(j-twok-1,l)*
     coschi(j-twok-1-1)*sinchi(l)
     lfact = -lfact
   enddo
  enddo
 enddo
 end
```

A.9 setup_C.f

```
subroutine setup_C
implicit none
real*16 lfact
integer j,k,l, twok
include 'main.h'
do j=0,maxj
 do k=0,maxj/2
  do l=0,maxj
   T(1,j,k,l) = ZERO
  enddo
 enddo
enddo
do j = 0, maxj
 do k = 0, j/2
  twok = 2*k
  lfact = ONE
```

```
        do l = 0, j-twok
          T(1,j,k,l) = lfact*bnom(j,twok)*bnom(j-twok,l)*
     .    coschi(j-twok-l)*sinchi(l)
          lfact = -lfact
        enddo
      enddo
    enddo
    end
```

A.10 setup_T.f

```
      subroutine setup_T(r_m)
      implicit none
      real*16 r_m, term, c(0:60)
      integer j,k,l,m,n
      include 'main.h'
      c(0) = r_m*r_m
      c(1) = ZERO
      c(2) = -0.5q0
      do j = 3, maxj
        c(j) = -c(j-1)*(j-1)/(sqrt2*r_m*(j-2))
      enddo
      do j = maxj, 2, -1
         do k = 0, j/2
            do l = 0, j-2*k
               T(1,j,k,l) = c(j) * T(1,j-2,k,l)
            end do
         end do
      end do
c  now do additional term due to higher L which multiplies a spin matrix
      do j=4,maxj
        do k=0,(j-4)/2
          do l=0,j-2*k-4
          T(2,j,k,l) = ZERO
            do m=0,j-4
              term = ZERO
```

```
            do n=0, min(m,l)
              term = term + B(j-m-3,k,l-n)*cot(m,n)
            enddo
            T(2,j,k,l) = T(2,j,k,l) - term*2.q0*(j-m-2)*
     . c(j-m)/(j-m-1)
          enddo  !m
        enddo    !l
      enddo      !k
    enddo        !j
    end
```

A.11 setup_U.f

```
subroutine setup_U(r_m, s_m)
implicit none
integer i, j, k, l, m, mmin, mmax
real*16 r_m, s_m, term, prefact
real*16 g(0:60),c(0:60)
include 'main.h'
g(0) = 1.q0 / (s_m*s_m)
do j = 1, maxj
   g(j) = ZERO
   do m = 1, j
      g(j) = g(j) + (m+ONE) * a1(j,m)
   end do
   g(j) = g(j) * g(0)
end do
term = sqrt2 / r_m
prefact = ONE
do j = 0, maxj
   g(j) = g(j) * prefact
   prefact = prefact * term
end do
do j=0,maxj
 do i=0,maxj
  s(j,i) = ZERO
```

```
        enddo
      enddo
      do j = 0, maxj
         do i = 0, j
            s(j,i) = bnom(j,i)*coschi(i)*sinchi(j-i)
         end do
      end do
      c(0) = ONE / (4.0q0 * r_m * r_m)
      do j = 1, maxj
         c(j) = -c(j-1) * (j+1) / (j*sqrt2*r_m)
      end do
c  See s-wave potential expansion notes for U1,U2,U3. See higherL
c  potential expansion notes for U4,U5,U6.
      do j=0,maxj
       do k=0,maxj/2
        do l=0,maxj
         do i=1,6
          U(i,j,k,l) = ZERO
         enddo
        enddo
       enddo
      enddo
      do j = 0, maxj
         do k = 0, j/2
            do l = 0, j-2*k
               do i = 0, j-2*k
                  term = ZERO
                  mmin = l+2*k+i-j
                  if (mmin.lt.0) mmin=0
                  mmax = i
                  if (l.lt.mmax) mmax=l
                  do m = mmin, mmax
                     term = term + s(i,m)*T(1,j-i,k,l-m)
                  end do
                  U(1,j,k,l) = U(1,j,k,l) + c(j-i)*g(i)*term
               end do
```

```
            end do
         end do
         do k = 0, (j-2)/2
            do l = 0, j-2-2*k
               U(2,j,k,l) = -U(1,j-2,k,l) * 6.0q0
            end do
         end do

         do k = 0, (j-4)/2
            do l = 0, j-4-2*k
               U(6,j,k,l) = c(j-4)*T(1,j-4,k,l)
               U(3,j,k,l) = 8.q0 * U(1,j-4,k,l) - U(6,j,k,l)
            end do
         end do
c Higher L terms  U(4,j,k,l) and U(5,j,k,l) multiply a spin matrix
c U(6,j,k,l) is multiplied by the square of a spin matrix and is calculated
c above.
         do k=0, (j-3)/2
            do l=0, j-3-2*k
               do i= 0, j-3
                 term = ZERO
                 mmax = l
                 if (i.lt.mmax) mmax = i
                 do m= 0, mmax
                    term = term + s(i,m)*B(j-i-2,k,l-m)
                 enddo
                 U(4,j,k,l) = U(4,j,k,l) + g(i)*2.q0*c(j-i-2)*term
               enddo  !i
            enddo     !l
         enddo        !k
         do k=0, (j-5)/2
            do l=0, j-5-2*k
               U(5,j,k,l) = -2.q0*U(4,j-2,k,l)
            enddo
         enddo
      end do
```

```
end
```

A.12 setup_V.f

```
subroutine setup_V(r_m,lam,lam1,lam2,c_m)
implicit none
real*16 r_m, lam,lam1,lam2, c_m
integer i,j,k,l,k2,r,p,pmax,m,n2,n,k1
real*16 pfact,lfact
real*16 prefact, vtj,vtl
real*16 vtu, vtk1, vtk2, vtn, vtn2, vtq, k2fact
real*16 a,b2,c,e,jfact,nfact,n2fact
real*16 F(0:60,0:30,0:60), D(0:60,0:30,0:60)
real*16 V(0:60,0:30,0:60)
include 'main.h'
vtj = -ONE / (sqrt2 * r_m)
prefact = -2.0q0 / r_m
do j = 0, maxj
   do k = 0, j/2
      do l = 0, j-2*k
         U(1,j,k,l) = U(1,j,k,l) + prefact*T(1,j,k,l)
      end do
   end do
   prefact = prefact * vtj
end do
a = sqrt2 / r_m
b2 = ONE / (2.0q0 * r_m * r_m)
c = c_m
e = (ONE + c) / (ONE - c)
c = c / (ONE - c)
n2fact = b2 / (a*a)
nfact = -n2fact * c / a
jfact = c/a
k2fact = a*c / (b2*e)
do j = 0, maxj
   do k=0,j/2
```

```
      do r = 0,j-2*k
         D(j,k,r) = ZERO
      end do
   end do
end do
vtj = ONE
do j = 0, maxj
   vtq = vtj
   do m = 0, j/2
      vtn = vtq
      do n = 0, min(m, j-2*m)
         vtl = vtn*bnom(j-m-n,m)*bnom(m,n)
         do l = 0, j-2*m-n
            vtk1 = vtl*bnom(j-2*m-n,l)
            do k1 = 0, m-n
               vtk2 = vtk1*bnom(m-n,k1)
               do k2 = 0, k1
                  vtn2 = vtk2*bnom(k1,k2)
                  do n2 = 0, n
                     D(j,k1-k2+n-n2,n+l+k2) =
                     D(j,k1-k2+n-n2,n+l+k2) + bnom(n,n2) * vtn2
                     vtn2 = -vtn2
                  end do
                  vtk2 = -vtk2 * k2fact
               end do
               vtk1 = vtk1 * e
            end do
            vtl = -vtl * jfact
         end do            !l
         vtn = vtn * jfact * (j-m-n) / (0.5q0 - j + m + n)
      end do               !n
      vtq = vtq * (j-m) / (4.0q0*(0.5q0 - j + m))
   end do                  !m
   vtj = -vtj * a*(0.5q0+j) / (ONE+j)
end do                     !j
do j=0, maxj
```

```
            vtu = ONE
            do r = 0, j
               do k = 0, (j-r)/2
                  F(j,k,r) = ZERO
                  do i = 0, r
                     F(j,k,r) = F(j,k,r) + D(j-i,k,r-i)*vtu*a2(r,r-i)
                  end do
               end do
               vtu = vtu * a
            end do
         end do
         prefact = ONE / (r_m*sqrt2*sqrt(ONE-c_m))
         do j = 0, maxj
            do k=0,j/2
               do r=0,j-2*k
                  if (F(j,k,r) .ne. ZERO) F(j,k,r) = F(j,k,r) * prefact
               end do
            end do
         end do
C        Convert F(j,k,r) expansion coefficients to V(j,k,l)
         do j=0,maxj
          do k=0,j/2
           k2 = 2*k
           lfact=ONE
           do l=0,j-k2
            V(j,k,l) = ZERO
             do r=0,j-k2
              pmax = l
              if (pmax.gt.r) pmax = r
              do p=max(0,l+r+k2-j),pmax
               if ((p/2)*2.eq.p) then
                pfact=ONE
               else
                pfact=-ONE
               endif
               V(j,k,l)=V(j,k,l) + bnom(j-r-k2,l-p)*bnom(r,p)*F(j,k,r)*
```

```
      coschi(j-r-k2-l+2*p)*sinchi(l+r-2*p)*pfact*lfact
     enddo     !p
    enddo      !r
   U(1,j,k,l) = U(1,j,k,l) + lam*V(j,k,l)
   lfact=-lfact
  enddo        !l
 enddo         !k
 do k=0,(j-2)/2
  do l=0,j-2-2*k
   U(2,j,k,l) = U(2,j,k,l) + lam1*V(j-2,k,l)
  enddo
 enddo
 do k=0,(j-4)/2
  do l=0,j-4-2*k
   U(3,j,k,l) = U(3,j,k,l) + lam2*V(j-4,k,l)
  enddo
 enddo
end do                    !j
end
```

A.13 setup_W.f

```
subroutine setup_W(r_m, s_m)
implicit none
real*16 r_m,s_m,W(3,0:60,0:30,0:60)
real*16 jfact, kfact,lfact
real*16 factor
real*16 R12(0:60,0:60,0:60)
integer j,k,l,m,n,p,factor1
include 'main.h'
call setup_W1(W,r_m,s_m)
jfact = ONE
do j=0,maxj
  kfact = jfact
  do k = 0,j
    lfact = kfact
```

```
      do l=0,j-k
        factor1 = 0
        if ((k.le.(j-1)).and.(j.ge.1)) then
          if (l.le.(j-k-1)) factor1 = factor1 - (j-k-l)
          if (l.ge.1) factor1 = factor1 - l
        endif
        if ((k.ge.1).and.(j.ge.1)) factor1 = factor1 + k
        if (j.eq.0) then
          factor = ONE
        else
          factor = (factor1*ONE)/(j*ONE) + ONE
        endif
        R12(j,k,l)=lfact*coschi(j-k-l)*sinchi(l)*
     .   bnom(j,k)*bnom(j-k,l)*factor
        lfact=-lfact
      enddo  !l
      kfact = -kfact
    enddo    !k
    jfact = -jfact/(sqrt2*r_m)
  enddo      !j
  do j = 2,maxj
    do k = 0,j-2
      do l = 0,j-k-2
        factor = ZERO
        do m=2,j
          do n = 0,min(k/2,(m-2)/2)
            do p = 0,min(l,m-2*n-2)
              factor = factor + R12(j-m,k-2*n,l-p)*W(1,m,n,p)
            enddo
          enddo
        enddo
        R12W(1,j,k,l) = factor
      enddo
    enddo
    do k = 0,j-3
      do l = 0,j-k-3
```

```
        factor = ZERO
        do m=3,j
          do n = 0,min(k/2,(m-3)/2)
            do p = 0,min(l,m-2*n-3)
             factor = factor + R12(j-m,k-2*n,l-p)*W(2,m,n,p)
            enddo
          enddo
        enddo
        R12W(2,j,k,l) = factor
      enddo
    enddo
    do k = 0,j-4
      do l = 0,j-k-4
        factor = ZERO
        do m=4,j
          do n = 0,min(k/2,(m-4)/2)
            do p = 0,min(l,m-2*n-4)
             factor = factor + R12(j-m,k-2*n,l-p)*W(3,m,n,p)
            enddo
          enddo
        enddo
        R12W(3,j,k,l) = factor
      enddo
    enddo
  enddo
  end
```

A.14 setup_W1.f

```
subroutine setup_W1(W,r_m, s_m)
implicit none
real*16 r_m, W2(0:60,0:30,0:60),s_m
real*16 factor,W(3,0:60,0:30,0:60)
integer j,k,l,m,n,nmax
include 'main.h'
call setup_W2(W2,r_m,s_m)
```

```
 factor = r_m/sqrt2
 do j = 2, maxj
   do k=0,(j-2)/2
     do l=0,j-2*k-2
       W(1,j,k,l) = ZERO
       do m=0,j-2
         nmax = m
         if (l.lt.nmax) nmax = l
         do n=0,nmax
           W(1,j,k,l) = W(1,j,k,l) -0.5d0*W2(j-m-2,k,l-n)*
. cot(m,n)
         enddo
       enddo
     enddo
   enddo
   do k=0,(j-3)/2
     do l=0,j-2*k-3
       W(2,j,k,l) = factor*W2(j-3,k,l)
     enddo
   enddo
   do k = 0,(j-4)/2
     do l=0,j-2*k-4
       W(3,j,k,l) = -2.d0*W(1,j-2,k,l)
     enddo
   enddo
 enddo
 end
```

A.15 setup_W2.f

```
subroutine setup_W2(W2,r_m,s_m)
implicit none
real*16 r_m, s_m
integer i,j,k,l,k2,r,p,pmax,m,n2,n,k1
real*16 prefact, vtj,vtl,lfact,pfact
real*16 vtu, vtk1, vtk2, vtn, vtn2, vtq
```

```
real*16 a,b2
real*16 F(0:60,0:30,0:60), D(0:60,0:30,0:60)
real*16 W2(0:60,0:30,0:60)
include 'main.h'
a = sqrt2 / r_m
b2 = ONE / (2.q0 * r_m * r_m)
do j = 0, maxj
   do k=0, j/2
      do r=0,j-2*k
         D(j,k,r) = ZERO
      end do
   end do
end do
vtj = ONE
do j = 0, maxj
   vtq = vtj
   do l = 0, j/2
      vtn = vtq
      do n = 0, min(l, j-2*l)
         vtl = vtn*bnom(j-l-n,l)*bnom(l,n)
         do m = 0, j-2*l-n
            vtk1 = vtl*bnom(j-2*l-n,m)
            do k1 = 0, l-n
               vtk2 = vtk1*bnom(l-n,k1)
               do k2 = 0, k1
                  vtn2 = vtk2*bnom(k1,k2)
                  do n2 = 0, n
                     D(j,k1-k2+n-n2,n+m+k2) =
                     D(j,k1-k2+n-n2,n+m+k2) + bnom(n,n2) * vtn2
                     vtn2 = -vtn2
                  end do
                  vtk2 = vtk2*a/b2
               end do     !k2
               vtk1 = -vtk1
            end do        !k1
            vtl = -vtl/a
```

```
            end do            !m
            vtn = -vtn/a
          end do              !n
          vtq = -vtq*(1.d0/4.d0)
        end do                !l
        vtj = -vtj * a
      end do                  !j
      do j=0, maxj
        do k=0,j/2
          vtu = ONE
          do r=0,j-2*k
            F(j,k,r) = ZERO
            do i = 0, r
              F(j,k,r) = F(j,k,r) + D(j-i,k,r-i)*a1(r,r-i)
            end do
          F(j,k,r) = F(j,k,r)*vtu
          vtu = vtu*a
          end do
        end do
      end do
      prefact = ONE / (r_m*r_m*s_m)
      do j = 0, maxj
        do k=0,j/2
          do r=0,j-2*k
            if (F(j,k,r) .ne. ZERO) F(j,k,r) = F(j,k,r) * prefact
          end do
        end do
      end do
C   Convert F(j,k,r) expansion coefficients to W2(j,k,l)
      do j=0,maxj
       do k=0,j/2
        k2 = 2*k
        lfact=ONE
        do l=0,j-k2
         W2(j,k,l) = ZERO
          do r=0,j-k2
```

```
            pmax = l
            if (pmax.gt.r) pmax = r
            do p=max(0,r+l+k2-j),pmax
             if ((p/2)*2.eq.p) then
              pfact=ONE
             else
              pfact=-ONE
             endif
             W2(j,k,l)=W2(j,k,l) + bnom(j-r-k2,l-p)*bnom(r,p)*F(j,k,r)*
     .       coschi(j-r-k2-l+2*p)*sinchi(l+r-2*p)*pfact*lfact
            enddo    !p
           enddo     !r
          lfact=-lfact
c          if (W2(j,k,l).ne.ZERO) write(10,*) j,2*k,j-2*k-l,l,W2(j,k,l)
         enddo       !l
        enddo        !k
       end do        !j
       end
```

A.16 save.f

```
      subroutine save_params(omega,E0,E2)
      implicit none
      integer i,j,k,l
      real*16 omega(4), E0, E2
      real*16 prefact, fact1, fact2, mulj, mulk, mull, prej, prek
      real*16 fact3
      include 'main.h'
      open(unit=10, file='params.lis', status='unknown')
      write(10,*) maxj
      do i = 1, 4
         write(10,*) omega(i)
      end do
      write(10,*) sinchi(1)
      write(10,*) coschi(1)
      write(10,*) E0
```

```
      write(10,*) E2
      close(10)
      open(unit=10, file='T1.lis', status='unknown')
      open(unit=11, file='T2.lis', status='unknown')
      open(unit=12, file='UV1.lis', status='unknown')
      open(unit=13, file='UV2.lis', status='unknown')
      open(unit=14, file='UV3.lis', status='unknown')
      open(unit=15, file='UV4.lis', status='unknown')
      open(unit=16, file='UV5.lis', status='unknown')
      open(unit=17, file='UV6.lis', status='unknown')
      fact1 = 2.q0*omega(2)
      fact2 = fact1*fact1
      fact3 = ONE/sqrt(2.q0*omega(1))
      mulj = ONE / sqrt(2.q0*omega(2))
      mulk = omega(2) / omega(1)
      mull = sqrt(omega(2) / omega(3))
      prej = mulj*mulj*mulj
      do j = 3, maxj
         prek = prej
         do k = 0, j/2
            prefact = prek
            do l = 0, j-2*k
               if (T(1,j,k,l).ne.ZERO) write(10,*) j,k,l,
     .              prefact*omega(2)*T(1,j,k,l)
               if (T(2,j,k,l).ne.ZERO) write(11,*) j,k,l,
     .              prefact*fact2*fact3/sqrt2*T(2,j,k,l)
               if (U(1,j,k,l) .ne. ZERO) write(12,*) j,k,l,
     .              prefact*U(1,j,k,l)
               if (U(2,j,k,l) .ne. ZERO) write(13,*) j,k,l,
     .              prefact*fact1*U(2,j,k,l)
               if (U(3,j,k,l) .ne. ZERO) write(14,*) j,k,l,
     .              prefact*fact2*U(3,j,k,l)
               if (U(4,j,k,l) .ne. ZERO) write(15,*) j,k,l,
     .              prefact*fact3*fact1/mulj*U(4,j,k,l)
               if (U(5,j,k,l) .ne. ZERO) write(16,*) j,k,l,
     .              prefact*fact2*fact3/mulj*U(5,j,k,l)
```

```
            if (U(6,j,k,l) .ne. ZERO) write(17,*) j,k,l,
     .           prefact*fact2*U(6,j,k,l)
            prefact = prefact * mull
         end do
         prek = prek * mulk
      end do
      prej = prej * mulj
   end do
   write(10,*) -1,0,0,ZERO
   write(11,*) -1,0,0,ZERO
   write(12,*) -1,0,0,ZERO
   write(13,*) -1,0,0,ZERO
   write(14,*) -1,0,0,ZERO
   write(15,*) -1,0,0,ZERO
   write(16,*) -1,0,0,ZERO
   write(17,*) -1,0,0,ZERO
   close(10)
   close(11)
   close(12)
   close(13)
   close(14)
   close(15)
   close(16)
   close(17)
   open(unit=10, file='R12W1.lis', status='unknown')
   open(unit=11, file='R12W2.lis', status='unknown')
   open(unit=12, file='R12W3.lis', status='unknown')
   fact1 = 2.q0*omega(2)
   fact2 = fact1*fact1
   mulj = ONE / sqrt(2.q0*omega(2))
   mulk = sqrt(omega(2) / omega(1))
   mull = sqrt(omega(2) / omega(3))
   prej = mulj*mulj*mulj
   do j = 3, maxj
      prek = prej
      do k = 0, j
```

```
      prefact = prek
      do l = 0, j-k
         if (R12W(1,j,k,l).ne.ZERO) write(10,*) j,k,l,
     .        prefact*fact1*R12W(1,j,k,l)
         if (R12W(2,j,k,l).ne.ZERO) write(11,*) j,k,l,
     .        prefact*fact1/(mulj*sqrt2)*R12W(2,j,k,l)
         if (R12W(3,j,k,l) .ne. ZERO) write(12,*) j,k,l,
     .        prefact*fact2*R12W(3,j,k,l)
         prefact = prefact * mull
      end do
      prek = prek * mulk
   end do
   prej = prej * mulj
end do
write(10,*) -1,0,0,ZERO
write(11,*) -1,0,0,ZERO
write(12,*) -1,0,0,ZERO
close(10)
close(11)
close(12)
end
```

Appendix B

Code For Solving Perturbation Equations

B.1 qcommon.h

```
C---- constants; SIZE is max order in sqrt(1/D) and LEN is the
c---- maximum array dimension
      integer SIZE, LEN,anglen
c 40th order for p-odd
c      data SIZE, LEN, anglen /40,63,2/
c 54th order for p-odd
      data SIZE, LEN, anglen /54,81,2/
c 20th order for d-even
c      data SIZE, LEN, anglen /20,33,3/
c  LEN is equal to 3*(maxj-2)/2 + statemax where
c   statemax = 1,2,3,.... is the maximum quantum
c   number after it is increased by one. The ground
c   state 000 would have a statemax = 1.
      real*16 ZERO,ONE
      data ZERO,ONE /0.q0,1.q0/
C----- wavefunction tensors and temporary storage
C               A(0:SIZE,LEN,LEN,LEN)
C 40th order p-odd
c      REAL*16 A(32,63,63,2,0:38), T1(32,63,63,2), T2(32,63,63,2),
c     . T3(32,63,63,2)
c      real*16 TT(63), sqt(63), R2(63)
c      INTEGER asize(0:38)
C 54th order p-odd
```

```
      REAL*16 A(41,81,81,2,0:52), T1(41,81,81,2), T2(41,81,81,2),
     . T3(41,81,81,2)
      real*16 TT(81), sqt(81), R2(81)
      INTEGER asize(0:52)
C 20th order for d-even
c      REAL*16 A(17,33,33,3,0:18), T1(17,33,33,3), T2(17,33,33,3),
c     .  T3(17,33,33,3)
c      real*16 TT(33), sqt(33), R2(33)
c      INTEGER asize(0:18)
C----- potential expansion coefficients and associated pointers
C 40th order for any state
c      real*16 R12W1(10660),R12W2(9880),R12W3(9139),UV1(6391),UV2(5530)
c      real*16 TK1(5530),UV4(5130),UV3(4750),TK2(4750),UV6(4750)
c      real*16 UV5(4389)
c      real*16 E(-1:19)
c      integer PTR2(0:40,0:40),PTR(0:40,0:20)
C 54th order for any state
      real*16 R12W1(26235),R12W2(24804),R12W3(23426)
      real*16 UV1(15022),UV2(13482),TK1(13482)
      real*16 UV4(12753),UV3(12051),TK2(12051),UV6(12051)
      real*16 UV5(11375)
      real*16 E(-1:26)
      integer PTR2(0:54,0:54),PTR(0:54,0:27)
c--Angular momentum matricies
c  p-odd
      real*16 MM(2,2),Sbar(2,2),Sbar2(2,2)
c  d-even
c      real*16 MM(3,3),Sbar(3,3),Sbar2(3,3)
c  Quadruple precision takes about 180 MB for 40th order p-odd
c  Quadruple precision takes about 250 MB for 40th order d-even
      COMMON /ARRAYS/ R12W1,R12W2,R12W3,UV1,UV2,TK1,UV4,UV3,TK2,UV6,
     . UV5,TT,sqt,R2,MM,Sbar,Sbar2,E,PTR2,PTR
      COMMON /WVF/ A, T1, T2, T3, asize
```

B.2 qinput.f

```
C
C     Reads pre-computed expansion coefficients from files
C
      SUBROUTINE INPUT(maxj,omega,sinchi,coschi,lambda)
      INCLUDE 'qcommon.h'
C---- variables
      INTEGER maxj, j, k, l, n,m
      REAL*16 omega(4), tmp, sinchi,coschi
      Character*4 lambda
      character*48 path1
      m=0
      Do i=1,4
        If(lambda(i:i).ne.' ') m=m+1
      enddo
      path1='/home/carzoli/helium/higherL/Setup/'//
     . 'potterms/lam='
      OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/params.lis',
     . STATUS='OLD')
      READ(10,*) maxj
      if (maxj.gt.SIZE) maxj = SIZE
      write(*,*) 'maxj = ',maxj
      do n = 1,4
         READ(10,*) omega(n)
      enddo
      read(10,*) sinchi
      read(10,*) coschi
      READ(10,*) E(-1)
      READ(10,*) E(0)
      CLOSE(UNIT=10)
      n = 1
      do j = 0,maxj
         do k = 0, j/2
            PTR(j-2*k,k) = n
            n = n + j + 1 - 2*k
```

```
      end do
   end do
   n = 1
   do j = 0,maxj
      do k = 0, j
         PTR2(j-k,k) = n
         n = n + j + 1 - k
      end do
   end do
   OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/UV1.lis',
  . STATUS='OLD')
   read(10,*) j,k,l,tmp
   n = j - 2*k
   do while ((n.ge.0).and.(j.le.maxj))
      UV1(PTR(n,k)+l) = tmp
      read(10,*) j,k,l,tmp
      n = j - 2*k
   end do
   CLOSE(UNIT=10)
   OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/UV2.lis',
  . STATUS='OLD')
   read(10,*) j,k,l,tmp
   n = j - 2*k - 2
   do while ((n.ge.0).and.(j.le.maxj))
      UV2(PTR(n,k)+l) = tmp
      read(10,*) j,k,l,tmp
      n = j - 2*k - 2
   end do
   CLOSE(UNIT=10)
   OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/T1.lis',
  . STATUS='OLD')
   read(10,*) j,k,l,tmp
   n = j - 2*k - 2
   do while ((n.ge.0).and.(j.le.maxj))
      TK1(PTR(n,k)+l) = tmp
      read(10,*) j,k,l,tmp
```

```
      n = j - 2*k - 2
    end do
    CLOSE(UNIT=10)
    OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/UV4.lis',
   . STATUS='OLD')
    read(10,*) j,k,l,tmp
    n = j - 2*k - 3
    do while ((n.ge.0).and.(j.le.maxj))
      UV4(PTR(n,k)+l) = tmp
      read(10,*) j,k,l,tmp
      n = j - 2*k - 3
    end do
    CLOSE(UNIT=10)
    OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/R12W1.lis',
   . STATUS='OLD')
    read(10,*) j,k,l,tmp
    n = j - k - 2
    do while ((n.ge.0).and.(j.le.maxj))
      R12W1(PTR2(n,k)+l) = tmp
      read(10,*) j,k,l,tmp
      n = j - k - 2
    end do
    CLOSE(UNIT=10)
    OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/R12W2.lis',
   . STATUS='OLD')
    read(10,*) j,k,l,tmp
    n = j - k - 3
    do while ((n.ge.0).and.(j.le.maxj))
      R12W2(PTR2(n,k)+l) = tmp
      read(10,*) j,k,l,tmp
      n = j - k - 3
    end do
    CLOSE(UNIT=10)
    if (maxj.ge.5) then
     OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/UV5.lis',
   .  STATUS='OLD')
```

```
  read(10,*) j,k,l,tmp
  n = j - 2*k - 5
  do while ((n.ge.0).and.(j.le.maxj))
    UV5(PTR(n,k)+l) = tmp
    read(10,*) j,k,l,tmp
    n = j - 2*k - 5
  end do
  CLOSE(UNIT=10)
 endif
 if (maxj.ge.4) then
    OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/UV3.lis',
.    STATUS='OLD')
    read(10,*) j,k,l,tmp
    n = j - 2*k - 4
    do while ((n.ge.0).and.(j.le.maxj))
       UV3(PTR(n,k)+l) = tmp
       read(10,*) j,k,l,tmp
       n = j - 2*k - 4
    end do
    CLOSE(UNIT=10)
    OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/T2.lis',
.    STATUS='OLD')
    read(10,*) j,k,l,tmp
    n = j - 2*k - 4
    do while ((n.ge.0).and.(j.le.maxj))
       TK2(PTR(n,k)+l) = tmp
       read(10,*) j,k,l,tmp
       n = j - 2*k - 4
    end do
    CLOSE(UNIT=10)
    OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/UV6.lis',
.    STATUS='OLD')
    read(10,*) j,k,l,tmp
    n = j - 2*k - 4
    do while ((n.ge.0).and.(j.le.maxj))
       UV6(PTR(n,k)+l) = tmp
```

```
         read(10,*) j,k,l,tmp
         n = j - 2*k - 4
      end do
      CLOSE(UNIT=10)
      OPEN(UNIT=10, FILE=path1//lambda(1:m)//'/R12W3.lis',
     .  STATUS='OLD')
      read(10,*) j,k,l,tmp
      n = j - k - 4
      do while ((n.ge.0).and.(j.le.maxj))
         R12W3(PTR2(n,k)+l) = tmp
         read(10,*) j,k,l,tmp
         n = j - k - 4
      end do
      CLOSE(UNIT=10)
   endif
   RETURN
   END
```

B.3 qhelium.f

```
c
c     Matrix method for two-electron atoms (3 dof)
c     for higher angular momentum.
c     4/29/97: Converted to q1=anti-symmetric, q2=bend, q3=symmetric
c     5/??/97: Fixed tim's bug where he multiplied derivatives and
c      coordinates in the wrong order!
c     6/23/97: Improved calculation of asize so as to truncate the
c      wavefunction beginning at (maxj-2)/2 +1. Also fixed bug in
C      comp_H_A.f where coordinate derivatives are calculated and loop
c      limits were too small for the calculation of the maxj-2 wavefunction.
      PROGRAM MATRIX_He
      IMPLICIT NONE
      include 'qcommon.h'
C---- misc local variables
      INTEGER maxj, state(4), i, j, n, i1,i2,i3,i4,smax,angmom
      INTEGER even1,even2,even3,even4
```

```
      LOGICAL evenE, savewf
      REAL*16 omega(4), temp, sinchi,coschi, pre2, pre3, pre32
      REAL*16 pre4,pre5
      CHARACTER*14 fname
      character*4 lambda
C
C     Input pre-computed potential expansion coefficients
C
      OPEN(UNIT=10, FILE='states.lis', STATUS='OLD')
      read(10,*) lambda
      read(10,*) angmom
      READ(10,*) state(1), state(3), state(2), state(4)
      close(unit=10)
      call input(maxj,omega,sinchi,coschi,lambda)
      if (angmom.gt.(anglen-1)) then
       write(*,*) 'You must increase the value of anglen in common.h'
       write(*,'(1x,a,I2)') 'to calculate t-2*gamma_2 = ',angmom
       stop
      endif
      if ((state(4) .gt. angmom+1).or.(state(4).lt.1)) then
       write(*,*) 'Fourth quantum number is invalid: should be from'
       write(*,'(1x,a,I2)') '1 to ',angmom+1
       stop
      endif
      savewf = .True. !do we wish to save the wavefunctions?
      do i = 1, 3
         E(0) = E(0) + (state(i) + 0.5*ONE) * omega(i)
      enddo
      E(0) = E(0) + omega(4)/(2*ONE) * (angmom - 2*ONE* (state(4) -1))
C
C     Prefactors for derivative terms
C
      pre2 = sinchi
      pre3 = coschi
      pre32 = 2.q0*pre2*pre3*sqrt(omega(2)*omega(3))
      pre2 = pre2*pre2*omega(2)
```

```
      pre3 = pre3*pre3*omega(3)
      pre4 = sinchi*sqrt(omega(2))
      pre5 = coschi*sqrt(omega(3))
C
C     Shift state(i) to compensate for 1-based arrays
C
      smax = 0
      do i = 1,3
         state(i) = state(i) + 1
         if (state(i).gt.smax) smax = state(i)
      end do
C
C     Axis contraction --> either even or odd elements are used depending
C     on
C
      if (((state(1)/2)*2.eq.state(1)).eqv.
     .                    ((state(4)/2)*2.eq.state(4))) then
       even1=1
       even2=0
      else
       even1=0
       even2=1
      endif

      even4=state(1)-(state(1)/2)*2
      state(1) = (state(1) + 1) / 2
C
C     Initialize arrays sqt and R2 for use in recursion multiplications
C
      do i = 1,LEN
         sqt(i) = sqrt(ONE*i)
         R2(i) = sqrt(ONE*i*(i+1))
      end do
c  Initialize angular momentum matricies Sbar, Sbarsquared and MM
      do i=1,anglen
       do n=1,anglen
```

```
          Sbar(i,n) = ZERO
          Sbar2(i,n) = ZERO
          MM(i,n) = ZERO
         enddo
        enddo
        MM(1,1) =  angmom/(2*ONE)
        do i=2,angmom+1
         n=i-1
         MM(i,i) =  (angmom/(2.q0) - i + ONE)
         MM(n,i) =  0.5q0*sqrt(n*(angmom - i +2)*ONE)
         MM(i,n) = - MM(n,i)
         Sbar(i,n) =  - sqrt(n*(angmom-i+2)*ONE)
         Sbar(n,i) = Sbar(i,n)
        enddo
        do i=1,anglen
         do n=1,anglen
          do j=1,anglen
           Sbar2(i,n) = Sbar2(i,n)+Sbar(i,j)*Sbar(j,n)
          enddo
         enddo
        enddo
C Initialize zeroth order wavefunction
        asize(0) = smax
        do i1 = 1,(smax+1)/2
         do i2 = 1,smax
          do i3 = 1,smax
           do i4=1,anglen
            A(i1,i2,i3,i4,0) = ZERO
            T1(i1,i2,i3,i4) = ZERO
           enddo
          end do
         end do
        end do
        A(state(1),state(2),state(3),state(4),0) = ONE
        T1(state(1),state(2),state(3),state(4)) = ONE
c  Wavefunction axis size increases by three up to a_(maxj-2)/2,
```

```
c  then the sizes
c  start to decrease by three.
c First check to see if largest wavefunction, a_(maxj-2)/2,
c  will fit in the array
      if (LEN.lt.(3*(maxj-2)/2 + smax)) then
       write(*,*) 'LEN, in common.h, is too small for the largest'
       write(*,*) 'quantum number you entered. Set LEN to'
       write(*,*) 3*(maxj-2)/2 + smax,' and change wavefunction'
       write(*,*) ' arrays also.'
       stop
      endif
      do j=1,(maxj-2)/2
         asize(j) = asize(j-1) + 3
      enddo
      write(*,*) 'NOTE: wavefunction truncation will begin with ',
     . 'a(',(maxj-2)/2+1,')'

      do j=(maxj-2)/2+1,maxj-2
       asize(j) = asize(j-1) - 3
      enddo
      do n = 1, maxj-2
       do i1 = 1,(asize(n)+1)/2
        do i2 = 1,asize(n)
         do i3 = 1,asize(n)
          do i4=1,anglen
            A(i1,i2,i3,i4,n) = ZERO
          enddo
         enddo
        enddo
       enddo
      enddo
C
C     output file for energy expansion coefficients
C
      open(unit=9,file='Ecoeff.lis',status='unknown')
      write(9,*) maxj/2
```

```
      write(9,*) E(-1)
      write(9,*) E(0)
      write(*,*)
      write(*,*) '  j           E(j)  '
      write(*,142) -1, E(-1)
      write(*,142) 0, E(0)
      evenE = .FALSE.
      if (savewf) then
       fname = 'A00.lis'
       open(unit=55,file=fname,status='unknown')
       write(55,*) 2*state(1)-even4,state(2),state(3),state(4),ONE
       write(55,*) -1,0,0,0,ZERO
       close(unit=55)
      endif
C     ********************
C     **** MAIN LOOP ****
C     ********************
C
      do 900 n = 0, maxj-3
C
C     Compute H * A contributions from A(n) to A(n+1), A(n+2), ...
C
         CALL compute_H_A(n,maxj,pre2,pre3,pre32,pre4,pre5,angmom,
     .    even1)
C
C     Extract energy coefficients on every other iteration
C
         if (evenE) E((n+1)/2) =
     .    -A(state(1),state(2),state(3),state(4),n+1)
C
C     Final corrections to wavefunction tensor
C
         do j = 1,(n+1)/2
            i = n+1-2*j
            do i1 = 1, (min(asize(i),asize(n+1))+1)/2
             do i2 = 1, min(asize(i),asize(n+1))
```

```
                do i3 = 1, min(asize(i),asize(n+1))
                 do i4 = 1,angmom+1
                  if (A(i1,i2,i3,i4,i).ne.ZERO) A(i1,i2,i3,i4,n+1) =
     .              A(i1,i2,i3,i4,n+1) + A(i1,i2,i3,i4,i) * E(j)
                 enddo
                end do
               end do
              end do
             end do
C
C     Scale a(n+1) by factor K-tilde
C
c  orthogonality condition
           A(state(1),state(2),state(3),state(4),n+1) = ZERO
           if (savewf) then
              fname(2:2) = char(ichar('0') + int((n+1)/10))
              fname(3:3) = char(ichar('0') + n+1 - 10*int((n+1)/10))
              open(unit=55,file=fname,status='unknown')
           endif
           do i4 = 1, anglen
            if((i4/2)*2.eq.i4) then
             even3=even2
            else
             even3=even1
            endif
            do i1 = 1,(asize(n+1)+1)/2
             do i2 = 1,asize(n+1)
              do i3 = 1,asize(n+1)
               if (A(i1,i2,i3,i4,n+1).ne.ZERO) then
                temp = omega(1)*(2*(i1-state(1))-even3+even4) +
     .           omega(2)*(i2-state(2))+
     .           omega(3)*(i3-state(3)) + omega(4)*(state(4)-i4)
                if (temp.eq.ZERO) then
                  A(i1,i2,i3,i4,n+1) = ZERO
                else
                  A(i1,i2,i3,i4,n+1) = A(i1,i2,i3,i4,n+1) / temp
```

```
                endif
               if (abs(temp).le.0.q-20) write(*,*) 'Warning: Ktilda ',
     . 'element is zero or very small without being the state(1) ',
     . 'state(2),state(3) element which should be zero.'
                if (savewf) write(55,*) 2*i1-even3,i2,i3,i4,
     .           A(i1,i2,i3,i4,n+1)
               endif
               T1(i1,i2,i3,i4) = A(i1,i2,i3,i4,n+1)
              enddo
             end do
            end do
           end do
           if (savewf) then
              write(55,*) -1,0,0,0,ZERO
              close(unit=55)
           endif
C
C     Only even energy terms are nonzero
C
           if (evenE) then
              write(*,142) (n+1)/2, E((n+1)/2)
              write(9,*) E((n+1)/2)
           endif
           evenE = .not.evenE
 900   continue
       close(unit=9)
 142   format(2x,i2,2x,e40.33)
c 955   format(4i5,3x,e24.17)
       end
```

B.4 qcomp_H_A.f

```
C
C  This subroutine takes the tensor T1, which is initialized with
C    a copy of the tensor a(n) prior to the subroutine call, and
C    computes all product tensors of the form
```

```
C
C           /  m1       m2       m3 \
C          |  x    *   x    *   x    | a
C           \  1        2        3  /   n
C
C    which contribute to a(n+1), a(n+2), ..., a(maxj).  To follow
C    the notation in the implementation section of Dunn et al.,
C    (The program counts the order
C    in 1/D beginning with the E(-1) infinite-dimensional term,
C    but this is usually referred to as the zeroth term, Bender et
C    al. being one exception to this.  Therefore, the slight
C    discrepency in counting terms.)
C
      SUBROUTINE compute_H_A(n,maxj,pre2,pre3,pre32,pre4,pre5,angmom,
     . even1)
      IMPLICIT NONE
      include 'qcommon.h'
C----- local variables
C   axis1, axis2, axis3 represent size of current tensor,
C
      REAL*16 pre2,pre3,pre32,pre4,pre5,term,termp,factor,factor2
      real*16 factor3,factor4
      INTEGER m,m1,m2,m3,i1,i2,i3,i4,axis1,axis2,axis3,lim1,lim2,lim3
      INTEGER n,maxj,p,angmom,even1
      logical even3,even5
      even3=(even1.eq.0)
      axis1 = asize(n)
      do m1 = 0, maxj-n
C  T2 = T1
        axis2 = asize(n)
        axis3 = asize(n)
        do i1 = 1,(axis1+1)/2
         do i2 = 1,axis2
          do i3 = 1,axis3
           do i4=1,angmom+1
            T2(i1,i2,i3,i4) = T1(i1,i2,i3,i4)
```

```
            enddo
           end do
          end do
         end do
        do m3 = 0, maxj-n-m1
C  T3 = T2
         axis2 = asize(n)
         do i1 = 1,(axis1+1)/2
          do i2 = 1,axis2
           do i3 = 1,axis3
            do i4 = 1,angmom+1
             T3(i1,i2,i3,i4) = T2(i1,i2,i3,i4)
            enddo
           end do
          end do
         end do
        do m2 = 0, maxj-n-m3-m1
         m = m1+m2+m3+n
           if (m.le.(maxj-4)) then
            lim1 = (min(axis1,asize(m+2))+1)/2
            lim2 = min(axis2,asize(m+2))
            lim3 = min(axis3,asize(m+2))
            if (m1.eq.(2*(m1/2))) then
             factor = UV3(PTR(m2+m3,m1/2)+m3) + 4*pre2*(m2+2)*
     .        (m2+1)*TK1(PTR(m2+m3+2,m1/2)+m3) +4*
     .        pre32*(m3+1)*(m2+1)*TK1(PTR(m2+m3+2,m1/2)+m3+1) + 4*
     .        pre3*(m3+2)*(m3+1)*TK1(PTR(m2+m3+2,m1/2)+m3+2)
             factor2 = UV6(PTR(m2+m3,m1/2)+m3)
            else
             factor = - 2*pre4*(m2+1)*
     .        TK2(PTR(m2+m3+1,(m1-1)/2)+m3) -2*pre5*
     .        (m3+1)*TK2(PTR(m2+m3+1,(m1-1)/2)+m3+1)
             if((m-n).ge.1) factor=factor+UV5(PTR(m2+m3,(m1-1)/2)+m3)
            endif
            factor3 = 2*R12W3(PTR2(m2+m3,m1)+m3) -4*pre4*
     .        (m2+1)*R12W2(PTR2(m2+m3+1,m1)+m3) -4*pre5*
```

```
     .         (m3+1)*R12W2(PTR2(m2+m3+1,m1)+m3+1)
              do i1 = 1,lim1
               do i2 = 1,lim2
                do i3 = 1,lim3
                 do i4 = 1,angmom+1
                  if (T3(i1,i2,i3,i4).ne.ZERO) then
                   if (m1.eq.(2*(m1/2))) then
c  U3, T1_3, T1_7, T1_10
                    A(i1,i2,i3,i4,m+2) =
     .               A(i1,i2,i3,i4,m+2) - factor * T3(i1,i2,i3,i4)
                    do p = 1,angmom+1
                     A(i1,i2,i3,p,m+2) = A(i1,i2,i3,p,m+2) -        !
     .                T3(i1,i2,i3,i4)*Sbar2(p,i4)*factor2           !U6
                    enddo
c  R12W3, R12W2_2, R12W2_4 diagonal term
                    A(i1,i2,i3,i4,m+2) = A(i1,i2,i3,i4,m+2) - factor3*
     .               MM(i4,i4)*T3(i1,i2,i3,i4)
                   else  !m1 is odd
c  R12W3, R12W2_2, R12W2_4, U5, T2_2, T2_4 top diagonal
                    if(i4.gt.1) A(i1,i2,i3,i4-1,m+2) =
     .               A(i1,i2,i3,i4-1,m+2)- (factor*Sbar(i4-1,i4) +
     .               factor3*MM(i4-1,i4))*T3(i1,i2,i3,i4)
c  R12W3, R12W2_2, R12W2_4, U5, T2_2, T2_4 bottom diagonal
                    if(i4.lt.(angmom+1)) A(i1,i2,i3,i4+1,m+2) =
     .               A(i1,i2,i3,i4+1,m+2) - (factor3*MM(i4+1,i4) +
     .               factor*Sbar(i4+1,i4))*T3(i1,i2,i3,i4)
                   endif  !(m1.eq.(2*(m1/2)))
                  endif  !(T3(i1,i2,i3,i4).ne.ZERO)
                 enddo
                end do
               end do
              end do
             endif !(m.le.(maxj-4))
             if (m.le.(maxj-3)) then
              lim1 = (min(axis1,asize(m+1))+1)/2
              lim2 = min(axis2,asize(m+1)+1)
```

```
                lim3 = min(axis3,asize(m+1)+1)
                if (m1.eq.(2*(m1/2))) then
                 factor = - 4*pre2*(m2+1)*
     .            TK1(PTR(m2+m3+1,m1/2)+m3) - 2*pre32*
     .            (m3+1)*TK1(PTR(m2+m3+1,m1/2)+m3+1)
                 factor2 = - 2*pre32*(m2+1)*
     .            TK1(PTR(m2+m3+1,m1/2)+m3) - 4*pre3*
     .            (m3+1)*TK1(PTR(m2+m3+1,m1/2)+m3+1)
                else
                 if ((m-n).ge.1) then
                  factor = pre4*TK2(PTR(m2+m3,(m1-1)/2)+m3)
                  factor2 = pre5*TK2(PTR(m2+m3,(m1-1)/2)+m3)
                 else
                  factor = ZERO
                  factor2 = ZERO
                 endif
                endif
                factor3 = 2*pre4*R12W2(PTR2(m2+m3,m1)+m3)
                factor4 = 2*pre5*R12W2(PTR2(m2+m3,m1)+m3)
                do i1 = 1,lim1
                 do i2 = 1,lim2
                  do i3 = 1,lim3
                   do i4 = 1,angmom+1
                    if (T3(i1,i2,i3,i4).ne.ZERO) then
                     if (m1.eq.(2*(m1/2))) then
c  T1_2, T1_5, diagonal of R12W2_1
                      if (i2.gt.1) A(i1,i2-1,i3,i4,m+1) =
     .                 A(i1,i2-1,i3,i4,m+1) - sqt(i2-1)*(factor+
     .                 factor3*MM(i4,i4))*T3(i1,i2,i3,i4)
                      if (i2.lt.LEN) A(i1,i2+1,i3,i4,m+1) =
     .                 A(i1,i2+1,i3,i4,m+1)+sqt(i2)*(factor+factor3*
     .                  MM(i4,i4))*T3(i1,i2,i3,i4)
c  T1_6, T1_9, diagonal of  R12W2_3
                      if (i3.gt.1) A(i1,i2,i3-1,i4,m+1) =
     .                 A(i1,i2,i3-1,i4,m+1) - sqt(i3-1)*(factor2+factor4*
     .                 MM(i4,i4))*T3(i1,i2,i3,i4)
```

```
                  if (i3.lt.LEN) A(i1,i2,i3+1,i4,m+1) =
     .             A(i1,i2,i3+1,i4,m+1) + sqt(i3)*(factor2+factor4*
     .             MM(i4,i4))*T3(i1,i2,i3,i4)
                 else   ! m1 odd
                  if (i4.gt.1) then
c  upper diagonal of R12W2_1 and T2_1
                   if (i2.gt.1) A(i1,i2-1,i3,i4-1,m+1) =
     .              A(i1,i2-1,i3,i4-1,m+1) - sqt(i2-1)*(factor3*
     .              MM(i4-1,i4)+factor*Sbar(i4-1,i4))*T3(i1,i2,i3,i4)
                   if (i2.lt.LEN) A(i1,i2+1,i3,i4-1,m+1) =
     .              A(i1,i2+1,i3,i4-1,m+1) + sqt(i2)*(factor3*
     .              MM(i4-1,i4) +factor*Sbar(i4-1,i4))*T3(i1,i2,i3,i4)
c  upper diagonal of R12W2_3 and T2_3
                   if (i3.gt.1) A(i1,i2,i3-1,i4-1,m+1) =
     .              A(i1,i2,i3-1,i4-1,m+1) - sqt(i3-1)*(factor4*
     .              MM(i4-1,i4)+factor2*Sbar(i4-1,i4))*T3(i1,i2,i3,i4)
                   if (i3.lt.LEN) A(i1,i2,i3+1,i4-1,m+1) =
     .              A(i1,i2,i3+1,i4-1,m+1) + sqt(i3)*(factor4*
     .              MM(i4-1,i4)+factor2*Sbar(i4-1,i4))*T3(i1,i2,i3,i4)
                  endif
                  if (i4.lt.angmom+1) then
c  lower diagonal of R12W2_1 and T2_1
                   if (i2.gt.1) A(i1,i2-1,i3,i4+1,m+1) =
     .              A(i1,i2-1,i3,i4+1,m+1) - sqt(i2-1)*(factor3*
     .              MM(i4+1,i4)+factor*Sbar(i4+1,i4))*T3(i1,i2,i3,i4)
                   if (i2.lt.LEN) A(i1,i2+1,i3,i4+1,m+1) =
     .              A(i1,i2+1,i3,i4+1,m+1) + sqt(i2)*(factor3*
     .              MM(i4+1,i4)+factor*Sbar(i4+1,i4))*T3(i1,i2,i3,i4)
c  lower diagonal of R12W2_3 and T2_3
                   if (i3.gt.1) A(i1,i2,i3-1,i4+1,m+1) =
     .              A(i1,i2,i3-1,i4+1,m+1) - sqt(i3-1)*(factor4*
     .              MM(i4+1,i4)+factor2*Sbar(i4+1,i4))*T3(i1,i2,i3,i4)
                   if (i3.lt.LEN) A(i1,i2,i3+1,i4+1,m+1) =
     .              A(i1,i2,i3+1,i4+1,m+1) + sqt(i3)*(factor4*
     .              MM(i4+1,i4)+factor2*Sbar(i4+1,i4))*T3(i1,i2,i3,i4)
                  endif
```

```
        endif
       endif
      enddo
     end do
    end do
   end do
  endif !(m.le.(maxj-3))
  if (((m-n).ge.3).and.(m1.eq.(2*(m1/2)))) then
   lim1 = (min(axis1,asize(m-2))+1)/2
   lim2 = min(axis2,asize(m-2))
   lim3 = min(axis3,asize(m-2))
   factor = UV1(PTR(m2+m3,m1/2)+m3)
   do i1 = 1,lim1
    do i2 = 1,lim2
     do i3 = 1,lim3
      do i4 = 1,angmom+1
       if (T3(i1,i2,i3,i4).ne.ZERO) then
         A(i1,i2,i3,i4,m-2) =                              ! U1
          A(i1,i2,i3,i4,m-2) - factor * T3(i1,i2,i3,i4) !
       endif
      enddo
     end do
    end do
   end do
  endif !(((m-n).ge.3).and.(m1.eq.(2*(m1/2))))
  if (((m-n).ne.0).and.(m.le.(maxj-2))) then
   lim1 = (min(axis1,asize(m))+1)/2
   lim2 = min(axis2,asize(m)+2)
   lim3 = min(axis3,asize(m)+2)
   if (m1.eq.(2*(m1/2))) then
    factor = UV2(PTR(m2+m3,m1/2)+m3)
   else
    factor = UV4(PTR(m2+m3,(m1-1)/2)+m3)
   endif
   factor2 = 2*R12W1(PTR2(m2+m3,m1)+m3)
   do i1 = 1,lim1
```

```
                do i2 = 1,lim2
                 do i3 = 1,lim3
                  do i4 = 1,angmom+1
                   if (T3(i1,i2,i3,i4).ne.ZERO) then
                    if (m1.eq.(2*(m1/2))) then
                     A(i1,i2,i3,i4,m) = A(i1,i2,i3,i4,m) - factor*    ! U2
                .     T3(i1,i2,i3,i4)                                  !
                     term = T3(i1,i2,i3,i4)*TK1(PTR(m2+m3,m1/2)+m3)
                     termp = term * pre2                              !
                     if ((i2+2).le.LEN) A(i1,i2+2,i3,i4,m) =          !
                .     A(i1,i2+2,i3,i4,m) - termp*R2(i2)              !  T1_1
                     A(i1,i2,i3,i4,m) = A(i1,i2,i3,i4,m) +            !
                .     termp * (2*i2-1)                               !
                     if (i2.gt.2) A(i1,i2-2,i3,i4,m) =                !
                .     A(i1,i2-2,i3,i4,m) - termp*R2(i2-2)            !
                     termp = term * pre32                             !
                     if (i2.lt.LEN) then                              !
                      if (i3.lt.LEN) A(i1,i2+1,i3+1,i4,m) =           !
                .      A(i1,i2+1,i3+1,i4,m) - termp *                 !
                .      sqt(i2) * sqt(i3)                              !
                      if (i3.ne.1) A(i1,i2+1,i3-1,i4,m) =             !
                .      A(i1,i2+1,i3-1,i4,m) + termp *                 !
                .      sqt(i2) * sqt(i3-1)                            !  T1_4
                     endif                                            !
                     if (i2.ne.1) then                                !
                      if (i3.lt.LEN) A(i1,i2-1,i3+1,i4,m) =           !
                .      A(i1,i2-1,i3+1,i4,m) + termp *                 !
                .      sqt(i2-1) * sqt(i3)                            !
                      if (i3.ne.1) A(i1,i2-1,i3-1,i4,m) =             !
                .      A(i1,i2-1,i3-1,i4,m) - termp *                 !
                .      sqt(i2-1) * sqt(i3-1)                          !
                     endif                                            !
                     termp = term * pre3                              !
                     if ((i3+2).le.LEN) A(i1,i2,i3+2,i4,m) =      !
                .     A(i1,i2,i3+2,i4,m) - termp*R2(i3)      !
                     A(i1,i2,i3,i4,m) = A(i1,i2,i3,i4,m) +      !  T1_8
```

```
     .              termp * (2*i3-1)        !
                   if (i3.gt.2) A(i1,i2,i3-2,i4,m) =     !
     .              A(i1,i2,i3-2,i4,m) - termp*R2(i3-2)     !
c  diagonal of R12W1
                   A(i1,i2,i3,i4,m) = A(i1,i2,i3,i4,m) - factor2*
     .              MM(i4,i4)*T3(i1,i2,i3,i4)
                  else !m1 odd
c  top diagonal of R12W1 and U4
                   if(i4.gt.1) A(i1,i2,i3,i4-1,m) = A(i1,i2,i3,i4-1,m)-
     .              (factor2*MM(i4-1,i4)+factor*Sbar(i4-1,i4))*
     .              T3(i1,i2,i3,i4)
c  bottom diagonal of R12W1 and U4
                   if(i4.lt.(angmom+1)) A(i1,i2,i3,i4+1,m) =
     .              A(i1,i2,i3,i4+1,m) - (factor2*MM(i4+1,i4)+
     .              factor*Sbar(i4+1,i4))*T3(i1,i2,i3,i4)
                  endif !(m1.eq.(2*(m1/2)))
                 endif !(T3(i1,i2,i3,i4).ne.ZERO)
                enddo
               enddo
              end do
             end do
            endif !(((m-n).ne.0).and.(m.le.(maxj-2)))
C        /          \
C  T   = | I  * x * I | T
C   3    \      2   /   3
           do i3 = 1,axis3
            do i1 = 1,(axis1+1)/2
             do i4 = 1,angmom+1
              do i2 = 2,axis2
               TT(i2-1) = sqt(i2-1)*T3(i1,i2,i3,i4)
              end do
              TT(axis2) = ZERO
              if (axis2.lt.LEN) T3(i1,axis2+1,i3,i4) = sqt(axis2)*
     .         T3(i1,axis2,i3,i4)
              do i2 = axis2,2,-1
               T3(i1,i2,i3,i4) = TT(i2) + sqt(i2-1)*T3(i1,i2-1,i3,i4)
```

```
                end do
                T3(i1,1,i3,i4) = TT(1)
               enddo
              enddo
             enddo
            axis2=axis2 + 1
            if (axis2.gt.LEN) axis2 = LEN
           end do !m2

C         /          \
C  T   = | I * I * x  | T
C   2    \          3/   2
          do i2 = 1, axis2
           do i1 = 1,(axis1+1)/2
            do i4 = 1,angmom+1
             do i3 = 2,axis3
              TT(i3-1) = sqt(i3-1)*T2(i1,i2,i3,i4)
             end do
             TT(axis3) = ZERO
             if (axis3.lt.LEN) T2(i1,i2,axis3+1,i4) = sqt(axis3)*
     .        T2(i1,i2,axis3,i4)
             do i3 = axis3,2,-1
              T2(i1,i2,i3,i4) = TT(i3) + sqt(i3-1)*T2(i1,i2,i3-1,i4)
             end do
             T2(i1,i2,1,i4) = TT(1)
            enddo
           enddo
          enddo
          axis3 = axis3 + 1
          if (axis3.gt.LEN) axis3 = LEN
         enddo !m3
C         /          \
C  T   = | x * I * I | T
C   1    \ 1        /   1
         do i2 = 1,axis2
          do i3 = 1,axis3
```

```
do i4 = 1,angmom+1
 if ((i4/2)*2.eq.i4) then
  even5=.not.even3
 else
  even5=even3
 endif
 if(.not.even5) then
  TT((axis1+1)/2)=ZERO
  if (axis1.gt.2) then
   do i1=2,(axis1+1)/2
    TT(i1-1)=sqt(2*i1-2)*T1(i1,i2,i3,i4)
   enddo
  endif
  do i1=1,(axis1+1)/2
   T1(i1,i2,i3,i4)=sqt(2*i1-1)*T1(i1,i2,i3,i4)+
    TT(i1)
  enddo
  do i1=(axis1+3)/2,(LEN+1)/2
   T1(i1,i2,i3,i4)=ZERO
  enddo
 else
  TT(1)=ZERO
  if (axis1.gt.1) then
   do i1=1,axis1/2
    TT(i1+1)=sqt(2*i1)*T1(i1,i2,i3,i4)
   enddo
   do i1=1,axis1/2
    T1(i1,i2,i3,i4)=sqt(2*i1-1)*T1(i1,i2,i3,i4)+
     TT(i1)
   enddo
  endif
  T1(axis1/2+1,i2,i3,i4)=TT(axis1/2+1)
  do i1=axis1/2+2,(LEN+1)/2
   T1(i1,i2,i3,i4)=ZERO
  enddo
 endif
```

```
     enddo
    enddo
   enddo
   axis1 = axis1 + 1
   if (axis1.gt.LEN) axis1 = LEN
  even3=.not.even3
end do !m1
return
end
```

Appendix C

Mathematica Notebook for Wavefunction Symmetries

This notebook takes a wavefunction list generated from the helium matrix method code and puts a mark in an array where there are non-zero elements. The array is written out as a matrix of columns. In reality, for higher angular momentum, the array is four dimensional so we should have a matrix of matricies. The fourth index has a small range. For p-odd states it can be 1 or 2. For d-even states it can be 1 or 2 or 3, etc. So when we place a mark in the array to say that there is a nonzero element there, we will use a "1" as the mark when the element has a fourth index of 1 and we will use a "2" when the element has a fourth index of 2, etc. If elements with different fourth indices but exact first, second and third indices exist then we will use a mark consisting of both fourth indices such as "12".

To see how Mathematica arranges indicies we can create a sample three dimensional array and place a non-zero number at some location. In this example the non-zero numbers have indicies 1,1,2 and 1,2,1. When the array is displayed notice that third index represents the location in the inner column. The first and second index give the row and column, respectively, of the outer matrix structure.

```
wavearray=Table["0",{x,1,3},{y,1,3},{z,1,3}];
wavearray[[1,1,2]]="1";
wavearray[[1,2,1]]="1";
MatrixForm[wavearray]
```

$$\left(\begin{pmatrix}0\\1\\0\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}\right)\left(\begin{pmatrix}0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}\right)\left(\begin{pmatrix}0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}\right)$$

For the wavefunction analysis we arrange the array so that ais along the inner column and aand agive the matrix row and column. This means that the indicies for abecome the third index for the array. We set up a function that reads a wavefunction from a directory and displays an array corresponding to that wavefunction as described above. The variable "file1" must contain the path and filename as shown.

```
wavefn[file1_] := (wavearray=Table["0",{x,1,3},{y,1,3},{z,1,6}];
file2=OpenRead[file1];n1=Read[file2,Number];n2=Read[file2,Number];
n3=Read[file2,Number];n4=Read[file2,Number];Skip[file2,Number];
While[n1>0,
If[(n1<7)&&(n2<4)&&(n3<4),
If[wavearray[[n3,n2,n1]]=="0",wavearray[[n3,n2,n1]]=ToString[n4],
n5=wavearray[[n3,n2,n1]];wavearray[[n3,n2,n1]]=n5<>ToString[n4]]];
n1=Read[file2,Number];n2=Read[file2,Number];n3=Read[file2,Number];
n4=Read[file2,Number];Skip[file2,Number]];Close[file2];
StandardForm[MatrixForm[wavearray]])
```

An inner column can be labeled like $\begin{pmatrix}x_1\\x_2\\x_3\\\vdots\end{pmatrix}$. We see that there are two cases.

A) $x_1 = x_3 = x_5 = \cdots = 0$ so that we transform $x_2 \rightarrow x_1$, $x_4 \rightarrow x_2$, ..., $x_{2i} \rightarrow x_i$.

B) $x_2 = x_4 = x_6 = \cdots = 0$ so that we transform $x_1 \rightarrow x_1$, $x_3 \rightarrow x_2$, ..., $x_{2i-1} \rightarrow x_i$.

The states are labeled like podd0001 or deven1001 where the four integers give the four large dimension quantum numbers n_a, n_s, n_θ, and i. The wavefunction array file names are given by AXX.lis where XX is p. For example, A00.lis holds the elements for $\mathbf{a}_0$ and A01.lis holds the elements of $\mathbf{a}_1$. Here are some examples:

wavefn["Research:helium:higherL:MemoryIntensive:quadrup:podd0001:A00.lis"]

$$\left(\begin{pmatrix}1\\0\\0\\0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\right)$$
$$\left(\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\right)$$
$$\left(\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\begin{pmatrix}0\\0\\0\\0\\0\\0\end{pmatrix}\right)$$

wavefn["Research:helium:higherL:MemoryIntensive:quadrup:podd0001:A01.lis"]