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A study of the variational aspects for the Fock expansion of the solution of hydrogenic atoms in constant magnetic fields

James B. Sternberg

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I am submitting herewith a dissertation written by James B. Sternberg entitled "A study of the variational aspects for the Fock expansion of the solution of hydrogenic atoms in constant magnetic fields." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

Joseph Macek, Major Professor

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Vice Provost and Dean of the Graduate School

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I am submitting herewith a dissertation written by James B. Sternberg entitled "A Study of the Variational Aspects of the Fock Expansion of the Solution of Hydrogenic Atoms in a Constant Magnetic Field". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

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Joseph Macek, Major Professor

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F. A.

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and Dean of the Graduate School

A STUDY OF THE VARIATIONAL ASPECTS FOR THE FOCK EXPANSION OF THE SOLUTION OF HYDROGENIC ATOMS IN CONSTANT MAGNETIC FIELDS

A Dissertation
Presented for the
Doctor of Philosophy Degree at
The University of Tennessee, Knoxville

James B. Sternberg December 1999

DEDICATION

This dissertation is dedicated to my parents, for their support and to Alexis Balderflüf for her dedicated study of hydrogen.

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ABSTRACT

The study of hydrogen in a constant magnetic field has been one of the most persistent problems in non-relativistic quantum mechanics. Although it is conceptually one of the simplest problems that one can think of, the non-separability of the Schrödinger equation containing both a Coulombic term and a constant magnetic term in the Hamiltonian has made the problem especially difficult. In this dissertation, we apply a solution in the form of the Fock expansion to this problem. It is shown that the logarithmic terms which are associated with the Fock expansion vanish. We then derive and solve a three term recurrence relation in order to find a set of solutions to this Schrödinger equation. Linear combinations of these Fock solutions which satisfy the physical boundary conditions are found, and at the same time upper bounds for the binding energies are found using the Raleigh-Ritz variational principal. It is shown that these same Fock solutions produce lower bounds for the binding energies when the Schwinger variational principal is employed. Therefore, the eigenenergies for bound states of hydrogen in a constant magnetic field can be bracketed from both above and below. We furthermore examine another recent method, that of Kravchenko, Liberman and Johansson[15] for solving the hydrogen atom in a constant magnetic field problem. We show that their method is equivalent to examining an eigenchannel in the R-matrix method of Bohm and Fano, and compare their results to the ones we obtain through variational methods on the Fock solution. We find that their method is both accurate and efficient for calculating the binding energies.

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CHAPTER 1

Introduction

The computation of binding energies for hydrogenic atoms in arbitrary, constant magnetic fields has been one of the most persistent problems in quantum mechanics. The early spectroscopy experiments date back to those of Zeeman in 1897 [1], and attempts to accurately describe this system are still actively sought. The advent of modern quantum mechanics allowed the differential equation which produces the solutions to this physical system to be written down easily in the form of the Schrödinger equation.

$$\left(-\frac{1}{2}\nabla_r^2+\frac{L^2}{2r^2}-\frac{\vec{B}\cdot\vec{L}}{c}-\frac{Z}{r}+\frac{B^2}{8c^2}r^2\sin^2\theta\right)\psi=E\psi \tag{1.1}$$

Here, Z is the charge of the nucleus, B is the magnitude of the applied magnetic field, and E is the energy of the state. Atomic units $\hbar = m_e = e = 1$ are used where m_e is the mass of the electron and e is the charge of the electron. The advantage of these units is that large numbers of numerical factors do not need to be carried throughout the calculation. Atomic units are discussed extensively in Bethe and Salpeter[2].

This Schrödinger equation can be refined to include small corrections. For example, the form written in equation (1.1) assumes an infinitely massive nucleus. The motion of the nucleus is a small correction which can be treated as a perturbation. This correction is not made in this work, however. Other work on this correction is discussed in the review article by Clark, Lu and Starace [3]. Spin-orbit corrections, corrections for the anomalous moment of the electron, and other relativistic corrections can also be made. These are all discussed in Bethe and Salpeter[2].

Obtaining general solutions to the Schrödinger equation has been extremely difficult. This difficulty arises because the natural symmetry of the system changes radically between the high B field and the low B field cases. For small fields, the solutions have a spherical symmetry because the Coulomb potential, $-\frac{Z}{r}$ is spherically symmetric. For large fields, however, the solutions have cylindrical symmetry because the dominant potential is the magnetic potential. This potential has a form of $\frac{B^2}{2}r^2 \sin^2\theta$, where θ is an angle measured from the direction of the applied magnetic field. Throughout this work, it will be assumed that the direction of the applied field is the $\hat{z}$ direction. Because of the change of symmetry between low and high field, the Schrödinger equation is not separable in any coordinate system. Therefore, one reason for interest in this problem is that it is a conceptually simple, non-separable problem. By studying the hydrogenic atom in a constant magnetic field problem, methods can be developed for studying other, more general non-separable systems.

A second reason for studying this problem was given by Fano in 1980 [4], who points out that a hydrogenic atom in a constant magnetic field can be used as a prototype for studying wave propagation along a potential ridge. Such ridges are common in physical systems. For example, the potential surfaces for many molecules show the features of a potential ridge. Such ridges also arise in the potential describing resonances in two electron atoms and in the "transition states" for many chemical reactions [5]. The magnetic potential displays such a ridge in a very simple form. If the magnetic potential $V_\mathrm{m} = \frac{1}{2}B^2r^2\sin^2\theta$ is plotted, it is clear that such a potential vanishes for $\theta = 0$ and $\theta = \pi$. However, the potential is maximum at $\theta = \frac{\pi}{2}$, and rises to infinity as r goes to infinity. The ridge is clearly visible in Figure (1.1) which shows the combined Coulomb and magnetic potential for hydrogen with a magnetic field of 13.7 atomic units. By solving the Schrödinger equation, the behavior of the solutions along this ridge can be studied and perhaps can give insight into more general ridge problems.

The study of hydrogenic atoms in magnetic fields is not confined to the discipline of theoretical atomic physics. While it is true that the magnetic fields currently produced in the laboratory only show a large effect for highly excited states, even the lowest states of this system are still studied. One discipline where such systems are of interest are in the study of excitons in magnetic fields [9]. An exciton is a system which is found in some semiconductors in which an electron becomes

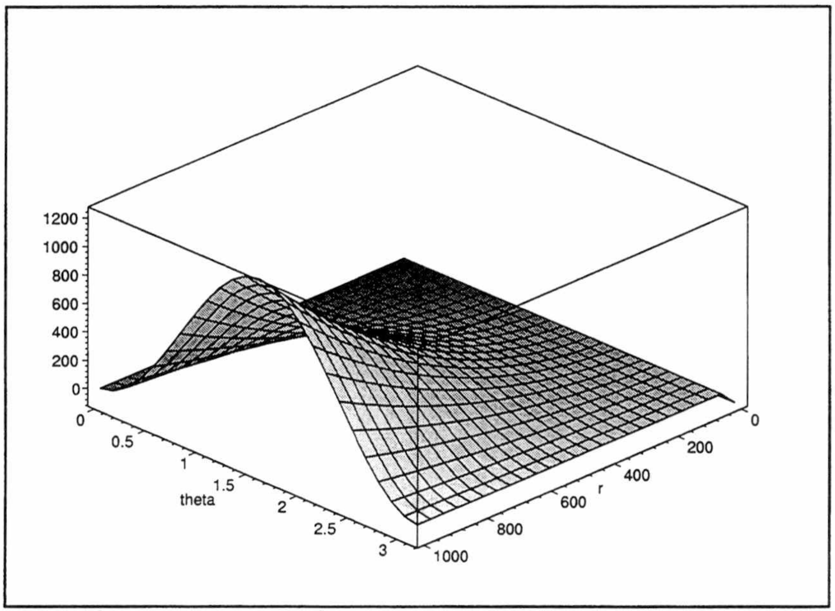

Figure 1.1: Plot of the combined Coulomb and magnetic potentials: The combined potentials of for the hydrogenic atom in a constant magnetic field are plotted for an applied magnetic field of 13.7 au. The potential ridge caused by the magnetic term is clearly seen.

bound to a charged defect. The system is very similar to that of hydrogen. The effective Coulomb potential is much less because of the dielectric constant of the semiconductor. The mass is also replaced by an effective mass[10]. The result is that excitons in a constant magnetic field present systems which are extremely similar to that of hydrogen atoms in a constant magnetic fields. The effects seen only on highly excited states of hydrogen can be seen in even the lowest states of excitons at laboratory attainable fields.

Some branches of astrophysics involve matter in much more intense magnetic fields that can currently be produced in the laboratory. For example, magnetic fields up to 5×10^8 Gauss have been detected near the white dwarf PG 1031+234 [11]. White dwarfs are formed when medium sized stars are no longer able to sustain fusion at their cores. The outer layers of these stars, which are mostly composed of hydrogen, are violently blown off. The core which is left behind becomes a white dwarf. These events are quite common in the universe and lead to many opportunities to observe hydrogen and other atoms in very intense fields. In fact, hydrogen has been observed around PG 1031+234, and attempts have been made to understand the spectrum[12]. More recently, even larger fields have been detected around a special class of neutron stars called magnetars. These produce magnetic fields ranging from 1×10^{13} Gauss to 1×10^{14} Gauss[13]. This is well into the regime where even the ground state is strongly affected by the star's magnetic field.

One consequence of the history and interest in hydrogenic atoms in constant magnetic fields has been the countless methods which have been used to describe the system. The most popular methods have been the variational approaches. The calculation of Smith et al.[27] uses a three parameter trial function of the form

$$\psi_m^{\pm}(\vec{r}) = \sum_{il} \left(a_i^{(t)} r^l + b_i^{(t)} r^{l+1} \right) e^{-\beta_i^{(t)} r} Y_{lm}(\theta, \phi). \tag{1.2}$$

Such a trial function is able to produce good ground state energies for fields between 10^6 and 10^8 Gauss. Brandi[21] was able to calculate more intense magnetic fields by using a trial function which is a linear combination of hydrogen atom wavefunctions.

$$\psi(\vec{r}) = \sum_i a_i \frac{2}{n^2} \left[\frac{(n-l-1)!}{[(n+l)!]^3} \right]^{\frac{1}{2}} x^l e^{-\frac{x}{2}} L_{n-l-1}^{2l+1}(x)\, Y_{l_i}^{m_i}(\theta, \phi), \tag{1.3}$$

where $x = \frac{2r}{n}$. This approach was able to produce good ground state energies from 10^8 to 10^9 Gauss. The high field limit has been calculated by Rech et al.[22]. In this calculation, the Schrödinger equation is written in parabolic coordinates ε,η, and ϕ and a trial function of the form

$$\psi(\varepsilon, \eta, \phi) = Ne^{\pm im\phi} \sum_{ij=0}^{\infty} d_{ij} \varepsilon^i \eta^i e^{-\frac{1}{2}(a\varepsilon + b\eta + c\varepsilon\eta)} \tag{1.4}$$

is used in the Raleigh-Ritz variational principle. This calculation was made for fields between 4.7×10^8 and 1.2×10^{14} Gauss. Relativistic variational calculations have been made by Goldman and Chen[23, 24]. These calculations are able to avoid the collapse of the variational energies to the negative energy sea by carefully specifying the boundary conditions. These calculations were made from fields of 2.35×10^8 to 4.7×10^{12} Gauss.

The earliest methods were the simple perturbative methods. Although the full Schrödinger equation is not separable in this case, it is separable in the two extremes of the applied magnetic field. The simple perturbative methods work in the two cases where either the Coulomb potential dominate or the magnetic field dominates. In the case of the magnetic interaction being very small compared to that of the Coulomb attraction the solutions behave approximately like those of hydrogen with no applied field. In the case of the Coulomb attraction being very small compared to that of the applied magnetic field, the solutions appear similar to those of the harmonic oscillator. Unfortunately, the direct perturbative approach only works for a limited range of external magnetic fields. More terms can be taken in the perturbation expansion in order to make the calculation accurate over a wider range of applied fields, however the series always eventually diverges. Higher order terms in the perturbation series expansion causes this divergence to become much more severe as the order increases. As a result, one has to be very careful to use higher order perturbation theory only in the range in which it is valid. Otherwise, the result can be extremely inaccurate. Figure (1.2) shows the divergent behavior of the results of perturbation theory. As one can see, fifth order perturbation theory becomes extremely divergent when pushed beyond its range of validity. Although perturbative approaches are less common than variational approaches, a few are still notable.

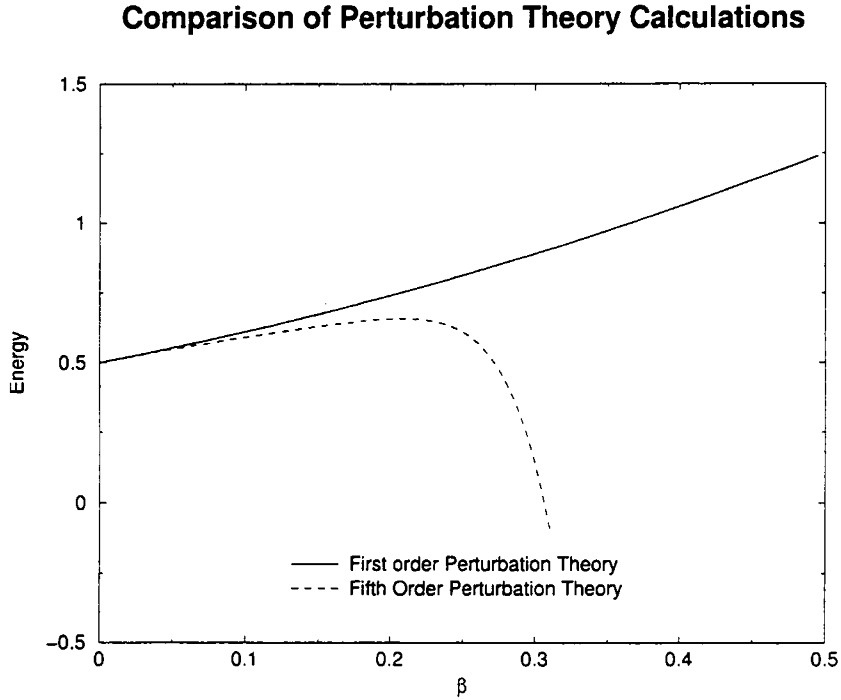

Figure 1.2: Plot of first and fifth order perturbation theory calculations: Both the first and fifth order perturbation results for hydrogen in a constant magnetic field are plotted as a function of the applied magnetic field β. The higher order perturbation result shows a drastic divergence as the calculation is pushed beyond its range of validity. In fact, the perturbation results diverge (yield non-physical energies) for any order perturbation expansion.

Killingbeck[18] improved the standard perturbative method by including only what is necessary as the perturbation. This was done by writing the angular term, $\sin^2\theta$ for the low field case in terms of the zeroth and second order Legendre functions P_0 and P_2. The zeroth order Legendre function P_0 is spherically symmetric. Therefore adding this term to the unperturbed Schrödinger equation does not change the natural symmetry of the system. The Schrödinger equation was solved exactly with this Legendre term included. Only the second order part was used as a perturbation. Doing this allowed accurate results to be calculated with less terms in the perturbation expansion than the standard method. Another notable perturbation calculation uses perturbation theory for both the high and low fields. Padé approximants were then used to interpolate between the two extremes and yield a result which applied for all fields[19]. The results were quite good in the two asymptotic regions, but were inaccurate in the intermediate region.

Adiabatic approximations have been used to find the lowest energies of this system[25, 26]. These calculations were adiabatic in the context that r varied slowly. This allowed separability between r and θ to be assumed. The advantage of this approach was that it produced rigorous upper and lower bounds to the exact eigenenergies. This allowed the eigenenergies to be bracketed and the errors in the calculation to be bounded. In these calculations an infinite set of coupled differential equations was derived. The set of differential equations can not be solved exactly, but approximations were made to allow calculation. If all of the coupling matrix elements were neglected, then the system of equations could be solved and the solutions were lower bounds to the exact energies. If only the off-diagonal coupling matrix elements were neglected then upper bounds were produced. One disadvantage of this method was that the lower bound was not variational and therefore could not be improved by adding more terms. Additional terms simply allowed the calculation of higher states, but did not improve the accuracy of the lower states. Therefore, although the energies were rigorously bounded from both above and below, the errors in the calculation could not be reduced easily. In the work discussed in this thesis, upper and lower bounds are also calculated, but both bounds are produced variationally. The advantage of the variational approach is that both the upper and lower bounds converge towards the exact eigenenergies as the number of terms in the expansion is increased. These convergent bounds allow the errors in the calculation to be rigorously known and for the calculation to be improved easily.

Because of the seemingly chaotic nature of the energy levels in the intermediate region of the magnetic field strength classical methods have recently been applied to the hydrogenic atom in a constant magnetic field problem [14]. The system has been studied extensively using quantum mechanics and many calculations yield very good results for certain ranges of the applied magnetic field. Classically the hydrogen atom in a constant magnetic field is a simple system which displays chaotic dynamics. In the two asymptotic regions of zero and extremely high B fields, the system is completely separable and only stable, periodic orbits are found. As a magnetic field is applied, the stable orbits found in the standard hydrogen atom begin to become unstable. These unstable orbits begin to bifurcate for increasing fields to create new stable orbits. These stable orbits then become unstable and bifurcate again until the entire phase space is filled with unstable trajectories. The constant process of bifurcating unstable orbits becoming stable orbits which bifurcate again leads to a system with many chaotic orbits and several regular orbits. This feature can be seen as a consequence of wave propagation along the potential ridge seen in Figure (1.1). Most solutions propagating along this ridge are unstable. Metastable states can be found propagating along the center of the ridge.

To date, the best calculation of the bound states of hydrogen in a constant magnetic field is probably the one of Kravchenko et al. [15]. These calculations use an iterative method to essentially diagonalize the R-matrix of Fano and Bohn [6, 7]. They were able to produce results for an extremely wide range of magnetic field strengths and for many excited states to high precision. This is a very practical method of calculating the bound states of the system. In order to perform the calculation to high precision, special numerical libraries were developed which enabled thousands of significant figures to be kept. This allowed the large numbers of terms of nearly the same magnitude, but different signs to be added without a complete loss of numerical accuracy. Although the calculation performs quite well, it shares the feature with the Fano-Bohn R-matrix method that it does not produce bounds. Therefore it is not truly a mathematically "exact" solution to the problem in the sense that both the accuracy and the precision can be specified.

The goal of my thesis work is to solve the non relativistic Schrödinger equation for the hydrogenic atom in a constant magnetic field "exactly" in two senses. The first sense is that the solutions should converge to the exact solutions. In other words, the solution can be improved to arbitrary accuracy by adding more terms to the expansion for the wavefunction or by considering more wavefunctions in the system. Normally convergence is assumed in that the Raleigh-Ritz principle converges when a complete set of basis functions is employed. Convergence may be deceptive, however, if the basis sets which are employed are not well adapted to the known properties of the exact solution. Although the results may converge in the mathematical sense, practical calculations can rarely utilize all elements of an infinite basis set. Therefore, calculations can converge slowly, if at all when a finite subset of a basis is used. Examples of this effect are well known in atomic physics. For example, Hylleraas improved the convergence of calculations for helium atoms by adding r_{12} explicitly into the trial wavefunctions [16]. Similar effects were found by adding log terms. The addition of both of these terms were motivated by the Fock expansion.

The second sense in which the solutions should be "exact" is that the energy eigenvalues are bracketed from both above and below and the gap between the upper and lower bounds can be made arbitrarily small. Therefore, the errors in the eigenenergies are known rigorously because the theories which are employed produce rigorous upper and lower bounds. If the solutions to the Schrödinger equation could be found in closed form, the eigenenergies would lie between these upper and lower bounds. Furthermore, it will be shown that both the upper and lower bounds converge to the exact solution. Therefore, the calculations in this work are able to specify that the exact solution lies between the two bounds and furthermore, the bounds can be "squeezed" to any desired precision. Since the methods used to compute upper bounds are well known, this work emphasizes the accurate computation of lower bounds. In essence, the development of such methods constitutes my original contribution to the study of atoms in constant magnetic fields. This work can also contribute to the study of many other systems. The mathematical foundations are quite general and other systems can be put into a form in which convergent upper and lower bounds to the exact eigenenergies are able to be calculated.

The first step in solving any quantum mechanical system is to write the Schrödinger equation. This is derived in chapter two. Because it is already known that there is no closed form solution to this equation, a series solution known as the Fock expansion is used. The logarithmic terms which are normally associated with the Fock expansion are found to be absent for equation (1.1). The Fock expansion[15, 8] is substituted into the Schrödinger equation and a three term recurrence relation is derived. The Fock expansion has previously been used to describe the wavefunctions of hydrogenic atoms in constant magnetic fields by Kravchenko et. al[15]. The success of that method suggests that the Fock expansion basis can describe the properties of the exact wavefunction quite well.

In chapter three, upper bounds to the binding energies are calculated using the Raleigh-Ritz variational principle and the Fock wavefunction. The form of the Fock expansion is such that when it is used for the Raleigh-Ritz principle, all of the integrals can evaluated in closed form, and all intermediate series terminate. Because of this, no approximations need to be made beyond the approximation made in terminating the Fock expansion and beyond choosing the number of Fock wavefunctions. It is demonstrated that the upper bounds found by this method converge to the exact result as the number of Fock wavefunctions used is increased.

In chapter four, lower bounds to the binding energies are calculated using the Schwinger variational principle. Normally the Schwinger principle is used to compute continuum states and phase shifts. The Schwinger principle was extended by Maleki[31, 32] in order to apply to bound states as well. The Schwinger variational principle is discussed, and it is shown that in the special case where the interaction potential is always positive, that the Schwinger variational principle produces lower bounds to the exact eigenenergies. The condition for bound states is also derived. The same Fock expansion wavefunctions which were used to calculate the Raleigh-Ritz upper bounds are used with the Schwinger principle. Once again, the form of the Fock expansion allows all of the integrals to be evaluated in closed form. All intermediate series terminate so that no approximations are needed beyond terminating the expansion and choosing the number of Fock wavefunctions. It is demonstrated that the lower bounds converge to the exact eigenenergies as more Fock solutions are considered.

Chapter five describes the calculation of excited states. It is shown that in unmodified form, the Raleigh-Ritz variational principle does not yield very accurate upper bounds to the exact eigenenergies. The reasons for this lack of accuracy is given and methods for improving the upper bounds are described. Furthermore, it is shown that the Schwinger variational principle yields accurate lower bounds to the exact eigenenergies even for excited states.

Chapter six discusses several aspects of the problem which are suggested by my method. It is shown that if an expansion in terms of hydrogenic Sturmian functions are used instead of the Fock expansion, all of the matrix elements can be calculated independently of the physical parameters B and Z. They are also independent of the variational parameter. This allows one to calculate all of the matrix elements only once and use them for many different magnetic fields and charges. A method for finding the bounds for the high field case is also shown. Finally, the Fano-Bohn R-matrix method is briefly described and applied to the lowest state in the manifold.

Chapter seven contains conclusions and results of the calculations which have been made. Appendix A gives the Wigner 3-J symbols which were used in the calculation. Appendix B describes the Feynman theorem used in Chapter four.

CHAPTER 2

Derivation of the Hamiltonian and the Recurrence Relation

2.1 The Hamiltonian

The goal of this work is to find the eigenvectors and convergent upper and lower bounds to the eigenvalues for the bound states of hydrogenic atoms in a constant magnetic field. Throughout this report, the constant magnetic field is assumed to be aligned along the $\hat{z}$ axis. Relativistic corrections are ignored because they are small for the magnetic fields considered. The nucleus is assumed to be infinitely massive. Corrections for the effects of a finite mass nucleus could be added later, but were not employed in this work. Finally, the entire calculation is carried out in atomic units [2].

Recently classical analysis of this problem has become popular. This popularity is due to the chaotic behavior of some of the classical orbits of the electron [14]. An accurate description of the system must be quantum mechanical, however. The first step in solving any quantum mechanical problem is to write a Hamiltonian which describes the system. For a hydrogenic atom in an arbitrary magnetic field, the Hamiltonian is

$$H = \frac{1}{2}\left(-i\vec{\nabla} + \frac{\vec{A}}{c}\right)^2 - \frac{Z}{r} \tag{2.1}$$

Here, $-i\vec{\nabla}$ represents the momentum operator in the Hamiltonian, $\vec{A}$ is the vector potential, and Z is the nuclear charge. The vector potential is taken to be $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$. This potential is in the Coulomb gauge so that $\vec{\nabla} \cdot \vec{A} = 0$ and describes a constant magnetic field $\vec{B} = \vec{\nabla} \times \vec{A}$. The vector potential $\vec{A}$ is then substituted into the Hamiltonian to obtain,

$$H = -\frac{1}{2}\nabla_r^2 + \frac{L^2}{2r} + \frac{B}{2c}L_z + \frac{B^2}{8c^2}r^2 \sin^2(\theta) - \frac{Z}{r} \tag{2.2}$$

where $\vec{L}$ is the orbital angular momentum vector. It is common to introduce a strength parameter $\beta \equiv \frac{B}{2c}$ to scale the magnitude of the magnetic field. Doing so results in the Hamiltonian

$$H = -\frac{1}{2}\nabla_r^2 + \frac{L^2}{2r} + \beta L_z + \frac{\beta^2}{2}r^2 \sin^2(\theta) - \frac{Z}{r} \tag{2.3}$$

The first and second terms of equation (2.3) represent the radial and angular components of the kinetic energy. These terms are found in any single particle Hamiltonian that is written in spherical coordinates. The second two terms represent the interaction of the electron with the magnetic field. The first is a linear term which is easily removed from the Hamiltonian. The second is the quadratic term which is of interest. It is this quadratic term which mixes the natural geometry of the system and causes the Schrödinger equation to become non-separable. The final term is the Coulombic term, which represents the interaction of the electron with the nucleus. As one can see, in the limit as $B \to 0$, equation (2.3) becomes the magnetic field-free hydrogenic Hamiltonian. In the limit as $Z \to 0$, equation (2.3) is the spherical representation of the harmonic oscillator. This is exactly as one would expect. This Hamiltonian is then inserted into the Schrödinger equation to obtain

$$\left[-\frac{1}{2}\nabla_r^2 + \frac{L^2}{2r} + \beta L_z + \frac{\beta^2}{2}r^2 \sin^2(\theta) - \frac{Z}{r}\right]\psi = E\psi \tag{2.4}$$

Unfortunately, it is known that this Hamiltonian has no closed form solutions. This is because of the change in the natural coordinate system between the high and low field cases. Since the direct approach can not solve the Schrödinger equation, another method must be employed. This will be discussed in the next section.

2.2 The Fock Ansatz

The approaches taken in this work are variational. Normally, in a variational approach, the trial wavefunctions are not solutions to the Schrödinger equation. However, in the present case the trial solution is chosen in such a way that each basis function ψ_ν is an approximate solution to the Schrödinger equation. It is relatively easy to find these basis functions and several methods can be used to do this. In this work an expansion is substituted into the Schrödinger equation to obtain a recurrence relation. This recurrence relation is solved to obtain expansion coefficients which allow the series solution to solve the Schrödinger equation. Unfortunately, each of these solutions diverges exponentially if taken to infinite order. Therefore very specific linear combinations of truncated solutions are needed in order to satisfy the physical boundary conditions. This linear combination is found by using the basis functions variationally. The matrices which are calculated using these variational principles are then diagonalized. Finally, the expectation value of the Hamiltonian is minimized to find the optimal eigenenergies. The eigenvectors then yield the constants which represent the linear combination of the basis functions which best satisfy the boundary conditions. This differs from the standard variational approach where the basis functions are arbitrary. Choosing basis states which are solutions to the Schrödinger equation insures that any linear combinations of these basis states which are used are also solutions to the Schrödinger equation.

The trial solution is in the form of the Fock expansion. The Fock ansatz is,

$$\psi_\nu = \sum_{n=0}^{\infty} e^{-\sqrt{-2\varepsilon}r} r^{n+\nu} X_n^\nu(\theta, \phi) \tag{2.5}$$

where

$$\varepsilon = E - m\beta \tag{2.6}$$

In equation (2.6) m is the familiar magnetic quantum number. In this particular case, m is a good quantum number. This is because $[\vec{B} \cdot \vec{L}, H] = 0$. Since $\vec{B} \cdot \vec{L} = B_z L_z$, and L_z gives the quantum number m, m is conserved throughout the calculation. The substitution made in equation (2.6) removes the linear magnetic term so that it does not need to be explicitly calculated. Equation (2.5) is substituted into the Schrödinger equation, which is then evaluated term by term. The first term is the radial kinetic energy term.

$$\begin{aligned}-\frac{1}{2}\nabla_r^2\psi_\nu &= \sum_{n=0}^{\infty}\Big[-\frac{1}{2}(n+\nu)(n+\nu+1)\,e^{-\sqrt{-2\varepsilon}r}r^{n+\nu-2} \\ &\quad + \sqrt{-2\varepsilon}(n+\nu+1)\,e^{-\sqrt{-2\varepsilon}r}r^{n+\nu-1} + \varepsilon e^{-\sqrt{-2\varepsilon}}r^{n+\nu}\Big] X_n^\nu(\theta,\phi)\,.\end{aligned}$$

The centrifugal term yields,

$$\frac{L^2}{2r^2}\psi_\nu = \sum_{n=0}^{\infty}\frac{L^2}{2}e^{-\sqrt{-2\varepsilon}r}r^{n+\nu-2}X_n^\nu(\theta,\phi)\,.$$

The magnetic terms give,

$$\beta L_z\psi_\nu = \sum_{n=0}^{\infty} m\beta e^{-\sqrt{-2\varepsilon}r}r^{n+\nu}X_n^\nu(\theta,\phi)\,,$$

and

$$\frac{\beta^2}{2}r^2\sin^2(\theta)\,\psi_\nu = \sum_{n=0}^{\infty}\frac{\beta^2}{2}\sin^2(\theta)\,e^{-\sqrt{-2\varepsilon}r}r^{n+\nu-2}X_n^\nu(\theta,\phi)\,.$$

Finally, the Coulombic term is

$$-\frac{Z}{r}\psi_\nu = \sum_{n=0}^{\infty} -Ze^{-\sqrt{-2\varepsilon}r}r^{n+\nu-1}X_n^\nu(\theta,\phi)\,.$$

These terms are collected into powers of r, and a three term recurrence relation is written. In order to do this, it is recognized that since the the final sum must be zero, all terms in the same power of r must vanish. Therefore, the recurrence relation is,

$$\begin{gathered}\Big[(n+\nu)(n+\nu+1)-L^2\Big]X_n^\nu(\theta,\phi) = \\ +\Big[2\sqrt{-2\varepsilon}(n+\nu)-2Z\Big]X_{n-1}^\nu(\theta,\phi)+\beta^2\sin^2(\theta)\,X_{n-4}^\nu(\theta,\phi)\end{gathered}\qquad(2.7)$$

It is important to note that the recurrence relation in equation (2.7) always has non-zero solutions. In the Helium atom case considered by Fock, this was not true and it was found necessary to add logarithmic terms to Equation (2.5) in order to obtain a recurrence relation with non-trivial solutions. Each term in the recurrence relation depends only upon known operators and upon previous terms in the expansion. These are already specified as starting conditions or calculated in a previous step when the recurrence relation is solved iteratively. It was not known *a* *priori* that a solution in the form of the Fock expansion with no logarithmic terms generates a solvable recurrence relation. The right-hand side of equation (2.7) can be expanded in eigenfunctions of L^2. If one of these eigenfunctions has an eigenvalue of $(n+\nu)(n+\nu+1)$ then the equation has no non-trivial solution. Such a case indicates a "resonance" in the recurrence relation which indicates that the expansion in Equation (2.5) is not correct. Such "resonances" in the recurrence relation are found in other systems such as the driven harmonic oscillator. If only trivial solutions could be found, the logarithmic terms would have to be put back into the Fock expansion. Then a new recurrence relationship would be found which might be solvable. It is essential to demonstrate that Equation (2.7) has solutions. This will be done in the next section. Doing so shows that the Fock expansion with the logarithmic terms removed can be used as a basis set to form solutions to this Schrödinger equation.

2.3 Solution of the three-term recurrence relations

2.3.1 Spherical Harmonic Expansion

Now that a recurrence relation has been derived, solutions to the recurrence relation in equation (2.7) must be found. These solutions will form a basis with which the physical solutions to the problem are constructed. The values of X_n^ν are set to 0 when $n < 0$. This starting condition allows the rest of the terms of the recurrence relation to be generated. The requirement that $n \geq 0$ rules out irregular solutions since such solutions can not be normalized and do not have expectation values of physical operators. This condition agrees with known solutions in the two asymptotic regions of the magnetic field. For a field of $\beta = 0$, the solution must be that of the "standard" hydrogen atom without any applied magnetic field. In this case, none of the solutions contain negative powers in r. The other asymptotic region is that in which the magnetic field is very large compared to the Coulombic field. In this case, $Z \to 0$, and the solution is that of a harmonic oscillator. In this case there are also no terms which contain negative powers in r.

With these starting conditions, the $n = 0$ term of the recurrence relation is examined. In this case,

$$\left[\nu\left(\nu+1\right)-L^2\right]X_0^\nu\left(\theta,\phi\right)=0 \tag{2.8}$$

The solution to this well known equation is the spherical harmonic, $Y_{\nu m}(\theta,\phi)$. The spherical harmonics are common in atomic physics and are often used to describe the angular state of one electron wavefunctions. It should be no surprise that the zeroth order term of the Fock expansion for our Hamiltonian would have this property.

To find the general solution to this problem, a spherical harmonic expansion is used as an ansatz. Therefore,

$$X_n^\nu\left(\theta,\phi\right)=\sum_l A_{nl}^\nu Y_{lm}\left(\theta,\phi\right). \tag{2.9}$$

This is then substituted into equation (2.5) to yield a new ansatz

$$\psi_\nu=\sum_n\sum_l A_{nl}^\nu e^{-\sqrt{-2\varepsilon}r}r^{n+\nu}Y_{lm}(\theta,\phi) \tag{2.10}$$

In general it is expected that since the spherical harmonics have two indices l and m, that both of these indices must be summed over in order to sum over the complete set of basis functions. This is substituted into recurrence relation (2.7) to obtain an equivalent recurrence relation.

$$\begin{aligned}\sum_l &\left[\left(n+\nu\right)\left(n+\nu+1\right)-L^2\right]A_{nl}^\nu Y_{lm}\left(\theta,\phi\right)\\ &-\left[2\sqrt{-2\varepsilon}\left(n+\nu\right)-2Z\right]A_{(n-1)l}^\nu Y_{lm}\left(\theta,\phi\right)\\ &-\beta^2\sin^2\left(\theta\right)A_{(n-4)l}^\nu Y_{lm}\left(\theta,\phi\right)=0\end{aligned} \tag{2.11}$$

If the $\sin^2\left(\theta\right)Y_{lm}\left(\theta,\phi\right)$ is written as a sum of single spherical harmonics, then the angular terms can be removed from the recurrence relation the same way that the radial terms were. This leaves a recurrence relation in A_{nl}^ν which no longer contains any spatial variables. To do this, the identity

$$\sin^2\left(\theta\right)=\frac{2}{3}\sqrt{4\pi}Y_{00}\left(\theta,\phi\right)-\frac{2}{3}\sqrt{\frac{4\pi}{5}}Y_{20}\left(\theta,\phi\right) \tag{2.12}$$

is used. Substituting equation (2.12) into equation (2.11) leaves a four term recurrence relation. The last two terms contain products of two spherical harmonics. $Y_{00}(\theta, \phi)$ is a constant, however. Therefore, this term is easily converted to one with only a single spherical harmonic. The $Y_{20}(\theta, \phi) Y_{lm}(\theta, \phi)$ term is not changed so easily. Products of two spherical harmonics can be written in terms of Wigner 3-J symbols, however. The 3-J symbols are very common in atomic physics and are a compact notation to describe the coupling of two angular momenta. These products of two spherical harmonics (which represent angular momenta) can be written in terms of Wigner 3-J symbols as a sum of single spherical harmonics by using the standard formula [17]

$$\begin{aligned} Y_{l_1 m_1}(\theta,\phi)\, Y_{l_2 m_2}(\theta,\phi) &= \sum_{l} \left[\frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi}\right]^{\frac{1}{2}} \\ &\quad \times \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} Y^*_{lm}(\theta,\phi) \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \qquad (2.13)$$

In this particular case the product $Y_{20}(\theta,\phi)\, Y_{lm}(\theta,\phi)$ needs to be calculated. The reason for this calculation is that since each term in the Fock expansion for the wavefunction will have a spherical harmonic term in it, and $\sin^2\theta$ can be written as a linear combination of the spherical harmonics Y_{00} and Y_{20}, such products will be common throughout the calculation. Equation (2.13) allows these products to be written as sums of single spherical harmonics which are much easier to calculate. Therefore, the appropriate substitutions are made into Equation (2.13) to obtain

$$\begin{aligned} Y_{20}(\theta,\phi)\, Y_{lm}(\theta,\phi) &= \sum_{l'} \left[\frac{5(2l+1)(2l'+1)}{4\pi}\right]^{\frac{1}{2}} \\ &\quad \times \begin{pmatrix} 2 & l' & l \\ 0 & -m' & m \end{pmatrix} \begin{pmatrix} 2 & l' & l \\ 0 & 0 & 0 \end{pmatrix} Y_{l'm'}(\theta,\phi). \end{aligned} \qquad (2.14)$$

Only a few of the Wigner 3-j symbols can contribute to the sum. The rest are zero and collapse the infinite sums into only three terms. Therefore,

$$Y_{20}(\theta,\phi)\, Y_{lm}(\theta,\phi) =$$

$$\left[\frac{5(2l+1)(2l-3)}{4\pi}\right]^{\frac{1}{2}} \begin{pmatrix} 2 & l & l-2 \\ 0 & -m & m \end{pmatrix} \begin{pmatrix} 2 & l & l-2 \\ 0 & 0 & 0 \end{pmatrix} Y_{(l-2)m}(\theta,\phi)$$

$$+\left[\frac{5\,(2l+1)^2}{4\pi}\right]^{\frac{1}{2}}\begin{pmatrix}2 & l & l\\ 0 & -m & m\end{pmatrix}\begin{pmatrix}2 & l & l\\ 0 & 0 & 0\end{pmatrix}Y_{lm}\,(\theta,\phi) \tag{2.15}$$
$$+\left[\frac{5\,(2l+1)\,(2l+5)}{4\pi}\right]^{\frac{1}{2}}\begin{pmatrix}2 & l & l+2\\ 0 & -m & m\end{pmatrix}\begin{pmatrix}2 & l & l+2\\ 0 & 0 & 0\end{pmatrix}Y_{(l+2)m}\,(\theta,\phi)$$

The notation in the above equation is simplified by setting the complicated terms in front of the spherical harmonics to functions of l and m to become,

$$Y_{20}\,(\theta,\phi)\,Y_{lm}\,(\theta,\phi) =$$
$$C_1\,(l,m)\,Y_{(l-2)m}\,(\theta,\phi) + C_2\,(l,m)\,Y_{lm}\,(\theta,\phi) + C_3\,(l,m)\,Y_{(l+2)m}\,(\theta,\phi) \tag{2.16}$$

where C_1, C_2, and C_3 correspond to the coefficients in front of the spherical harmonics in equation (2.15). This identity is then substituted into equation (2.11), and coefficients of like spherical harmonics are set to zero. Doing this finally leaves the five term recurrence relation,

$$[(n+\nu)\,(n+\nu+1) - l\,(l+1)]\,A^{\nu}_{nl} - \left[2\sqrt{-2\varepsilon}\,(n+\nu) - 2Z\right]A^{\nu}_{(n-1)l}$$
$$+\frac{2\beta^2}{3}\left[\sqrt{\frac{4\pi}{5}}C_2\,(l,m) - 1\right]A^{\nu}_{(n-4)l} + \frac{2\beta^2}{3}\sqrt{\frac{4\pi}{5}}C_1\,(l+2,m)\,A^{\nu}_{(n-4)(l+2)} \tag{2.17}$$
$$+\frac{2B^2}{3}\sqrt{\frac{4\pi}{5}}C_3\,(l-2,m)\,A^{\nu}_{(n-4)(l-2)} = 0$$

It should be noted that the recurrence relation in equation (2.17) that the values of l are limited. They are limited from below by the nature of the spherical harmonics which were used to generate the recurrence relation. Therefore $l \geq 0$. The maximum value is also limited, however. The first term of the recurrence relation is $[(n+\nu)(n+\nu+1) - l(l+1)]A^{\nu}_{nl}$. In this term, all of the variables n, ν and l are integers. When $l = n+\nu$ this entire term vanishes. Therefore, in order to prevent the solution to the recurrence relation from exploding, we must have $A^{\nu}_{(n-1)(n+\nu)} = 0$ and $A^{\nu}_{(n-4)(n+\nu)} = 0$. Thus we insure that $A^{\nu}_{nl} = 0$ if $l > n+\nu$.

It is important from a programming point of view to be sure that no values of the matrix representing A^{ν}_{nl} are accessed beyond the boundaries of the array. Therefore, the series in l should be properly terminated. Fortunately, the nature

Table 2.1: Scheme of recurrence relation matrix.

The pattern of the entries in the recurrence relation matrix A^{ν}_{nl} are shown.

					l ν			
	0			0	X	0		
	1			0	X	0		
n	2			0	X	0		
	3	0	X	0	X	0	X	0
	4	0	X	0	X	0	X	0
	5	0	X	0	X	0	X	0
					⋮			

of the recurrence relation prevents the artificial termination of the series in l from becoming necessary. Table (2.1) shows the scheme in which the values of A^{ν}_{nl} are calculated. In this table 'X' represents elements of the matrix which are non-zero. '0' was put into some of the matrix elements to make it clear that these elements are always zero. The values of l are along the horizontal axis and the values of n along the vertical axis. The matrix is initialized by putting a value into $A^{\nu}_{0,\nu}$. The recurrence relation only produces non-zero values for $l = \nu$ until the $n = 4$ term is reached. At this point, the angular momentum mixing caused by the $\sin^2\theta$ in the $A^{\nu}_{(n-4)l}$ term causes $l + 2$ and $l - 2$ terms to also be produced. The same pattern repeats itself every four terms by adding two more l terms to the matrix. As one can see, this limits the possible values of l so that they do not grow as fast as the value of n. From a practical point of view this is a very important result. If one wishes to produce the most accurate results possible, the series which are being calculated should be artificially terminated as little as possible. In this case, the series in n must be artificially terminated by choosing the order of the Fock expansion terms which are to be calculated. The angular series are self-terminating, however, if the proper number of l array elements are specified when the array is initialized. Therefore they can be calculated to the order of n which was taken in the Fock expansion.

There are many ways in which to solve this recurrence relation. The the method that we have chosen is to do this algorithmically. Since the recurrence relation must sum to zero, it is required that every term cancels. The approach which is taken is to set the entire set of A^{ν}_{nl} to values which make the recurrence relation equal to zero. The exact amount needed to cancel a previous term is added to A^{ν}_{nl}. This procedure is iterated until the desired number of terms in the expansion of the wavefunction has been reached. The notation

$$\{A^{\nu}_{nl} \Longrightarrow A^{\nu}_{nl} + C\}$$

is used for compactness. The symbol '$\Longrightarrow$' represents the assignment operator in a standard computer programming language such as *Fortran* or *C*. It is not the absolute assignment symbol '=' of mathematics. Instead, it can be a self-referential assignment as is seen above. The equation $\{A^{\nu}_{nl} \Longrightarrow A^{\nu}_{nl} + C\}$ means that the value C is added to the current value of A^{ν}_{nl}. The second term of the recurrence relation is examined.

$$\left[(n+\nu+1)(n+\nu) - l(l+1)\right] A^{\nu}_{nl} = \left[2\sqrt{-2\varepsilon}\,(n+\nu) - 2Z\right] A^{\nu}_{(n-1)l}$$

Using the algorithm described above yields,

$$\left\{ A^{\nu}_{nl} \Longrightarrow A^{\nu}_{nl} + \frac{\left[2\sqrt{-2\varepsilon}\,(n+\nu) - 2Z\right]}{\left[(n+\nu)(n+\nu+1) - l(l+1)\right]} A^{\nu}_{(n-1)l} \right\} \tag{2.18}$$

The terms which contains the magnetic interaction $-\beta^2 \sin^2(\theta)\, A^{\nu}_{nl} Y_{lm}(\theta,\phi)$ must be examined. They yield the contributions

$$\left\{ A^{\nu}_{nl} \Longrightarrow A^{\nu}_{nl} + \frac{-\frac{2}{3}\beta^2 \left(\sqrt{\frac{4\pi}{5}} C_2(l,m) - 1\right)}{\left[(n+\nu)(n+\nu+1) - l(l+1)\right]} A^{\nu}_{(n-4)l} \right\} \tag{2.19}$$

$$\left\{ A^{\nu}_{nl} \Longrightarrow A^{\nu}_{nl} + \frac{-\frac{2}{3}\sqrt{\frac{4\pi}{5}}\beta^2 C_1(l+2,m)}{\left[(n+\nu)(n+\nu+1) - l(l+1)\right]} A^{\nu}_{(n-4)(l+2)} \right\} \tag{2.20}$$

$$\left\{ A^{\nu}_{nl} \Longrightarrow A^{\nu}_{nl} + \frac{-\frac{2}{3}\sqrt{\frac{4\pi}{5}}\beta^2 C_3(l-2,m)}{\left[(n+\nu)(n+\nu+1) - l(l+1)\right]} A^{\nu}_{(n-4)(l-2)} \right\} \tag{2.21}$$

These coefficients are calculated iteratively. First, for a given value of ν which is chosen, the coefficient $A_{0,\nu}$ is set to be 1.0. This corresponds to the $n = 0$

term of the recurrence relation (2.7) which has a solution of a spherical harmonic $X_0^\nu(\theta, \phi) = Y_{\nu m}(\theta, \phi)$. For the $n = 1$ term, the substitution in equation (2.18) can be used since it only refers to the term directly before it. This term alone generates coefficients until the $n = 4$ term. The order in which these terms are calculated are very important. The A_{nl}^ν elements depend explicitly on all of the $A_{(n-1)l}^\nu$ elements and the $A_{(n-1)l}^\nu$ elements depend explicitly on the $A_{(n-4)l}^\nu$ elements. This makes the A_{nl}^ν terms indirectly dependent on the $A_{(n-4)l}^\nu$ terms. Therefore one must make sure that the $A_{(n-4)l}^\nu$ terms are calculated before the $A_{(n-1)l}^\nu$ terms. The magnetic terms which are calculated mix the angular momentum components so that the wavefunction is no longer a function of simply one value of l. It is important to note however that this mixing only changes l by factors of ± 2. Therefore, parity is a good quantum number and even and odd l wavefunctions are in different manifolds. As a result, only even or odd l states need to be computed in a single calculation.

2.4 Termination of the Fock Expansion Series

Although the Fock expansion series does not necessarily need to be artificially terminated beyond the approximation of taking n terms, it is convenient to terminate the series in a slightly different fashion. As will be seen in the next chapter, many of the integrals involving the Fock expansion result in terms which contain gamma functions or powers of $n + \nu$. In order to force all of these powers to be of nearly the same magnitude, the series is terminated in such a way that the maximum power of r is ν_{max}. This ν_{max} is chosen so that $\nu_{max} = n_{max}$. Such a termination scheme insures that the maximum power of r of all ψ_ν is the same.

The drawback to this termination method is that the number of spherical harmonic terms for a given ν_{max} (which will be seen in later chapters) is limited. Mathematically the results are only guaranteed to converge monotonically as the size of the matrix to be diagonalized is increased. However monotonic convergence as the maximum order of the Fock terms is increased is assured. Therefore such a termination scheme does not allow one to increase the maximum l independently of ν_{max}. This is a disadvantage for strong fields, or highly excited states where many l

values may contribute.

CHAPTER 3

Satisfying Boundary Conditions and the Raleigh-Ritz Variation Principle

In the chapter two, a three term recurrence relation which generates solutions to the Schrödinger equation was found in the form of the Fock expansion. Although these are solutions, they are divergent and do not satisfy the boundary conditions which are present in the physical problem. Ultimately linear combinations of these Fock solutions which satisfy the boundary conditions must be found. At the same time the goal is to bracket the eigenenergies from both above and below. Upper bounds to the eigenenergies and approximate linear combinations of the basis functions which satisfy the physical boundary conditions can be found using the Raleigh-Ritz variational principle.

The general method which is normally used for the Raleigh-Ritz principle is to write a trial wavefunction which is an approximation to a real solution to the Schrödinger equation. The functional,

$$\frac{\langle \Psi_{trial}\left(\alpha_1, \alpha_2, ...\alpha_n\right) | \hat{H} | \Psi_{trial}\left(\alpha_1, \alpha_2, ...\alpha_n\right)\rangle}{\langle \Psi_{trial}\left(\alpha_1, \alpha_2, ...\alpha_n\right) | \Psi_{trial}\left(\alpha_1, \alpha_2, ...\alpha_n\right)\rangle} \tag{3.1}$$

is minimized. These variational energies correspond to upper bounds to the exact eigenenergies. Most successful trial functions for the hydrogen atom in a constant magnetic field problem have used trial functions with many variational parameters in order to gain finer control over the behavior of the wavefunction. In the case of the Fock expansion as it has been chosen, there is only one non-linear variational parameter ε and a set of linear parameters which determine the linear combinations of the Fock functions ψ_ν of equation (2.5). Minimization with respect to the linear parameters requires diagonalization of the Hamiltonian matrix in the Fock basis. Since the Fock functions are not orthonormal one obtains the eigenvalue equation

$$\sum_{\nu'} \left[\langle \psi_\nu | H | \psi_{\nu'} \rangle - \varepsilon \langle \psi_\nu | \psi_{\nu'} \rangle \right] C_{\nu'} = 0 \tag{3.2}$$

3.1 Calculating the Raliegh-Ritz Matrix Elements

To use the Raleigh-Ritz principle, the matrix elements

$$v_{\nu\nu'}(\varepsilon) = \frac{\langle \psi_\nu | \hat{H} - \varepsilon | \psi_{\nu'} \rangle}{\sqrt{\langle \psi_\nu | \psi_\nu \rangle \langle \psi_{\nu'} | \psi_{\nu'} \rangle}} \tag{3.3}$$

must be calculated. This is the same as equation (3.1), however a pre-normalization factor has been inserted into the denominator. The reason for doing this is to aid in the numerical stability of the calculation. Dividing by this pre-normalization factor causes the terms in the summations which are shown later to become more nearly the same in magnitude. This pre-normalization does not actually normalize the final wavefunction because the Fock terms which are used as the trial functions for the calculation are not orthogonal to each other. When the Raleigh-Ritz matrix is diagonalized, the final wavefunction is found as a linear combination of these Fock expansion functions. These final wavefunctions will also have to be normalized because of the non-orthogonality of the chosen basis.

When the matrix given in equation (3.3) is diagonalized, it produces eigenvalues v_k and associated eigenvectors Ψ_k. These eigenvectors are linear combinations of the original Fock trial functions $\Psi_k = \sum_\nu C_\nu^k \psi_\nu$. As was stated above, the eigenvectors Ψ_k are not normalized. Therefore, in order to obtain proper eigenvectors,

$$\frac{\left\langle \Psi_k | \hat{H} - \varepsilon | \Psi_k \right\rangle}{\langle \Psi_k | \Psi_k \rangle} \tag{3.4}$$

is calculated. The approximate eigenenergies then become

$$E_k(\varepsilon) = \varepsilon + \frac{v_k(\varepsilon)}{\langle \Psi_k | \Psi_k \rangle} \tag{3.5}$$

Where $v_k(\varepsilon)$ are the eigenvalues of the matrix $v(\varepsilon)$. In order to find the optimal variational energies, $E_k(\varepsilon)$ is minimized. The lowest energies given by E_k should be the best upper bound to the exact eigenenergies which are possible with the Fock basis functions.

3.2 Pre-normalization of the wavefunction

In order to calculate the matrix elements in equation (3.3), the pre-normalization factor in the denominator should be calculated in order to make the computation of the Raleigh-Ritz matrix elements more numerically stable. This factor is easily found. Writing $\langle \psi_\nu | \psi_\nu \rangle$ in integral form and collecting terms,

$$\begin{aligned} \langle \psi_\nu | \psi_\nu \rangle \;=\; & \int_0^\infty \int_0^{2\pi} \int_0^\pi e^{-\sqrt{-2\varepsilon} r} \sum_n \sum_{n'} \sum_l \sum_{l'} A^\nu_{nl} A^\nu_{n'l'} r^{n+n'+2\nu} \\ & Y_{lm}(\theta, \phi)\, Y_{l'm}(\theta, \phi)\, r^2 \sin(\theta)\, dr d\theta d\phi \end{aligned} \tag{3.6}$$

must be evaluated. The spherical harmonics are orthonormal, however, causing most of the angular terms vanish. Only the radial integral

$$\langle \psi_\nu | \psi_\nu \rangle = \int_0^\infty e^{-2\sqrt{-2\varepsilon} r} \sum_n \sum_{n'} \sum_l r^{n+n'+2\nu+2} A^\nu_{nl} A^\nu_{n'l} dr \tag{3.7}$$

is left to evaluate. This integral is solvable in closed form and yields the pre-normalization factor,

$$\langle \psi_\nu | \psi_\nu \rangle = \sum_n \sum_{n'} \sum_l A^\nu_{nl} A^\nu_{n'l} \frac{\Gamma(n + n' + 2\nu + 3)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+2\nu+3}} \tag{3.8}$$

The integrals which pre-normalize the $\psi_{\nu'}$ states are exactly the same as those for the ψ_ν states. Therefore these will not be evaluated explicitly.

3.3 Calculation of the Raleigh-Ritz matrix elements

In order to calculate the matrix elements, the Hamiltonian operates on the Fock trial wavefunctions which have been previously calculated. Once the matrix given in equation (3.3) has been constructed, it is diagonalized. These eigenvalues are then used in equation (3.5) to obtain upper bounds for the exact eigenenergies. The eigenvectors which result from the diagonalization of equation (3.3) contain proportionality constants. These proportionality constants give the linear combination of the original Fock trial functions which best describe the exact wavefunction.

Since the Hamiltonian has many terms, it is easiest to operate the Hamiltonian on the trial wavefunctions term by term. In order to calculate $\hat{H}\left|\psi_{\nu'}\right\rangle$, first the radial kinetic term is evaluated.

$$\begin{aligned}
-\frac{1}{2}\nabla_r^2\psi_{\nu'} &= \varepsilon\sum_n\sum_l e^{-\sqrt{-2\varepsilon}r}r^{n+\nu'}A_{nl}^{\nu'}Y_{lm}(\theta,\phi) \\
&+ \sqrt{-2\varepsilon}\sum_n\sum_l (n+\nu'+1)\,e^{-\sqrt{-2\varepsilon}r}r^{n+\nu'-1}A_{nl}^{\nu'}Y_{lm}(\theta,\phi) \\
&- \frac{1}{2}\sum_n\sum_l (n+\nu')(n+\nu'+1)\,e^{-\sqrt{-2\varepsilon}r}r^{n+\nu'-2}A_{nl}^{\nu'}Y_{lm}(\theta,\phi).
\end{aligned} \tag{3.9}$$

The angular momentum operator operates on the wavefunction to yield,

$$\frac{\hat{L}^2}{2r^2}\psi_{\nu'} = \frac{1}{2}\sum_n\sum_l l(l+1)\,A_{nl}^{\nu'}e^{-\sqrt{-2\varepsilon}r}r^{n+\nu'-2}Y_{lm}(\theta,\phi) \tag{3.10}$$

The quadratic magnetic term evaluates to,

$$\begin{aligned}
\frac{\beta^2r^2\sin^2(\theta)}{2}\psi_{\nu'} &= \frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2\sum_n\sum_l A_{nl}^{\nu'}e^{-\sqrt{-2\varepsilon}r}r^{n+\nu'+2}Y_{lm}(\theta,\phi) \\
&- \frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2\sum_n\sum_l A_{nl}^{\nu'}e^{-\sqrt{-2\varepsilon}r}r^{n+\nu'+2}\times \\
&\quad \Big[C_1(l,m)\,Y_{(l-2)m}(\theta,\phi) + C_2(l,m)\,Y_{lm}(\theta,\phi) \\
&+ C_3(l,m)\,Y_{(l+2)m}(\theta,\phi)\Big]
\end{aligned} \tag{3.11}$$

Where, C_1, C_2 and C_3 are as defined in equation (2.16). Finally, the Coulombic term evaluates to,

$$-\frac{Z}{r}\psi_{\nu'} = -Z\sum_n\sum_l A_{nl}^{\nu'}e^{-\sqrt{-2\varepsilon}r}r^{n+\nu'-1}Y_{lm}(\theta,\phi) \tag{3.12}$$

All of these are evaluated and the results are combined. The results are then put into the integral $\langle\psi_\nu|\hat{H}-\varepsilon|\psi_{\nu'}\rangle$. These represent the matrix elements of the Raliegh-Ritz matrix. Since the integral contains many terms, it is easiest to integrate in several parts as was done above. As was seen in equation (3.9), there are three parts to the integral $\langle\psi_\nu|-\frac{1}{2}\nabla_r^2|\psi_{\nu'}\rangle$. The first term only multiplies the wavefunction by a factor of ε. This is canceled by the ε in each matrix element, and therefore does not have to be explicitly evaluated. The second term multiplies the wavefunction by $\sqrt{-2\varepsilon}\,(n'+\nu'+1)$ and reduces the power in r by one. This results in a known integral which evaluates to

$$\sqrt{-2\varepsilon}\sum_{n}\sum_{n'}\sum_{l}(n'+\nu'+1)\,A^{\nu}_{nl}A^{\nu'}_{n'l'}\frac{\Gamma(n+n'+\nu+\nu'+2)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+2}} \tag{3.13}$$

The third term multiplies the wavefunction by $-\frac{1}{2}(n'+\nu')(n'+\nu'+1)$ and reduces the power in r by two. This integral evaluates to

$$-\frac{1}{2}\sum_{n}\sum_{n'}\sum_{l}(n'+\nu')(n'+\nu'+1)\,A^{\nu}_{nl}A^{\nu'}_{n'l'}\frac{\Gamma(n+n'+\nu+\nu'+1)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+1}} \tag{3.14}$$

The angular momentum term $\frac{\hat{L}^2}{2r^2}$ multiplies the wavefunction by $l'(l'+1)$, and reduces the power in r by two. Evaluating this integral yields,

$$\frac{1}{2}\sum_{n}\sum_{n'}\sum_{l}l(l+1)\,A^{\nu}_{nl}A^{\nu'}_{n'l}\frac{\Gamma(n+n'+\nu+\nu'+1)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+1}} \tag{3.15}$$

The Coulombic term $-\frac{Z}{r}$ simply multiplies the wavefunction by $-Z$ and reduces the power in r by one. This integral evaluates to,

$$-Z\sum_{n}\sum_{n'}\sum_{l}A^{\nu}_{nl}A^{\nu'}_{n'l}\frac{\Gamma(n+n'+\nu+\nu'+2)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+2}} \tag{3.16}$$

The magnetic term has several parts. The integral involving the first term on the right hand side of equation (3.11) is

$$\frac{1}{3}\beta^2\int_0^\infty\int_0^{2\pi}\int_0^\pi\sum_{n}\sum_{n'}\sum_{l}\sum_{l'}A^{\nu}_{nl}A^{\nu'}_{n'l'}e^{-2\sqrt{-2\varepsilon}r}r^{n+n'+\nu+\nu'+2} \tag{3.17}$$

$$Y_{lm}(\theta,\phi)\,Y_{l'm'}(\theta,\phi)\,r^2\sin(\theta)\,dr\,d\theta\,d\phi$$

evaluates to

$$\frac{1}{3}\beta^2\sum_{n}\sum_{n'}\sum_{l}A^{\nu}_{nl}A^{\nu'}_{n'l}\frac{\Gamma(n+n'+\nu+\nu'+5)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+5}}. \tag{3.18}$$

The integral involving $C_1(l,m)$ on the right hand side of equation (3.11) is

$$-\frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2\int_0^\infty\int_0^{2\pi}\int_0^\pi\sum_{n}\sum_{n'}\sum_{l}\sum_{l'}A^{\nu}_{nl}A^{\nu'}_{n'l}C_1(l',m)\,e^{-2\sqrt{-2\varepsilon}r}r^{n+n'+\nu+\nu'+2} \tag{3.19}$$

$$Y_{lm}(\theta,\phi)\, Y_{l'm}(\theta,\phi)\, r^2 \sin(\theta)\, dr d\theta d\phi.$$

This becomes

$$-\frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2 \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'(l+2)} C_1(l+2,m) \frac{\Gamma(n+n'+\nu+\nu'+5)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+5}}. \tag{3.20}$$

The integral involving the $C_2(l,m)$ term in the right hand side of equation (3.11) is

$$-\frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2 \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} \sum_n \sum_{n'} \sum_l \sum_{l'} A^{\nu}_{nl} A^{\nu'}_{n'l'} C_2(l',m)\, e^{-2\sqrt{-2\varepsilon}r} r^{n+n'+\nu+\nu'+2} \tag{3.21}$$

$$Y_{lm}(\theta,\phi)\, Y_{l'm}(\theta,\phi)\, r^2 \sin(\theta)\, dr d\theta d\phi.$$

This evaluates to

$$-\frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2 \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'l} C_2(l,m) \frac{\Gamma(n+n'+\nu+\nu'+5)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+5}}. \tag{3.22}$$

Finally, the integral involving $C_3(l,m)$ on the right hand side of equation (3.11) is

$$-\frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2 \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} \sum_n \sum_{n'} \sum_l \sum_{l'} A^{\nu}_{nl} A^{\nu'}_{n'l'} C_3(l',m)\, e^{-2\sqrt{-2\varepsilon}r} r^{n+n'+\nu+\nu'+2} \tag{3.23}$$

$$Y_{lm}(\theta,\phi)\, Y_{l'm}(\theta,\phi)\, r^2 \sin(\theta)\, dr d\theta d\phi.$$

This evaluates to

$$-\frac{1}{3}\sqrt{\frac{4\pi}{5}}\beta^2 \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'(l-2)} C_3(l-2,m) \frac{\Gamma(n+n'+\nu+\nu'+5)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+5}}. \tag{3.24}$$

Gathering the magnetic terms terms together results in

$$-\frac{1}{3}\beta^2 \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} \frac{\Gamma(n+n'+\nu+\nu'+5)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+5}} \times \tag{3.25}$$

$$\left\{\sqrt{\frac{4\pi}{5}} C_1(l+2,m)\, A^{\nu'}_{n'(l+2)} + \left[1-\sqrt{\frac{4\pi}{5}} C_2(l,m)\right] A^{\nu'}_{n'l} + \sqrt{\frac{4\pi}{5}} C_3(l-2,m)\, A^{\nu'}_{n'(l-2)}\right\}.$$

If all of these terms are collected, a matrix can be formed which has elements which are labeled by the indices ν and ν'. Finally all of the terms which have previously been evaluated can be combined to give the Raleigh-Ritz matrix. This final matrix is

$$
\begin{aligned}
&\left\langle \psi_{\nu} \left| \hat{H} - \varepsilon \right| \psi_{\nu'} \right\rangle = \\
&\sum_{n} \sum_{n'} \sum_{l} \qquad \left\{ \sqrt{-2\varepsilon} \left(n' + \nu' + 1\right) A^{\nu}_{nl} A^{\nu'}_{n'l} \frac{\Gamma\left(n + n' + \nu + \nu' + 2\right)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+2}} \right. \\
&\quad - \ \frac{1}{2} \left(n' + \nu'\right) \left(n' + \nu' + 1\right) A^{\nu}_{nl} A^{\nu'}_{n'l'} \frac{\Gamma\left(n + n' + \nu + \nu' + 1\right)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+1}} \\
&\quad + \ \frac{1}{2} l \left(l + 1\right) A^{\nu}_{nl} A^{\nu'}_{n'l} \frac{\Gamma\left(n + n' + \nu + \nu' + 1\right)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+1}} \\
&\quad - \ Z A^{\nu}_{nl} A^{\nu'}_{n'l} \frac{\Gamma\left(n + n' + \nu + \nu' + 2\right)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+2}} \qquad (3.26) \\
&\quad - \ \frac{1}{3} \beta^2 A^{\nu}_{nl} \frac{\Gamma\left(n + n' + \nu + \nu' + 5\right)}{\left(2\sqrt{-2\varepsilon}\right)^{n+n'+\nu+\nu'+5}} \left[\sqrt{\frac{4\pi}{5}} C_1 \left(l + 2, m\right) A^{\nu'}_{n'(l+2)} \right. \\
&\quad + \ \left. \left. \left(1 - \sqrt{\frac{4\pi}{5}} C_2 \left(l, m\right)\right) A^{\nu'}_{n'l} + \sqrt{\frac{4\pi}{5}} C_3 \left(l - 2, m\right) A^{\nu'}_{n'(l-2)} \right] \right\}
\end{aligned}
$$

3.4 Diagonalization of the Raleigh-Ritz matrix

As was described above, the eigenvalues of the matrix

$$
\left\langle \hat{H} - \varepsilon \right\rangle = \frac{\left\langle \psi_{\nu} | \hat{H} - \varepsilon | \psi_{\nu'} \right\rangle}{\sqrt{\left\langle \psi_{\nu} | \psi_{\nu} \right\rangle \left\langle \psi_{\nu'} | \psi_{\nu'} \right\rangle}} \qquad (3.27)
$$

must be found. Here, $\langle \psi_{\nu} | \psi_{\nu} \rangle$ was calculated in equation (3.8) and $\left\langle \psi_{\nu} \left| \hat{H} - \varepsilon \right| \psi_{\nu'} \right\rangle$ was given explicitly in equation (3.26). This is easily done on the computer. To do so, first the coefficients of the wavefunctions, A^{ν}_{nl} are calculated and put into arrays. Two arrays are used corresponding to the indices ν and ν'. These arrays completely represent the Fock trial wavefunction because all other parameters of the Fock expansion are known functions. These coefficients are then used to explicitly calculate equations (3.8) and (3.26). Doing so yields the matrix elements of the Raliegh-Ritz matrix. These matrix elements are then stored in a two dimensional array to represent the complete matrix Raliegh-Ritz matrix. Once all of the elements of the array are calculated, it is passed to the standard `LAPACK` library, and the diagonalization routine `dgeevx()` is called. The eigenvalues $v_k(\varepsilon)$ and eigenvectors k of this matrix are returned from this routine.

The `LAPACK` libraries[28] are convenient because they are are free, accurate and highly portable. The diagonalization routine `dgeevx()` does not sort the eigenvalues, however. Therefore, sorting routines were written and the lowest eigenvalue was chosen to correspond to the ground state. The assumption that the ground state is the lowest eigenvalue is reasonable as long as no other levels cross that of the ground state. Examination of the eigenvalues indicate that this is a good assumption since there is a large separation between the values of the lowest and second lowest eigenvalues. This can be seen in figure (3.1).

3.5 Normalization of the final results

Although the Raleigh-Ritz matrix has been diagonalized, the results still need to be normalized so that

$$E_k(\varepsilon) = \varepsilon + \frac{v_k(\varepsilon)}{\langle\Psi_k|\Psi_k\rangle}. \tag{3.28}$$

Ordinarily, the pre-normalization process would be sufficient for this. In this case, however the Fock expansion basis functions are not orthogonal to each other. Therefore, a final normalization must be done at this point. To do this, the final wavefunction is written as

$$|\Psi_k\rangle = \sum_{\nu} C^k_{\nu}\,|\psi_\nu\rangle \tag{3.29}$$

Here, C^k_ν are the components of the k^{th} eigenvector and $|\psi_\nu\rangle$ represent the wavefunctions defined in equation (2.5). Therefore, the normalization factor is,

$$\langle\Psi_k|\,\Psi_k\rangle = \sum_{\nu}\sum_{\nu'} C^k_{nu}C^k_{\nu'}\,\langle\psi_{\nu'}|\,\psi_\nu\rangle \tag{3.30}$$

Substituting the Fock trial functions from equation (2.10) into $\langle\psi_{\nu'}|\psi_\nu\rangle$ gives

$$\langle\psi_{\nu'}|\,\psi_\nu\rangle \;=\; \int_0^\infty\int_0^{2\pi}\int_0^\pi \sum_n\sum_{n'}\sum_l\sum_{l'} A^\nu_{nl}A^{\nu'}_{n'l'}r^{n+n'+\nu+\nu'}\,\times$$

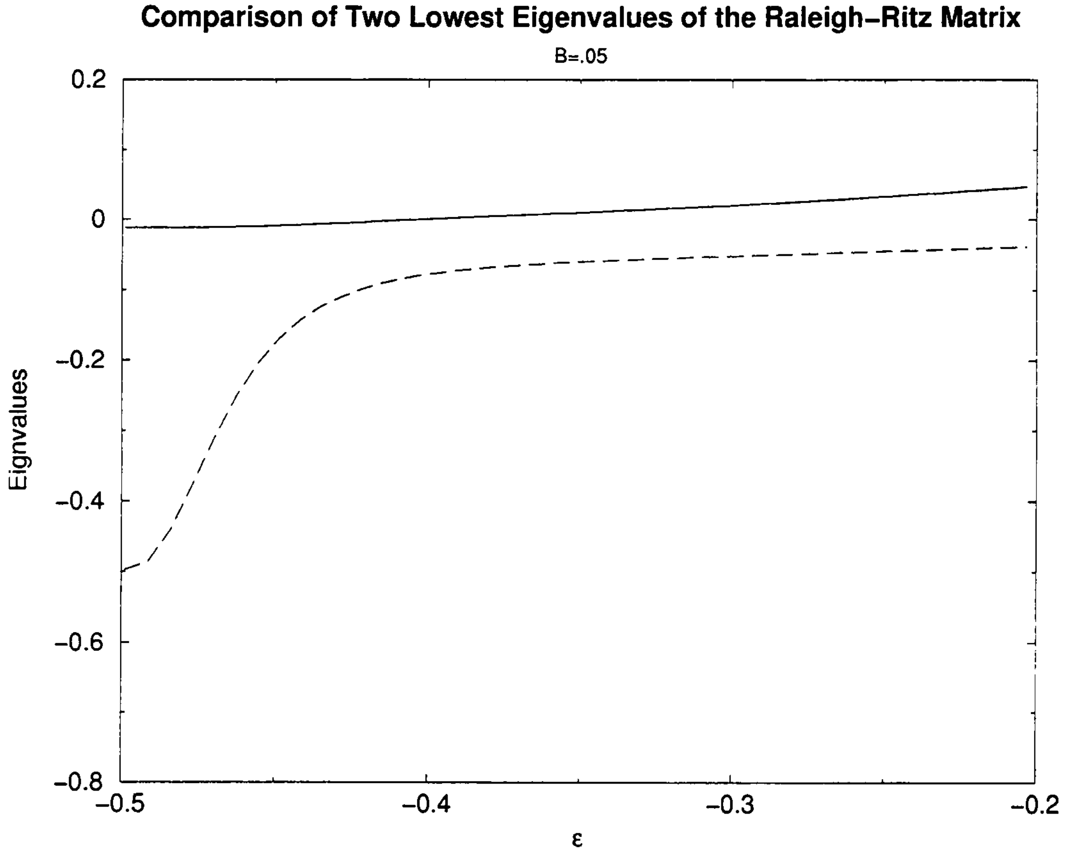

Figure 3.1: Two lowest matrix elements for the even manifold: The two lowest matrix elements in the even manifold are plotted here. It is shown that these two matrix elements are separated and do not appear to cross.

$$
\begin{aligned}
& e^{-2\sqrt{-2\varepsilon}r} Y^*_{l'm'}(\theta,\phi)\, Y_{lm}(\theta,\phi)\, r^2 \sin\theta dr d\theta d\phi \\
= & \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'l} \frac{\Gamma(n+n'+\nu+\nu'+3)}{(2\sqrt{-2\varepsilon})^{n+n'+\nu+\nu'+3}}
\end{aligned} \tag{3.31}
$$

Therefore, substituting the above equation into equation (3.30) yields the final normalization factor

$$
\langle \Psi_k |\, \Psi_k \rangle = \sum_n \sum_{n'} \sum_l \sum_{\nu} \sum_{\nu'} C^k_{\nu} C^k_{\nu'} A^{\nu}_{nlm} A^{\nu'}_{n'lm} \frac{\Gamma(n+n'+\nu+\nu'+3)}{(2\sqrt{-2\varepsilon})^{n+n'+\nu+\nu'+3}} \tag{3.32}
$$

This normalization factor is computed and substituted into the denominator of the second term in equation (3.28).

3.6 Minimization of the Raleigh-Ritz matrix eigenvalues

Once the eigenvalues of equation (3.3) are calculated, the value of the eigenvalues of

$$
E_k(\varepsilon) = \varepsilon + \frac{v_k(\varepsilon)}{\langle \Psi_k | \Psi_k \rangle}. \tag{3.33}
$$

should be minimized. The value of $E_k(\varepsilon)$ at its minimum represents the best upper bound to the exact eigenenergy which can be found with the chosen trial wavefunction using the Raleigh-Ritz method. Figure (3.2) shows this minimization process for the ground state of hydrogen in a field of $\beta = 0.05$. The vertical axis represents the value of the eigenvalue which corresponds to the ground state. The horizontal axis represents the variational parameter ε. The minimization occurs at $\beta = 0.4975264802548$ and gives an approximate ground state energy of $E = -0.49752648040$ au. If the solution were exact, then ε and E would be identical. Figure (3.2) also shows the intersection of the line $E = \varepsilon$ with the value of the eigenvalue which represents the ground state energy of the atom. It is clear that this intersection occurs very close to the minimum of the eigenvalue.

An estimate of the errors in the calculation can easily be found using the Raleigh Ritz method. In order to use this estimate, two assumptions must be made about the calculation, however. The first is that the Fock expansion converges to the exact wavefunctions if an infinite number of terms are taken in the expansion. This was proven by Hylleraas[16] in the case of Helium, and a similar method can

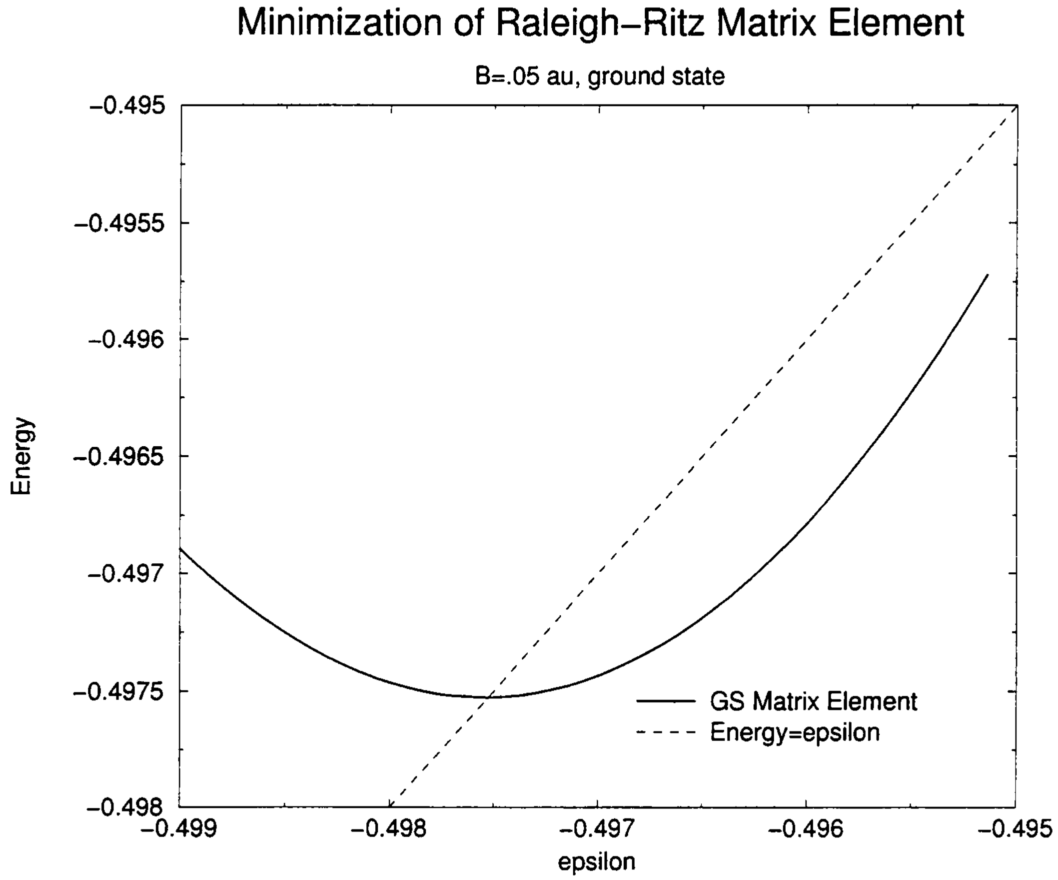

Figure 3.2: Minimization of Raleigh Ritz Matrix Element: In this figure the lowest eigenvalue of the Raleigh-Ritz matrix is plotted as a function of the variational parameter ε. The minimum of this eigenvalue is easily seen as well as that minimum's close proximity to the line $E = \varepsilon$. If the eigenvalue were a perfect eigenenergy, the minimum would occur exactly on this line.

be used to do this for the hydrogen atom in a constant magnetic field. The second assumption is that all solutions to the Schrödinger equation given in equation (1.1) can be represented by the Fock expansion. This has never been formally proven. If both of the assumptions are made, then because $\hat{H}\left|\Psi_k\right\rangle = \varepsilon\left|\Psi_k\right\rangle$,

$$\frac{v_k(\varepsilon)}{\langle \Psi_k | \Psi_k \rangle} = 0 \tag{3.34}$$

for a "perfect" solution. Therefore, the value of equation (3.34) at the ε which minimizes equation (3.28) should give an estimate of the errors in the calculation. This estimate is not absolute, however. Upper bounds to the eigenenergies must be found in order to bracket the eigenenergies.

Table (3.1) shows how the energy varies as the number of Fock functions and their order are varied. The third column of table (3.1) shows the convergence of these terms towards zero as the number of terms in the Fock expansion increases. This estimate of error seems to converge monotonically towards zero until thirteen terms are used in the Fock expansion. A possible explanation for this non-monotonic behavior is given in the next section.

3.7 Convergence of the upper bounds as a function of the order of the Fock expansion

Although the Fock expansion technically solves the Schrödinger equation for hydrogen in a constant magnetic field, this assumes that the Fock expansion is taken to infinite order.

$$\psi_\nu = \sum_{n=0}^{\infty} e^{-\sqrt{-2\varepsilon}r} r^{n+\nu} \sum_{l} A_{nl} Y_{lm}(\theta, \phi) \tag{3.35}$$

The recurrence relation in equation (2.16) produces solutions to the Schrödinger equation. These solutions are exact for an infinite expansion. For a finite expansion, however, there is always a remainder term. Furthermore, as the order n increases, so does the maximum power of the radial variable r. This leads to several interesting convergence properties of the Fock expansion when used with the Raleigh-Ritz principle. For small B-fields, the coefficients A_{nl} corresponding to large n are very small.

Table 3.1: Convergence of the Raleigh-Ritz calculation for $\beta = 0.05$.

The lowest energy for a Raleigh-Ritz calculation of the ground state of hydrogen is shown with an applied magnetic field of $\beta = 0.05$. The energy shown converges as the number of terms in the Fock expansion increases.

Number of Fock Terms and Order	*Energy (au)*	$\frac{v_k(\varepsilon)}{\langle\Psi_k\|\Psi_k\rangle}$
3	-0.49752069817	0.00289855022
4	-0.49752643540	0.00010184888
5	-0.49752646442	4.05067082261e-05
6	-0.49752647878	1.06244711858e-05
7	-0.49752648004	-1.89165839093e-06
8	-0.49752648033	-6.96123124561e-07
9	-0.49752648040	-1.01409166758e-07
10	-0.49752648039	5.65905132669e-08
11	-0.49752648040	1.29681568440e-08
12	-0.49752648040	-4.76531843997e-11
13	-0.49752648040	-4.88791618292e-10
14	-0.49752648040	-1.62756474964e-11

Therefore solutions depend mostly on small order coefficients A_{nl}. The energies will appear to converge before the remainder terms become very large.

Table (3.1) shows the convergence properties of the Raleigh-Ritz calculation as a function of the number of terms taken in the Fock expansion coupled with the order of the Fock expansions used. In the calculation which produced table (3.1), the order of the Fock expansion is not independent of the number of Fock expansion terms. For a small B-field it is shown that the results converge to an upper bound of the exact eigenenergy as the number of terms in the Fock expansion are increased. In the case of Table (3.1), the ground state energy is calculated at a magnetic field strength of $\beta = 0.05$ atomic units. Although such a field is well beyond the reach of simple first order perturbation theory, it is still small enough that the geometry is basically spherical and results to five significant figures can be calculated with only three terms. As the number of Fock terms is increased, the best upper bound to the exact eigenenergy begins to converge asymptotically to the exact value. After only eleven terms, the calculation converges to the number of significant figures calculated.

The result for ten terms show the feature that the upper bound does not converge monotonically. The trend appears that the result should have converged to the desired precision in only nine terms. However, the result for ten terms in the Fock expansion is actually slightly higher than the result for nine terms instead of the expected lower result. This is because of the way that the trial wavefunctions are calculated. If an infinite number of Fock basis states could be used, the exact wavefunction would be

$$\Psi = \sum_{\nu=0}^{\infty} C_\nu \psi_\nu \tag{3.36}$$

where the coefficients C_ν correspond to the eigenvectors of the matrix $\left\langle \psi_\nu | \hat{H} - \varepsilon | \psi_{\nu'} \right\rangle$. For practical purposes, however, only a finite matrix can be calculated and diagonalized. We define the notation

$$\Psi^{(N)} = \sum_{\nu=0}^{N} C_\nu^{(N)} \psi_\nu^{(N)} \tag{3.37}$$

Where N corresponds to the number of Fock basis states that are used. Ordinarily, adding a term to this basis should never lead to an increase in the upper bound to the eigenvalue. This is because the final coefficient in the expansion N_N can be set to zero in the expansion, making the final wavefunction equivalent to an expansion with one less term. This is not true in the case which has been calculated, however. The reason for this is that the Fock basis functions ψ_ν are not fixed, but are a function of the number of terms in the Fock expansion. In the calculation reported in Table (3.1), the number of terms taken in the Fock expansion is the same as the number of functions which are used. Therefore, increasing the number of functions which are used also increases the number of terms in each Fock function. This variability in the basis set leads to possible increases in the calculated upper bound as the number of terms is increased. This variability is also seen the error term when thirteen terms are used in the Fock expansion. The error decreases once again for fourteen terms.

In table (3.2) we see the same calculation as that shown in table (3.1) except that it is for a much larger applied field of $\beta = 0.2$. In this case we see that the convergence is no longer monotonic. The energy becomes lower until the number of Fock functions and their order reaches five. After this point the results diverge. In fact, for a large number of terms, this divergence is quite severe. This is because the remainder term from calculating the coefficients of the Fock expansion become quite large.

A detailed exploration of the convergence of this calculation is given in Table (3.3). In this case the Fock expansion is taken so that the number of terms can be specified independently of the number of functions. This also allows the number of Fock functions to be chosen independently from the order of the Fock functions used. As one can see, as the order of the Fock expansion is increased, the minimum energy becomes higher. Therefore an increase in the order of the Fock expansion makes the calculation less accurate. On the other hand, as the number of Fock functions used is increased, the energy becomes lower and improves monotonically.

We can see from these two cases that the Fock expansion is not convenient to use with the Raleigh-Ritz variational principle. The general trend is for the energies to increase (i.e. to get worse) as the order of the Fock functions is increased. On the other hand, the solutions always improve as the number of Fock functions is increased. This feature leads to a method of allowing the Raleigh-Ritz principle to

Table 3.2: Convergence of the Raleigh-Ritz calculation for $\beta = 0.2$.

The lowest energy for a Raleigh-Ritz calculation of the ground state of hydrogen is shown with an applied magnetic field of $\beta = 0.2$. It is seen in this case that the energy does not converge as the number of Fock terms increases.

Number of Fock Terms and Order	*Energy (au)*
3	-0.46386328339009
4	-0.46403613501216
5	-0.46456269423592
6	-0.46427491750252
7	-0.46399164930861
8	-0.46329016681068
9	-0.45993569807247
20	-0.24537462068371

Table 3.3: Convergence of the Raleigh-Ritz calculation as a function of the order of the Fock expansion and the number of functions.

Number of Fock Functions	*3rd order*	*4th order*
2	-0.463862833390090	-0.463567544677774
4	-0.46413796291041	-0.46368626905290
6	-0.46414991325643	-0.46369345622131
8	-0.46423345160191	-0.46369409130916
18	-0.46424666137469	-0.46374985816947

Number of Fock Functions	*5th order*	*6th order*
2	-0.45529332692395	-0.40571488070206
4	-0.46221365142844	-0.45218737666694
6	-0.46229468576427	-0.45298778470024
8	-0.46230291934447	-0.45306825873346
18	-0.46234571313618	-0.45319677878570

produce convergent upper bounds to the exact solutions. The most efficient method to calculate these upper bounds probably involves varying both the order and number of Fock functions. The best algorithm for doing this has yet to be discovered.

CHAPTER 4

Finding Lower Bounds using the Schwinger Variational Principle

In chapter two a series solution in terms of the Fock expansion was found for the hydrogenic atomic in a constant magnetic field problem. In chapter three upper bounds to the exact eigenenergies were found by using the Raleigh-Ritz variational method. The upper bounds could be improved by including more Fock functions in the basis. In principle if all terms were included the upper bound would equal the exact energy. In practice only a finite number of terms are taken, but the upper bound can be made to approach the exact value to an arbitrary accuracy. In other words, if a tolerance in the energy were specified one should be able to add enough terms to reach that goal. To do this it would be necessary to know the exact eigenvalue or to have an accurate lower bound to the exact energy. If the lower bound can also be made to approach the exact energy, then as the bound is improved then one could specify a definite tolerance ΔE and by improving both the upper and lower bounds until they differed by ΔE one would effectively have an exact solution within a given tolerance to the eigenvalue problem. Previous lower bounds, for example those given by the adiabatic method[20, 25] did not have this property. The lower bound by that method can never equal the exact energy except for the trivial case when $B = 0$. The goal of this dissertation, is to bracket the energy eigenvalues from both above and below. Therefore, a method must be found to calculate lower bounds to the energy eigenvalues as well as upper bounds.

The method used to calculate the lower bounds in this work is the Schwinger variational principle[38, 39]. The Schwinger variational principle was originally used for continuum states and has been used to calculate such quantities as phase shifts.

Maleki showed that the Schwinger variational principle is also applicable to bound states[31, 32]. We will derive the condition for bound states for the Schwinger variational principal. It will be also be shown that that the Schwinger variational principle gives lower bounds to the exact eigenenergies in the case of the hydrogenic atom in a constant magnetic field. The Schwinger principle will then be applied to this system. The Schwinger variational lower bounds do equal the exact eigenenergies when the trial function equals the exact eigenfunction. By using the Fock expansion as the trial function it is possible to improve the lower bound indefinitely (assuming that all solutions to the Schrödinger equation can be represented in the Fock form). Thus, by using the Fock expansion to compute upper and lower bounds it is possible to "squeeze" the exact energy from both above and below. In this way one can specify a desired tolerance and by computing both bounds, insure that the exact energy is computed within a desired tolerance. In this sense the Fock expansion together with the Raleigh-Ritz and Schwinger variational principals provide an exact solution for the energy eigenvalues. Neither method, however, gives an expression for the error in the wavefunctions. This means that the accuracy of important physical quantities such as the dipole matrix elements is not similarly insured. While there are methods to bound these quantities, perhaps using the Fock expansion, that is beyond the scope of this work.

In the Raleigh-Ritz calculation shown in Chapter three, the Schrödinger equation was solved approximately. In the Schwinger variational principle this same equation must be solved again. The Schrödinger equation can be written in compact form as,

$$|h - \epsilon + V_{\mathrm{I}}\rangle = 0 \tag{4.1}$$

where

$$h = -\frac{1}{2}\nabla^2 - \frac{Z}{r}. \tag{4.2}$$

In this notation, ϵ is the energy h contains the kinetic and Coulomb terms and V_{I} is the interaction potential. The interaction potential must contain all terms in the potential which is not contained in h, and in this case contains the non-Coulombic part of the potential. Other choices can be made for which terms are included in h_l

and which are included in V_{I}. This will be seen later.

It may not be possible to find closed form solutions to equation (4.1). If closed form solutions cannot be found, approximation methods must be used. In the Schwinger variational principle, the approximation used is to replace the exact interaction potential V_{I} with a separable potential of the form,

$$V^s = \frac{V_{\mathrm{I}}\,|\psi_t\rangle\,\langle\psi_t|\,V_{\mathrm{I}}}{\langle\psi_t|V_{\mathrm{I}}|\psi_t\rangle}. \tag{4.3}$$

In equation (4.3), $|\psi_t\rangle$ is a trial wavefunction. The potential V^s is a non-local potential. Its meaning is that V^s operating on an arbitrary state vector $|F\rangle$ is given by

$$V^s\,|F\rangle = \frac{V_I\,|\psi_t\rangle\,\langle\psi_t\,|V_I|\,F\rangle}{\langle\psi_t\,|V_I|\,\psi_t\rangle} \tag{4.4}$$

This property insures that when $|\psi_t\rangle$ equals the exact solution $|\psi\rangle$, then $V^s|\psi\rangle = V|\psi\rangle$ and it follows that when $|\psi_t\rangle = |\psi\rangle$, then the solution with V^s equals the exact solution. This insures that energies computed with V^s equal the exact energies when the trial function equals the exact eigenfunction. It will be shown in a later section that this substitution leads to lower bounds to the exact eigenenergies in the case of a hydrogenic atom in a constant magnetic field.

In order to perform this calculation, it will first be shown that in certain cases, substituting the Schwinger potential for the full interaction potential produces bounds. Furthermore, it will be seen that in the particular case of a hydrogenic atom in a constant magnetic field that lower bounds are produced. A method for solving the modified Schrödinger equation will the be demonstrated. To prove the lower bound properties of the Schwinger variational principal extensive use is made of the Feynman theorem discussed in the next section.

4.1 The Feynman Theorem

The Feynman theorem[29] relates small variations of the eigenenergies, or phase shifts in the case of continuum states, to small variations in the potential. Specifically if V depends upon a parameter λ then so will the eignenenergy E. Feynman's theorem states that

$$\frac{\partial E}{\partial \lambda} = \left\langle \psi(\lambda) \left| \frac{\partial V}{\partial \lambda} \right| \psi(\lambda) \right\rangle . \tag{4.5}$$

Integrating this equation between the limits a and b gives

$$E(b) - E(a) = \int_a^b \left\langle \psi(\lambda) \left| \frac{\partial V(\lambda)}{\partial \lambda} \right| \psi(\lambda) \right\rangle d\lambda \tag{4.6}$$

One can then choose the potential to be of the form $V(\lambda) = V_1 + \lambda(V_0 - V_1)$, where V_0 is the original potential and V_1 is a potential which is either always greater than or always less than the original potential[30]. If such a potential is used it is clear that $V(0) = V_1$ and that $V(1) = V_0$. Therefore, substituting this potential into equation (4.6) and making the limits of integration vary between 0 and 1, yields

$$E(1) - E(0) = \int_0^1 \langle \psi(\lambda) | V_0 - V_1 | \psi(\lambda) \rangle \, d\lambda \tag{4.7}$$

From equation (4.7) it is seen that that $E(1)$ represents the energy with the original potential and $E(0)$ represents the energy with a modified potential. If $V_0 - V_1$ is a positive quantity then $E(1) - E(0)$ also is positive and therefore the energy with the exact potential is greater than that with the modified potential. If $V_0 - V_1$ is negative then $E(1) - E(0)$ is negative and the energy with the exact potential is lower than that with the modified potential. In other words, if $V_0 - V_1$ is negative, then if V_1 was substituted into the Schrödinger equation, it would produce lower bounds to energies. If $V_0 < V_1$ is positive then if V_1 was substituted into the Schrödinger equation it would produce upper bounds to the energies.

4.2 Conditions for which upper and lower bounds are produced with the Schwinger variational principle

The results from the previous section are used to show the conditions which allow the Schwinger variational principle to produce bounds. The Schwinger potential given in equation (4.3) is employed as V_1 in the Feynman theorem equation (4.7). This yields,

$$E(1) - E(0) = \int_0^1 \left\langle \psi(\lambda) \left| V_I - \frac{V_I|\phi_t\rangle\langle\phi_t|V_I}{\langle\phi_t|V_I|\phi_t\rangle} \right| \psi(\lambda) \right\rangle d\lambda \tag{4.8}$$

Equation (4.8) is then rewritten as

$$\begin{aligned} E(1) - E(0) &= \frac{1}{\langle \phi_t | V_{\rm I} | \phi_t \rangle} \qquad (4.9) \\ &\times \int_0^1 \left[\langle \psi(\lambda) | V_{\rm I} | \psi(\lambda) \rangle \langle \phi_t | V_{\rm I} | \phi_t \rangle - \langle \psi(\lambda) | V | \phi_t \rangle \langle \phi_t | V_{\rm I} | \psi(\lambda) \rangle \right] d\lambda \end{aligned}$$

The Schwartz inequality [37] shows that if V_I has the same sign everywhere, then

$$\left[\langle \psi(\lambda) | V_{\rm I} | \psi(\lambda) \rangle \langle \phi_t | V_{\rm I} | \phi_t \rangle - \langle \psi(\lambda) | V_{\rm I} | \phi_t \rangle \langle \phi_t | V_{\rm I} | \psi(\lambda) \rangle \right] \geq 0$$

Taking into account the first factor on the right hand side of equation (4.9), if $V_{\rm I} > 0$ then the Schwinger potential gives a lower bound and if $V_{\rm I} < 0$ then the Schwinger potential gives an upper bound. This is because the integrand on the right hand side of equation (4.9) is always positive or zero. Therefore, the entire integral must also be non-negative. The Schwinger principle can not give bounds in general. However, if the potential $V_{\rm I}$ does not change sign, it follows from the above argument that upper or lower bounds are obtained.

4.3 Derivation of the condition for bound states in the Schwinger Variational Principle

In the previous section it was shown that the Schwinger potential V^s yields bounds for a potential V_I which does not change signs. The conditions for approximating the energies of bound states should be found. The Schwinger variational principle was originally derived for continuum states to compute approximate phase shifts and scattering lengths. It was recognized that bounds on these quantities could be derived in some cases[33]. Still later the bound properties of the Schwinger variational principle were employed to compute eigenenergies of atomic systems [31]. In this section the equation for bound states is derived. Normally one would solve the Schrödinger equation, $|h_l - \epsilon + V_{\rm I}\rangle = 0$. The solution to this can be written as

$$|\psi\rangle = |\phi_h\rangle + G V_{\rm I} |\psi\rangle \qquad (4.10)$$

Here, $|\phi_h\rangle$ is the homogeneous solution to the differential equation and G is the hydrogen atom Green's function. This Green's function is defined as the solution to the equation

$$(h-\epsilon)|G\rangle = -1 \tag{4.11}$$

In the case of the Schwinger potential, $V_{\rm I}$ is replaced with V^s given in equation (4.3). This yields,

$$|\psi^s\rangle = |\phi_h\rangle + G\frac{V_{\rm I}|\phi_t\rangle\langle\phi_t|V_{\rm I}}{\langle\phi_t|V_{\rm I}|\phi_t\rangle}\,|\psi^s\rangle \tag{4.12}$$

For bound states, the Green's function is for outgoing waves and there is no homogeneous solution to the differential equation. Here it is recognized that outgoing waves for negative energy decrease exponentially for large r, while incoming waves increase exponentially for large r. Therefore the bound state solution can be written as,

$$|\psi^s\rangle = G^o\frac{V_{\rm I}|\phi_t\rangle\langle\phi_t|V_{\rm I}}{\langle\phi_t|V_{\rm I}|\phi_t\rangle}\,|\psi^s\rangle \tag{4.13}$$

Equation (4.13) is multiplied on the left by $\langle\phi_t|V$ is divided by $\langle\phi_t|V|\psi^s\rangle$. Collecting all terms onto one side of the equation yields the condition [31]

$$\langle\phi_t\,|V_{\rm I} - V_{\rm I}G^oV_{\rm I}|\,\phi_t\rangle = 0 \tag{4.14}$$

In the case where the trial wavefunction is written as a finite linear combination of functions the determinant is used

$$\det(\langle\phi_t\,|V_{\rm I} - V_{\rm I}G^oV_{\rm I}|\,\phi_t\rangle) = 0 \tag{4.15}$$

Here, the Green's function G^o is a function of ϵ and solutions ϕ_t can only be found when ϵ corresponds to a bound state.

4.4 Evaluation of the Coulomb Green's function in terms of hydrogenic Sturmian functions

The condition for bound states was found in the previous section. The Schwinger variational principle will now be applied to the problem of finding the bound state energies of hydrogenic atoms in a constant magnetic field. In this case, the trial wavefunction ϕ_t remains the same Fock trial wavefunction used for the Raleigh-Ritz principal, given in equation (2.5). Next, the Green's function must be found. The Green's function is defined to be,

$$G \equiv \frac{1}{E-H} \tag{4.16}$$

If one expands the Green's function in an eigenfunction expansion and substitutes it into equation (4.15) then one would obtain an expression of the form

$$m(E) = \left\langle \phi_t \left| V_I - \frac{\sum_n V_I \left|\psi_n\right\rangle \left\langle\phi_n\right| V_I}{E - E_n^0} \right| \phi_t \right\rangle . \tag{4.17}$$

If the trial functions ϕ_t do not depend explicitly on E, then $m(E)$ would have the general form of an cotangent. This is because as E is varied there are poles at each energy eigenvalue of the Coulomb potential E_n^0. These poles cause discontinuities in $m(E)$ shown schematically in figure (4.1). Because of the cotangent like behavior, there are an infinite number of zeros in the function $m(E)$. It has been shown that zeros in this function correspond to bound states of the entire system. Therefore, a single trial function is able to reproduce not only the ground state of the system, but all of the excited states as well. This is different from the Raleigh-Ritz principle which can only produce lower bounds to the lowest state in any manifold. In order to use the Raleigh-Ritz method for excited states, the principle needs to be modified. The ground state is removed from the basis and the basis is then re-written so that it is orthogonal to the computed ground state. In the Schwinger variational principal, on the other hand, no re-orthogonalization needs to be done. The trial functions automatically produce the entire spectrum. Thus, the Schwinger variational principle is very convenient for calculating excited states.

In our case we are using the Fock expansion, which produces trial functions which depend explicitly on energy as a parameter. Because of this explicit dependence, a spectrum is produced which no longer contains all of the excited states. In the case of the Fock expansion the number of excited states produced is the same as the number of terms which are taken in the expansion. This does not cause a problem in producing results for excited states since the number of Fock terms is chosen arbitrarily. An alternative to the eigenstate expansion is an expansion in terms of

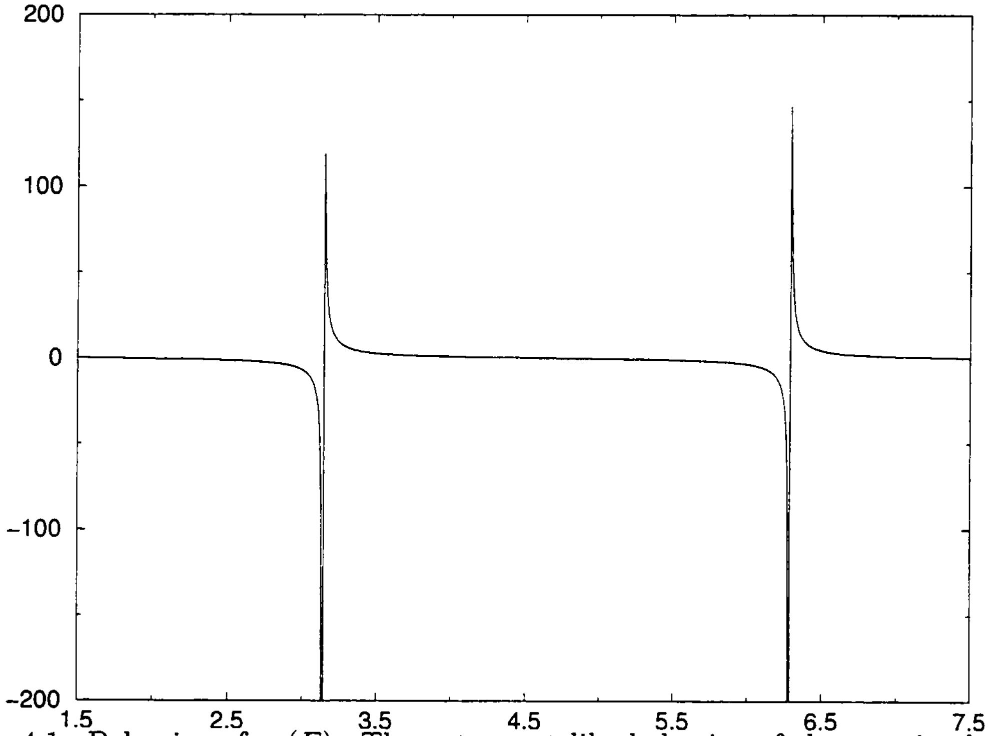

Figure 4.1: Behavior of $m(E)$: The cotangent like behavior of the matrix elements of the Schwinger matrix is shown schematically here. The poles occur at the bound state energies of hydrogen in no external field.

Sturmian functions. This will be seen in the next section. In this case, the Green's function can be expanded in terms of hydrogenic Sturmian functions.

4.4.1 Hydrogenic Sturmian Functions

The hydrogenic Sturmian functions are the solutions of a Sturm-Liouville equation very similar to the standard Schrödinger equation. The placement of the eigenvalue in this equation is different, however. In this case an equation of the form

$$T_{lm}\psi + \lambda_{nlm} V \psi = E\psi \tag{4.18}$$

is be solved. Instead of E being the eigenvalue, E is kept fixed. The Sturmian eigenvalue is then λ_{nlm} which is a function of E. For the hydrogenic Sturmian problem, the potential V is the Coulomb potential with unit charge. The solutions to this differential equation are hydrogenic Sturmian functions

$$S_{nlm}\left(r, \theta, \phi, E\right) = r^l e^{-\sqrt{-2E}r} L_{n-l-1}^{2l+1}\left(2\sqrt{-2E}r\right) Y_{lm}\left(\theta; \phi\right) \tag{4.19}$$

with Sturmian eigenvalues

$$E = -\frac{\lambda_{nlm}^2}{2n^2} \tag{4.20}$$

or

$$\lambda_{nlm}(E) = n\sqrt{-2E} \tag{4.21}$$

These hydrogenic Sturmian functions can are used as a basis in which the Green's function is expanded. First, the Green's function is written in terms of partial waves so that $g_{lm}(\vec{r}, \vec{r}'\Omega) = \langle \vec{r} | g_{lm}(\Omega) | \vec{r}' \rangle$. Here $g_{lm}(\Omega)$ is the lm component of equation (4.16). This can be written explicitly as

$$g_{lm}(\Omega) = \frac{1}{(\Omega - T_{lm} - V)} \tag{4.22}$$

It is convenient to expand this function in terms of known functions. Since the Sturmian functions defined in equation (4.19) form a complete basis, $g_{lm}(\Omega)$ can be expanded as

$$g_{lm}(\Omega) = \sum_q \sum_p a_{pq} | S_{qlm}^E \rangle \langle S_{plm}^E | \tag{4.23}$$

Multiplying both sides of equation (4.19) by $(\Omega - T_{lm} - V)$ and then using equation (4.18) yields

$$(\Omega - T_{lm} - V)g_{lm}(\Omega) = 1 = \sum_q \sum_p a_{pq}[\Omega - E + (\lambda^E_{qlm} - 1)V]|S^E_{qlm}\rangle\langle S^E_{plm}| \qquad (4.24)$$

Multiplying the above equation on the left by $\langle S^E_{nlm}|$ results in

$$\langle S^E_{nlm}| = \sum_q \sum_p a_{pq}[(\Omega - E)\langle S^E_{nlm}|S^E_{qlm}\rangle + (\lambda^E_{qlm} - 1)\langle S^E_{nlm}|V|S^E_{qlm}\rangle]\langle S^E_{plm}|\delta_{n,q} \qquad (4.25)$$

or defining $\beta = \left\langle S^E_{nlm} \left| \frac{1}{r} \right| S^E_{nlm} \right\rangle$ this can be rewritten as

$$\left\langle S^E_{nlm}\right| = \sum_p a_{pn} \left[(\Omega - E)\left\langle S^E_{nlm}|S^E_{nlm}\right\rangle + \left(\lambda^E_{nlm} - 1\right)\beta^E_{nlm}\left\langle S^E_{plm}\right|\right] \qquad (4.26)$$

For the case where $\Omega = E$, multiplying on the right by $\frac{1}{r}|S^E_{p'lm}\rangle$, the results in [34]

$$\delta_{n,p'} = a_{p'n}(\lambda^E_{nlm} - 1)\beta^E_{nlm} \qquad (4.27)$$

Therefore, $a_{p',n}$ can be written as

$$a_{p',n} = \frac{\delta_{n,p'}}{(\lambda^E_{nlm} - 1)\beta^E_{nlm}} \qquad (4.28)$$

Therefore, the hydrogenic Green's function can be written in terms of Sturmian functions by substituting equation (4.28) into equation (4.23) to obtain

$$g_{lm}(E) = \sum_q \frac{|S^E_{qlm}\rangle\langle S^E_{qlm}|}{(\lambda^E_{qlm} - 1)\beta^E_{qlm}} \qquad (4.29)$$

4.4.2 Evaluation of β^E_{nlm}

β^E_{nlm} is defined as

$$\beta^E_{nlm} \equiv \langle S^E_{nlm}|V|S^E_{nlm}\rangle = -Z\int_0^\infty r^{2l+1}e^{-2\sqrt{-2E}r}\left[L^{2l+1}_{n-l-1}\left(2\sqrt{-2E}r\right)\right]^2 dr \qquad (4.30)$$

If the substitution, $u = 2\sqrt{-2E}r$ is made, then the integral can easily be evaluated[35]. The result is

$$\beta^E_{nlm} = -\frac{Z}{(2\sqrt{-2E})^{2l+2}}\frac{\Gamma(n+l+1)}{(n-l-1)!} \qquad (4.31)$$

4.5 Application of the Schwinger variational principal to the hydrogenic atom in a constant magnetic field problem

The Fock expansion solutions shown in equation (2.5) can be used as trial functions for the Schwinger variational principle as well as the more common Raleigh-Ritz principal. In order to do this, the Fock solutions

$$\psi_\nu = \sum_n \sum_l A^{\nu}_{nl} e^{-\sqrt{-2\varepsilon} r} r^{n+\nu} Y_{lm}(\theta, \phi) \tag{4.32}$$

are substituted into the condition for bound states

$$F(E) = \det(\langle \psi_\nu | V_{\mathrm{I}} - V_{\mathrm{I}} G V_{\mathrm{I}} | \psi_{\nu'} \rangle = 0 \tag{4.33}$$

In the case of the hydrogenic atom in a constant magnetic field problem, the added "interaction" potential V_{I} is the magnetic field potential

$$V_{\mathrm{I}} = \frac{\beta^2}{2} r^2 \sin^2(\theta) \tag{4.34}$$

This interaction potential is substituted into equation (4.33) to obtain

$$\det\left(\left\langle \psi_\nu \left| \frac{\beta^2}{2} r^2 \sin^2(\theta) - \frac{\beta^2}{2} r^2 \sin^2(\theta) G \frac{\beta^2}{2} r^2 \sin^2(\theta) \right| \psi_{\nu'} \right\rangle\right) = 0 \tag{4.35}$$

4.5.1 Evaluation of $\left\langle \psi_\nu \left| \frac{\beta^2}{2} r^2 \sin^2(\theta) \right| \psi_{\nu'} \right\rangle$

The first term to calculate in equation (4.35) is

$$\begin{gathered}\left\langle \psi_\nu \left| \frac{\beta^2}{2} r^2 \sin^2(\theta) \right| \psi_{\nu'} \right\rangle = \\ \frac{\beta^2}{2} \int_0^\infty \int_\Omega \sum_n \sum_l \sum_m \sum_{n'} \sum_{l'} \sum_{m'} A^{\nu}_{nlm} A^{\nu'}_{n'l'm'} e^{-\sqrt{-2\varepsilon} r} r^{n+n'+\nu+\nu'+4} \\ Y^*_{lm}(\theta, \phi) Y_{l'm'}(\theta, \phi) \sin^2(\theta) dr d\Omega\end{gathered} \tag{4.36}$$

From equations (2.12) and (2.16)

$$\begin{aligned}\sin^2(\theta) Y_{l'm'}(\theta, \phi) &= \frac{2}{3} Y_{l'm'}(\theta, \phi) - \frac{2}{3}\sqrt{\frac{4\pi}{5}} \left[C_1(l', m') Y_{(l'-2)m'}(\theta, \phi)\right. \\ &+ \left. C_2(l', m')\, Y_{l'm'}(\theta, \phi) + C_3(l', m') Y_{(l'+2)m'}(\theta, \phi)\right]\end{aligned} \tag{4.37}$$

Evaluating the radial component of the integral and substituting equation (4.37) gives,

$$\left\langle \psi_\nu \left| \frac{\beta^2}{2} r^2 \sin^2\theta \right| \psi_{\nu'} \right\rangle = \frac{\beta^2}{2} \sum_n \sum_{n'} \frac{\Gamma(n+n'+\nu+\nu'+5)}{(2\sqrt{-2\varepsilon})^{n+n'+\nu+\nu'+5}} \sum_l \sum_{l'} \int_\Omega A^{\nu}_{nlm} A^{\nu'}_{n'l'm'}$$

$$\left[-\frac{2}{3}\sqrt{\frac{4\pi}{5}} C_1(l',m) Y^*_{lm}(\theta,\phi) Y_{(l'-2)m}(\theta,\phi) - \frac{2}{3}\sqrt{\frac{4\pi}{5}} C_2(l',m) Y^*_{lm}(\theta,\phi) Y_{l'm}(\theta,\phi) \right.$$

$$\left. -\frac{2}{3}\sqrt{\frac{4\pi}{5}} C_3(l',m) Y^*_{lm}(\theta,\phi) Y_{(l'+2)m}(\theta,\phi) + \frac{2}{3} Y^*_{lm}(\theta,\phi) Y_{l'm}(\theta,\phi) \right] d\Omega \tag{4.38}$$

The angular integrals are evaluated easily by taking advantage of the orthonormality of the spherical harmonic functions. The evaluation of this integral results in four terms.

$$\left\langle \psi_\nu \left| \frac{B^2}{2} r^2 \sin^2\theta \right| \psi_{\nu'} \right\rangle$$

$$\begin{aligned}
= & -\frac{\beta^2}{3}\sqrt{\frac{4\pi}{5}} \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'(l+2)} C_1(l+2,m) \frac{\Gamma(n+n'+\nu+\nu'+5)}{(2\sqrt{-2\varepsilon})^{n+n'+\nu+\nu'+5}} \\
- & \frac{\beta^2}{3}\sqrt{\frac{4\pi}{5}} \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'l} C_2(l,m) \frac{\Gamma(n+n'+\nu+\nu'+5)}{(2\sqrt{-2\varepsilon})^{n+n'+\nu+\nu'+5}} \\
- & \frac{\beta^2}{3}\sqrt{\frac{4\pi}{5}} \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'(l-2)} C_3(l-2,m) \frac{\Gamma(n+n'+\nu+\nu'+5)}{(2\sqrt{-2\varepsilon})^{n+n'+\nu+\nu'+5}} \\
+ & \frac{\beta^2}{3} \sum_n \sum_{n'} \sum_l A^{\nu}_{nl} A^{\nu'}_{n'l} \frac{\Gamma(n+n'+\nu+\nu'+5)}{(2\sqrt{-2\varepsilon})^{n+n'+\nu+\nu'+5}}
\end{aligned} \tag{4.39}$$

4.5.2 Evaluation of $\langle \psi_\nu | V_{\mathrm{I}} G^o V_{\mathrm{I}} | \psi_{\nu'} \rangle$.

The second term of the condition for bound states is

$$\langle \psi_\nu | V_{\mathrm{I}} G^o V_{\mathrm{I}} | \psi_{\nu'} \rangle = \sum_{n'} \sum_{l'} \sum_{m'} \frac{\left\langle \psi_\nu | V_{\mathrm{I}} | S^E_{n'l'm'} \right\rangle \left\langle S^E_{n'l'm'} | V_{\mathrm{I}} | \psi_{\nu'} \right\rangle}{\beta^E_{n'l'm'}(\lambda_{n'l'm'} - 1)}$$

The two integrals in the numerator must be evaluated. These are

$$\left\langle \psi_\nu | V_{\mathrm{I}} | S^E_{n'l'm'} \right\rangle \tag{4.40}$$

The infinite sums in equation (4.40) can be collapsed by evaluating the Green's function at ε instead of E. This does not give the optimum lower bound, but the result is still a lower bound as seen in the arguments given in section 4.2. This procedure makes it possible to avoid truncation of the series. We shall see that the lower bounds are still convergent. Therefore the integral $\langle\psi_\nu\,|V_{\mathrm{I}}|\,S^{\varepsilon}_{n'l'm'}\rangle$ is evaluated. This integral can be written explicitly as

$$\frac{\beta^2}{2}\sum_n\sum_{n'}\sum_l\sum_{l'}\int_0^\infty e^{-2\sqrt{-2\varepsilon}r}r^{n+\nu+l'+4}L^{2l'+1}_{n'-l'-1}\left(2\sqrt{-2\varepsilon}\right)dr \tag{4.41}$$

$$\int_\Omega A^\nu_{nl}Y^*_{lm}(\theta,\phi)Y_{l'm'}(\theta,\phi)\sin^2\theta d\Omega$$

The substitution $x = 2\sqrt{-2\varepsilon}r$ is made. The radial component of this integral then becomes

$$\frac{1}{(2\sqrt{-2\varepsilon})^{n+\nu+l'+5}}\int_0^\infty e^{-x}x^{n+\nu+l'+4}L^{2l'+1}_{n'-l'-1}(x)dx \tag{4.42}$$

Integrals of this form can be evaluated analytically [36]

$$\textstyle\int_0^\infty e^{-x}x^{\gamma-1}L^\mu_n(x)dx = \frac{\Gamma(\gamma)\Gamma(1+\mu+n-\gamma)}{n!\Gamma(1+\mu-\gamma)} \quad [Re(\gamma)>0]$$

Therefore, the radial component of the equation (4.41) evaluates to

$$\langle\psi_\nu\,|V_{\mathrm{I}}|\,S^{\varepsilon}_{n'l'm'}\rangle_r = \frac{1}{(2\sqrt{-2\varepsilon})^{n+\nu+l'+5}}\frac{\Gamma(n+\nu+l'+5)\Gamma(n'-n-\nu-4)}{(n'-l'-1)!\Gamma(l'-n-\nu-3)} \tag{4.43}$$

One problem with the above expression becomes immediately apparent. Because l' is always less than n, $(l'-n-\nu-3)$ is always a negative integer. The gamma function has poles at each of the negative integers, however. In order for equation (4.43) to yield a value other than zero, it must be evaluated for $n' \leq n+\nu+4$, so that the numerator is also evaluated at the poles of the Gamma function. Doing this allows the substitution

$$\frac{\Gamma(-m)}{\Gamma(-n)} = (-1)^{m-n}\frac{n!}{m!} \tag{4.44}$$

Equation (4.44) is then substituted into equation (4.43) to yield

$$\left\langle\psi_\nu\left|\frac{\beta^2}{2}r^2\sin^2(\theta)\right|S^{\varepsilon}_{n'l'm'}\right\rangle_r = \frac{(-1)^{l'-n'+1}}{(2\sqrt{-2\varepsilon})^{n+\nu+l'+5}}\frac{\Gamma(n+\nu+l'+5)(n+\nu-l'+3)!}{(n'-l'-1)!(n+\nu-n'+4)!} \tag{4.45}$$

Substituting this evaluated radial integral into the full integral leaves,

$$\begin{aligned}\left\langle\psi_{\nu}\left|V_{\mathrm{I}}\right|S_{nlm}^{\varepsilon}\right\rangle &= \frac{\beta^{2}}{2}\sum_{n}\sum_{n'}\sum_{l}\sum_{l'}\frac{(-1)^{l'-n'+1}}{(2\sqrt{-2\varepsilon})^{n+\nu-l'+5}} \\ &\quad \frac{\Gamma(n+\nu+l'+5)(n+\nu-l'+3)!}{(n'-l'-1)!(n+\nu-n'+4)!} \\ &\quad \int_{\Omega} A_{nl}^{\nu}Y_{lm}^{*}(\theta,\phi)Y_{l',m'}(\theta,\phi)\sin^{2}\theta d\Omega\end{aligned} \tag{4.46}$$

The angular integral was previously evaluated in equation (4.38). Therefore the integral becomes

$$\begin{aligned}\left\langle\psi_{\nu}\left|V_{\mathrm{I}}\right|S_{nlm}^{\varepsilon}\right\rangle &= -\frac{\beta^{2}}{3}\sqrt{\frac{4\pi}{5}}\sum_{n}\sum_{n'}\sum_{l}\sum_{l'}\frac{(-1)^{l'-n'+1}}{(2\sqrt{-2\varepsilon})^{n+\nu+l'+5}} \\ &\quad \frac{\Gamma(n+\nu+l'+5)(n+\nu-l'+3)!}{(n'-l'-1)!(n+\nu-n'+4)!} \\ &\quad [A_{nlm}^{\nu}C_{1}(l',m)\delta_{l',l-2}+A_{nlm}^{\nu}C_{2}(l',m)\delta_{l',l} \\ &+ \left. A_{nlm}^{\nu}C_{3}(l',m)\delta_{l',l+2}-\sqrt{\frac{5}{4\pi}}A_{nlm}^{\nu}\delta_{l',l}\right]\end{aligned} \tag{4.47}$$

With the above calculated, it is now possible to calculate the condition for bound states in equation (4.33). Such a calculation can be seen in figure (4.2) for the ground state of hydrogen and an applied field of $\beta = 0.05$. There is a bound state wherever this eigenvalue intersects zero. In this case the intersection occurs at $\varepsilon \approx -0.4975$.

4.6 Convergence of the lower bounds as a function of the number of terms in the Fock expansion

In chapter three it was shown that when the Fock expansion is used with the Raleigh-Ritz principle that the results do not converge monotonically as the order of the Fock functions is increased. However, the results converge monotonically as the number of Fock functions is increased. The remainder also exists in the Fock expansion when it is used with the Schwinger variational principle. Therefore, an analysis similar to that in chapter three is performed for the Schwinger variational principle.

For a small field of $\beta = 0.05$, the convergence properties can be seen in table (4.1). In this calculation the order of the Fock expansion is coupled with the number

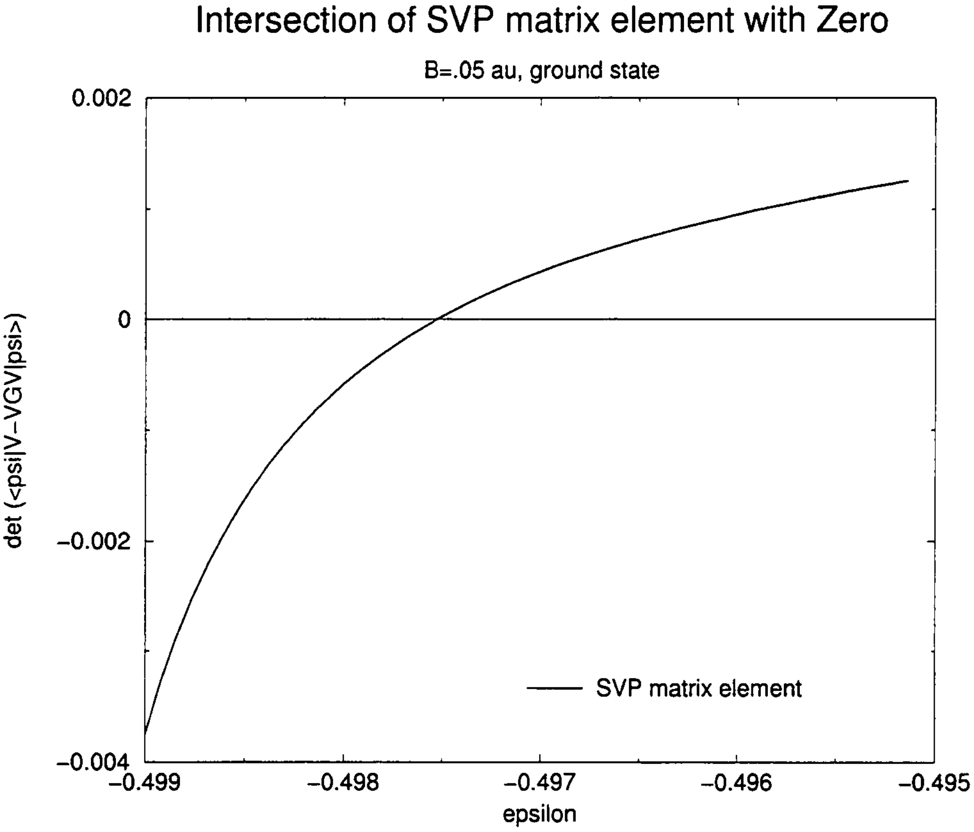

Figure 4.2: Intersection of Schwinger variational principle matrix element with zero.

Table 4.1: Convergence of the Schwinger variational calculation for a field of $\beta = 0.05$. The lowest energy for a Schwinger variational principle calculation of the ground state of hydrogen is shown with an applied magnetic field of $\beta = 0.05$. The energy shown converges as the order and number of Fock terms increases.

Number of Fock Functions and order	*Energy (au)*
3	-0.497526983572
4	-0.497526489977
5	-0.497526483433
6	-0.497526480834
7	-0.497526480509
8	-0.497526480430
9	-0.497526480423
10	-0.497526480407
11	-0.497526480402
12	-0.497526480401
13	-0.497526480401

of Fock functions. It is seen that the results appear to converge as the number of Fock functions and their orders are increased. Furthermore, this result converges to the same result as that of the Raleigh-Ritz calculation given in table (3.1). Figure (4.3) shows that the upper and lower bounds are "squeezed" by this calculation for an applied magnetic field of $\beta = 0.05$ as the number of Fock functions and their orders are increased. Both calculations eventually yield the same result to machine precision. This calculation is the first calculation of an energy level of hydrogen in a constant magnetic field which has been made "exactly" in the sense of having rigorous and convergent upper and lower bounds to the calculation.

For a larger field of $\beta = 0.2$, the same algorithm yields the results in table (4.2). Once again we find that as the order of the Fock expansions used increases that the energies produced become worse. This is expected because of the error produced by the remainder terms. As the number of Fock functions is increased, however, these results converge. One interesting feature is seen in the third order calculation of table (4.3). The energies calculated with four Fock functions and six Fock functions are identical to the precision shown. This is because different Fock functions do not necessarily contribute to the same class of solutions and may have a negligible effect on an individual energy level. Adding still more Fock terms causes the calculation to converge once again. The same behavior is seen for the fifth order calculation when six, eight, and ten Fock functions are used. This calculation is expected to converge also as more functions are used just as is seen in the third order calculation.

A detailed exploration of the convergence of this calculation is seen in table (4.3). We find behavior very similar to that of the Raleigh-Ritz calculation in chapter three. Once again, the Fock expansion is taken in such a way that the number of Fock functions can be chosen independently from the order of the Fock functions. As the order of the Fock functions is increased, the calculation diverges because of the remainder terms in the Fock expansion. On the other hand, the calculation converges monotonically as the number of Fock functions increases.

Just as was the case for the Raleigh-Ritz principle, the Fock expansion is not convenient to use with the Schwinger variational principle. The energies tend to decrease as the order of the Fock functions increases. As the number of Fock functions

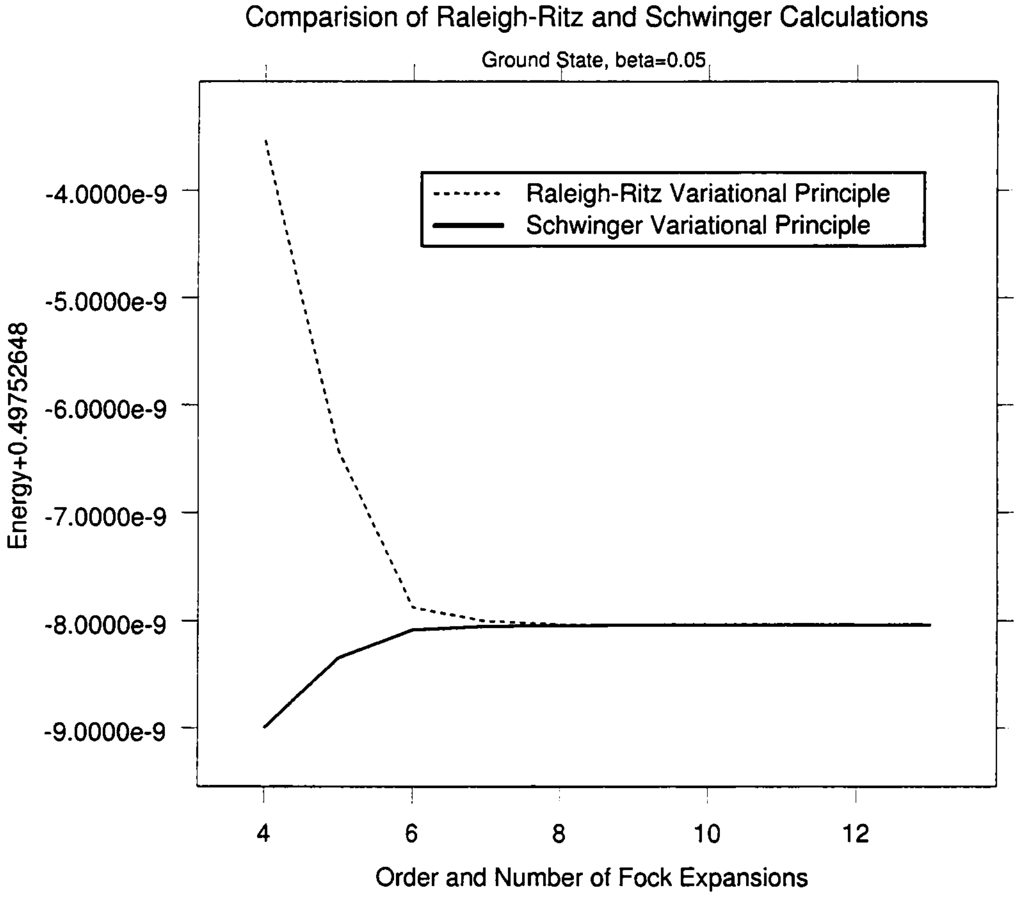

Figure 4.3: Comparison of Raleigh-Ritz and Schwinger Calculations: The Raleigh-Ritz and Schwinger variational principle calculations are plotted on the same graph. This shows that when combined, these two calculations "squeeze" the exact energy eigenvalue from above and below.

Table 4.2: Convergence of the Schwinger variational principle calculation for a field of $\beta = 0.2$.

The lowest energy for a Schwinger variational principle calculation if the ground state of hydrogen is shown with an applied magnetic field of $\beta = 0.2$. The energy shown diverges as the order and number of Fock terms increases.

Number of Fock functions and order	*Energy (au)*
3	-0.46496810908108
4	-0.46651159497317
5	-0.46481356154289
6	-0.465686499493251
7	-0.49103124777930
8	-0.49682027453290
9	-0.49912134026123

Table 4.3: Convergence of the Schwinger variational principle calculation as a function of the order of the Fock expansion and the number of functions.

Number of Fock Functions	*3rd order*	*4th order*	*5th order*	*6th order*
2	-0.46496810908108	-0.46706805565431	-0.47214216430168	-0.49190602232048
4	-0.46486706716073	-0.46631749486877	-0.46569000153895	-0.48059477822483
6	-0.46486706716073	-0.46557412244048	-0.46563676655388	-0.47686691518706
8	-0.46483438049915	-0.46535554436570	-0.46563676655388	-0.47612118646134
10	-0.46483130359737	-0.46522020306386	-0.46563676655388	-0.47534798259475

increases, the energy increases monotonically, allowing convergent lower bounds to the eigenenergies to be calculated. When combined with the Raleigh-Ritz variational principle, this allows the exact eigenenergies to be bounded from both above and below.

CHAPTER 5

Excited States

In the previous chapters two variational methods were used to calculate the binding energy of the ground state of hydrogenic atoms in constant magnetic fields. It was shown that both the Raleigh-Ritz and Schwinger variational principles gave convergent bounds to the exact eigenenergies as the number of Fock functions used was increased. There is a lot of interest in the energy levels of excited states of hydrogen in constant magnetic fields. One reason for this is that effects which are currently impossible to see for the ground state with laboratory achievable magnetic fields can be seen in excited states, which have a weaker interaction with the Coulomb potential. Variational calculations are normally applied to the ground state. In this chapter we will explore the properties of the Raleigh-Ritz and Schwinger variational principles for excited states.

5.1 Excited states and the Raleigh-Ritz variational principle

First the properties of the Raleigh-Ritz variational principle are examined in the case of excited states. In chapter three, the eigenvalues and eigenvectors of a matrix of the form

$$\left\langle \psi_{\nu} \middle| \hat{H} - \varepsilon \middle| \psi_{\nu'} \right\rangle \tag{5.1}$$

were calculated. For the ground state the lowest eigenvalue was examined and a minimum was found in this eigenvalue as a function of the variational parameter ε. The second lowest eigenvalue is now examined. This eigenvalue corresponds to the first excited state in the manifold. For the even l manifold and $m = 0$, this is the ${}^2S_0$ state. First the convergence of the ${}^2S_0$ state is examined in table (5.1).

Table 5.1: Convergence of the first excited state in the Raleigh-Ritz principle

The eigenvalue corresponding to the ${}^2S_0$ state of hydrogen in a constant magnetic field is shown as a function of the number of terms in the Fock expansion. This calculation is made for a magnetic field of $\beta = 0.05$. It can be seen that the eigenenergy does not converge for the first excited state.

Number of Terms	*Energy (au)*
3	-0.094064421667259
4	-0.0060926401333017
5	-0.0069673324363791
6	-0.0097025321547484
7	0.05320130772264
8	0.037259153500780
9	0.02639849000743
10	0.04337141609756
11	0.084472168771727

This calculation is made for an applied external magnetic field of $\beta = 0.05$. The minimum is then found in the second lowest eigenvalue. As one can see, the Raleigh-Ritz variational principle does not converge for the first excited state in hydrogen. The reason for this can be seen in figure (5.1). The lower, solid line in figure (5.1) represents the ground state eigenvalue as a function of the variational parameter ε. It was shown in chapter three that for an applied magnetic field of $\beta = 0.05$ that this minimum is located at approximately $\varepsilon = -0.4975$. This is seen in the minimum located in in the left-hand side of the plot for the lowest eigenvalue. The minimum for the first excited state occurs at approximately $\varepsilon = -0.09$. This is seen in the upper, dashed line in figure (5.1).

If the Schrödinger equation was solved exactly, all of the eigenvalues produced would be orthogonal to each other. In this case, however, the eigenvectors are not orthogonal to each other. The reason for this is that the variational parameter ε is not the same at each minimum. This causes the ground state wavefunction to be different at each value of ε. While it is true that upper bounds to the eigenenergies of excited states are produced when these excited states are orthogonal to approximate ground state wavefunctions[2], they are not expected to be very accurate because the best approximation for the ground state wavefunction occurs when $\varepsilon \approx -0.4975$. If $\varepsilon = -0.09$, the ground state wavefunction is not a very good approximation to the exact wavefunction.

The lack of orthogonality of the wavefunctions for different values of ε propagate throughout the calculations of the excited states. Just as the ground state and the first excited states are not orthogonal because they minimize at different ε, the same is true of the first and second excited states, as well as further excited states. Therefore, a straight-forward calculation of the excited states using the Raleigh-Ritz variational principle is not possible.

In order to obtain a better upper bound for the first excited state, this state would have to be written in a new basis which is orthogonal to the best possible ground state (i.e., that produced at $\varepsilon \approx -0.4975$). One procedure for doing this is as follows. First, the lowest local minimum in the ground state eigenvalue is found in order to find a linear combination of Fock expansion solutions which best describes

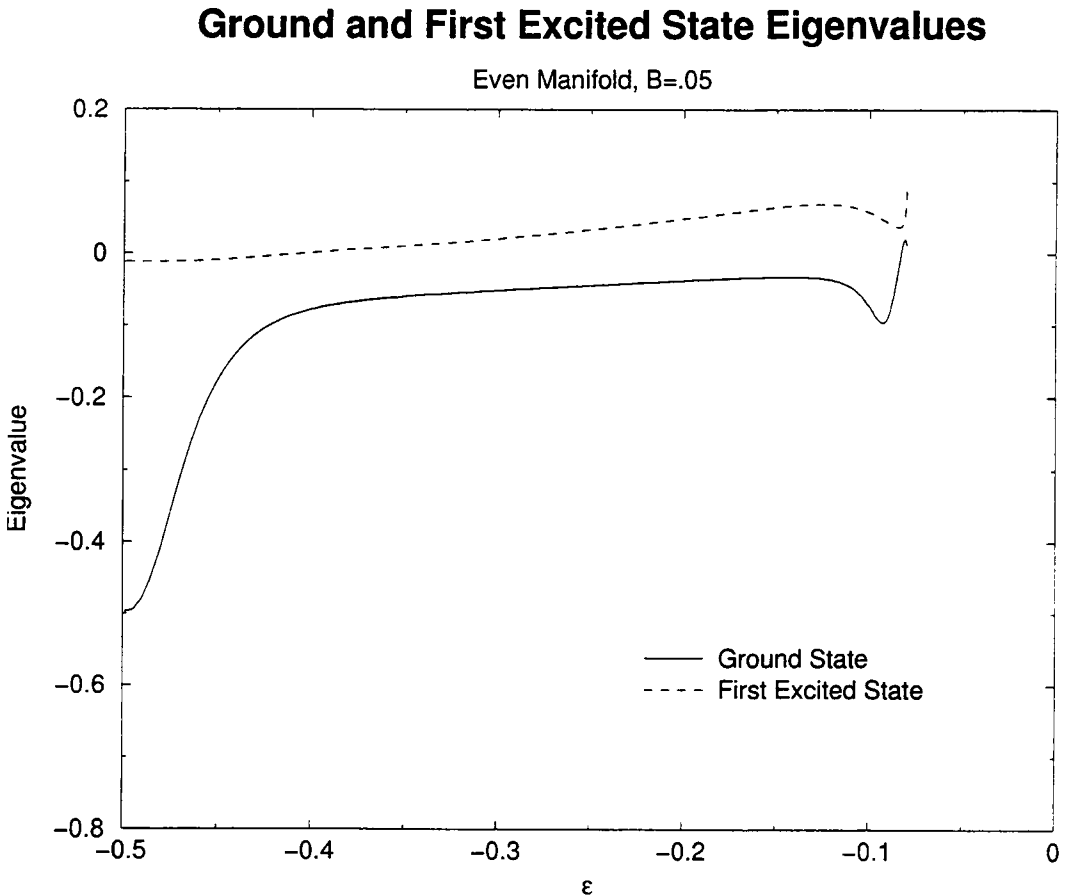

Figure 5.1: Plot of the ground state and first excited state eigenvalues: This is a plot of the ground state and first excited state eigenvalues for a Raleigh-Ritz calculation of hydrogen in a magnetic field of $\beta = 0.05$.

the ground state of hydrogen in a constant magnetic field. This calculation is exactly the same as was shown in chapter three. One result of the matrix diagonalization which produced this eigenvalue is a corresponding eigenvector. Each element of this eigenvector represents a proportionality constant such that if this the n^{th} element is C_n, then

$$\Psi = \sum_n C_n \psi_n \tag{5.2}$$

In this expression, Ψ represents an approximate solution to the Schrödinger equation. The linear combinations of Fock solutions which result from diagonalizing the Raleigh-Ritz matrix becomes a new basis. If the basis element which represents the ground state is removed from the basis, all states produced in this basis are automatically orthogonal to this state. In effect, the first excited state can become a new "ground state" for the calculation. This procedure can be repeated for more highly excited states.

A problem with such a procedure is that the bookkeeping becomes very complicated. Ultimately one needs to evaluate expressions which explicitly depend on the Fock expansion. Every time the basis is re-orthogonalized, the new basis has to be converted into the Fock expansion basis before any of the integrals can be evaluated. Although this can be done for the first excited state with little inconvenience, more highly excited states become much more complicated.

5.2 Excited States and the Schwinger Variational Principle

In the previous section the properties of the Raleigh-Ritz variational principle were examined for excited states. It was shown that without modification, the Raleigh-Ritz principle does not produce convergent upper bounds for excited states. The properties of the Schwinger variational principle are now examined for excited states.

Unlike the Raleigh-Ritz variational principle, the Schwinger variational principle does not depend upon the orthogonality of the functions which represent the final wavefunctions. The derivation of the Schwinger variational principle does not put strong constraints upon the form or properties of the trial wavefunction. In fact, as long as the trial wavefunction satisfies the conditions for bound states,

$$\langle\psi_t|V - VGV|\psi_t\rangle \tag{5.3}$$

then the wavefunction produces an approximate lower bound to the exact bound state energy. The Fock expansion, taking enough terms, can exactly represent the exact eigenfunctions to the Hamiltonian describing a hydrogenic atom in a constant magnetic field. Therefore it is reasonable to expect that the Fock wavefunctions should produce convergent lower bounds to the exact eigenenergies. This expectation relies on the assumption that all physical solutions to the Schrödinger equation can be represented accurately in terms of the Fock expansion. This is a reasonable assumption because the Fock expansion works very well for the ground state. Calculation of the $^2S_0$ state of hydrogen, which is the first excited state in the $l = even$ manifold gives the results in table (5.2). In table (5.2) we find results very similar to that of the ground state. For a small magnetic field of $\beta = 0.01$, the results converge as the number and order of the Fock expansion is increased until $N = 8$. At this point the remainder terms cause the calculation to begin to diverge. The results of table (5.3) show that the eigenenergy for the first excited state in the even manifold does not converge for as a function of the number of Fock functions and their order for a field of $\beta = 0.05$. In this case the effect of the remainder terms is much more pronounced. This behavior is seen in the ground state calculation discussed in chapter four. In fact, the convergence of the first excited state is nearly identical to that of the ground state.

For the ground state, we showed that as the order of the Fock expansion is increased, the energies become worse, but they improve as the number of Fock functions is increased. This same behavior can be seen in tables (5.3-5.18). One difference between the ground and first excited state calculations is that the divergence in the energies as the order of the Fock expansion is increased is much more pronounced for a small applied field. This fact makes the Fock expansion more difficult to use for excited states.

In chapter four, it was found that as the number of Fock functions was increased that the energies converged. The reason for this was not explained, however.

Table 5.2: Convergence of the Schwinger variational principle calculation of the first excited state for a field of $\beta = 0.01$.

The lowest energy for a Schwinger variational principle calculation of the first excited state of hydrogen is shown with an applied magnetic field of $\beta = 0.01$. The energy shown diverges as the order and number of Fock terms increases.

Number of Fock functions and order	*Energy (au)*
2	-0.12440676219299
3	-0.12440669241998
4	-0.12440650496050
5	-0.12440646694709
6	-0.12440646631362
7	-0.12440646602182
8	-0.12440646972656

Table 5.3: Convergence of the ${}^2S_0$ state of hydrogen in a constant magnetic field of $\beta = 0.05$ as a function of the number of terms in the Fock expansion.

Number of Fock Terms	*Energy (au)*
3	-0.10356944995453
4	-0.10115800106354
5	-0.11055115523515
6	-0.10866707914256
7	-0.11794963968629
8	-0.12104618943571

Table 5.4: Ground and Excited States for three Fock terms and diagonalizing a 1x1 matrix

State	*Energy (au)*
1	-0.49752698357173
2	-0.10356944995453
3	-0.04241779303271
4	-0.02120935499403

Table 5.5: Ground and Excited States for three Fock terms and diagonalizing a 2x2 matrix

State	*Energy (au)*
1	-0.49752673425308
2	-0.10105097121551
3	-0.04241729919206
4	-0.02120664759489

Table 5.6: Ground and Excited States for four Fock terms and diagonalizing a 1x1 matrix

State	*Energy (au)*
1	-0.49752655514451
2	-0.10115880435343
3	-0.03741099046707
4	-0.02363566822972
5	-0.01424713799904

Table 5.7: Ground and Excited States for four Fock terms and diagonalizing a 2x2 matrix

State	*Energy (au)*
1	-0.49752648753690
2	-0.10115800106354
3	-0.03730809743829
4	-0.02363207684448
5	-0.01424605143463

Table 5.8: Ground and Excited States for five Fock terms and diagonalizing a 1x1 matrix

State	*Energy (au)*
1	-0.49752730373767
2	-0.11352784529523
3	-0.04549359291833
4	-0.02522029385700
5	-0.01502642306314

Table 5.9: Ground and Excited States for five Fock terms and diagonalizing a 2x2 matrix

State	*Energy (au)*
1	-0.49752648343339
2	-0.11055115523515
3	-0.03688477482622
4	-0.02165352444543
5	-0.01497089429302

Table 5.10: Ground and Excited States for five Fock terms and diagonalizing a 3x3 matrix

State	*Energy (au)*
1	-0.49752648328641
2	-0.10956912897387
3	-0.03462215435880
4	-0.02164559978114
5	-0.01491737667402

Table 5.11: Ground and Excited States for six Fock terms and diagonalizing a 1x1 matrix

State	*Energy (au)*
1	-0.49753213533889
2	-0.11443410789833
3	-0.05211361414029
4	-0.02614706566632
5	-0.01553990065782

Table 5.12: Ground and Excited States for six Fock terms and diagonalizing a 2x2 matrix

State	*Energy (au)*
1	-0.49752648084453
2	-0.10923816889084
3	-0.04498398977888
4	-0.02250154331410
5	-0.01421715050698

Table 5.13: Ground and Excited States for six Fock terms and diagonalizing a 3x3 matrix

State	*Energy (au)*
1	-0.49752648083414
2	-0.10866707914256
3	-0.04365349980880
4	-0.02241403538203
5	-0.01418745141327

Table 5.14: Ground and Excited States for six Fock terms and diagonalizing a 3x3 matrix

State	*Energy (au)*
1	-0.49752648083414
2	-0.10866707914256
3	-0.04365349980880
4	-0.02241403538203
5	-0.01418745141327

Table 5.15: Ground and Excited States for seven Fock terms and diagonalizing a 1x1 matrix

State	*Energy (au)*
1	-0.49755746991220
2	-0.12088630587119
3	-0.05504466563092
4	-0.02803535668890
5	-0.01644658768464

Table 5.16: Ground and Excited States for seven Fock terms and diagonalizing a 2x2 matrix

State	*Energy (au)*
1	-0.49752648061549
2	-0.11863416727419
3	-0.05333966271402
4	-0.02800962056781
5	-0.01641140874644

Table 5.17: Ground and Excited States for seven Fock terms and diagonalizing a 3x3 matrix

State	*Energy (au)*
1	-0.49752648050873
2	-0.11794963968629
3	-0.04968591720881
4	-0.02799986288751
5	-0.01443722373590

Table 5.18: Ground and Excited States for seven Fock terms and diagonalizing a 4x4 matrix

State	*Energy (au)*
1	-0.49752648050322
2	-0.11761369320507
3	-0.04889372424387
4	-0.02799217493600
5	-0.01417969627680

This convergence can be analyzed by examining the diagonal matrix elements of the Schwinger matrix. Figure (5.2) shows the diagonal matrix elements for three Fock expansion terms. In this case only one diagonal matrix element is plotted. In figure (5.2) the transformation $n^* = \frac{1}{\sqrt{-2\varepsilon}}$ was made so that the poles which lie at the hydrogen atom bound states are transformed to integers. This transformation causes the poles to appear equally spaced. In this figure each n^* at which the curve intersects zero represents a lower bound to an exact bound state. Using the Fock expansion with the Schwinger variational principle allows rough lower bounds to any excited state to be calculated quite quickly and efficiently. In fact, if the Greens function had not been evaluated at $E = \varepsilon$, all excited states would be generated.

In figure (5.3), the diagonal matrix elements for four Fock functions are plotted. Because there are two diagonal terms, two curves appear on the graph. As in figure (5.2), each curve intersection with zero represents a lower bound with an exact eigenenergy. The original curves which are seen in figure (5.2) are still present in figure (5.3). New curves also appear which lie between the original curve and the pole. The existence of such a curve should tend to push the first state to higher energy when the matrix is diagonalized. This would improve the lower bound.

Another aspect of the diagonal matrix elements is seen in figure (5.4). In this case there are three diagonal matrix elements. The curve created by the third diagonal matrix element is not affected by the first two poles, however. This is because of the way that the Fock expansion has been truncated. The Fock expansion has been calculated so that each Fock expansion term ψ_ν is terminated to the same power in r. For six terms in the Fock expansion it is terminated at r^6. As a result, the ψ_6 term only has one Fock expansion term with an angular dependence of Y_{00}. The Fock expansion would have to be continued to include a Y_{40} term in order to be affected by the first two poles.

As has been shown here, the behavior of the Raleigh-Ritz variational principle is fundamentally different from that of the Schwinger variational principle. In the Raleigh-Ritz principle calculation of excited states is difficult because the excited states must be orthogonal to each of the lower states. Because the trial wavefunctions depend upon the variational parameter ε, the ground state is no longer correct

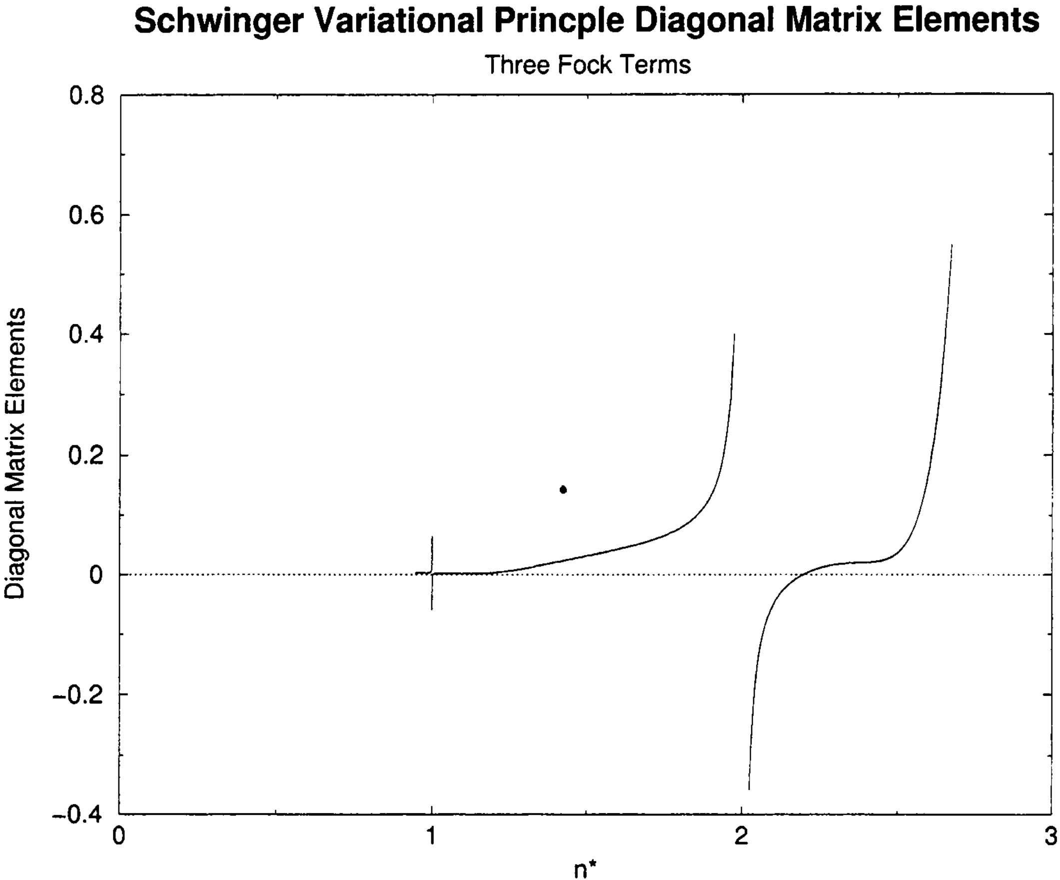

Figure 5.2: Plot of the diagonal matrix elements for the Schwinger variational matrix with three Fock terms: The diagonal matrix elements of the matrix which is to be diagonalized in the Schwinger variational principle is plotted here for an external field of $\beta = 0.05$ au. In this plot, $n^* = \frac{n}{\sqrt{-2\varepsilon}}$

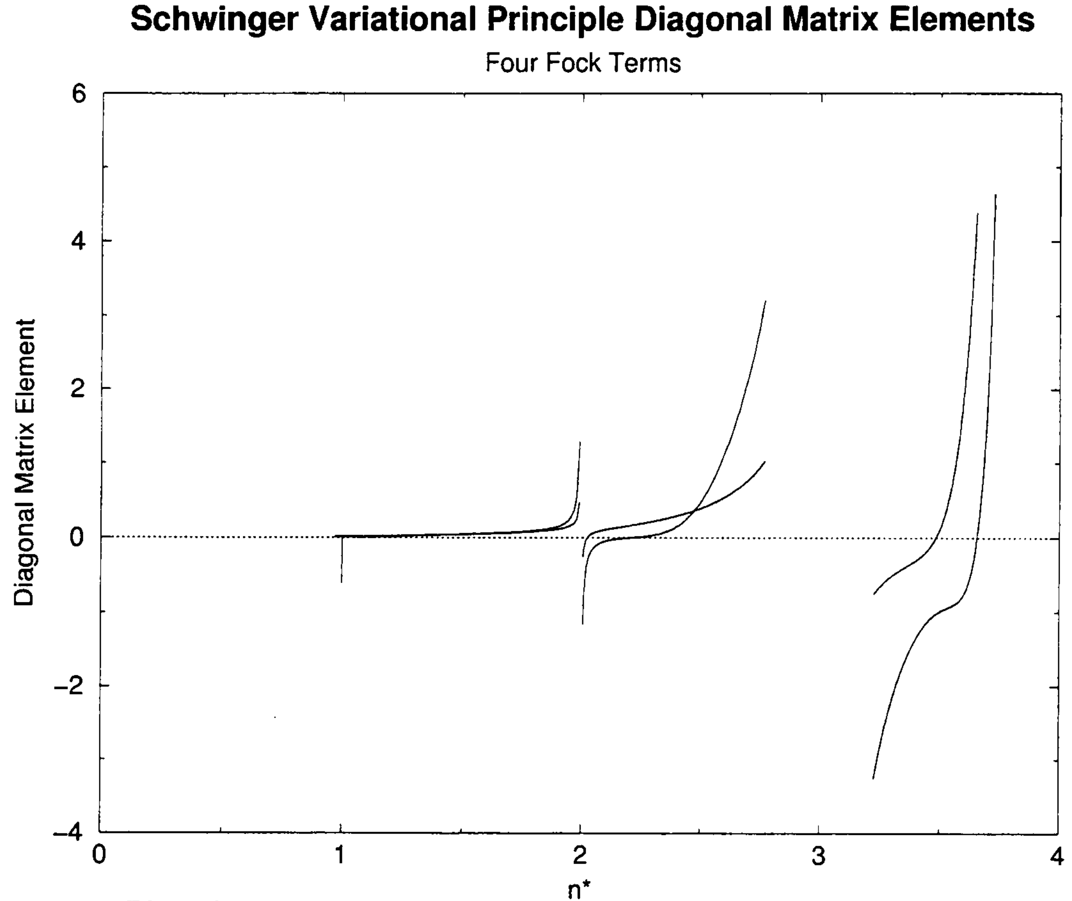

Figure 5.3: Plot of the diagonal matrix elements for the Schwinger variational principle matrix with four Fock terms: The diagonal matrix elements of the matrix which is to be diagonalized in the Schwinger variational principle is plotted here for an external field of $\beta = 0.05$ au. Because there are two diagonal terms, both are plotted on the same graph. In this plot, $n^* = \frac{n}{\sqrt{-2\varepsilon}}$

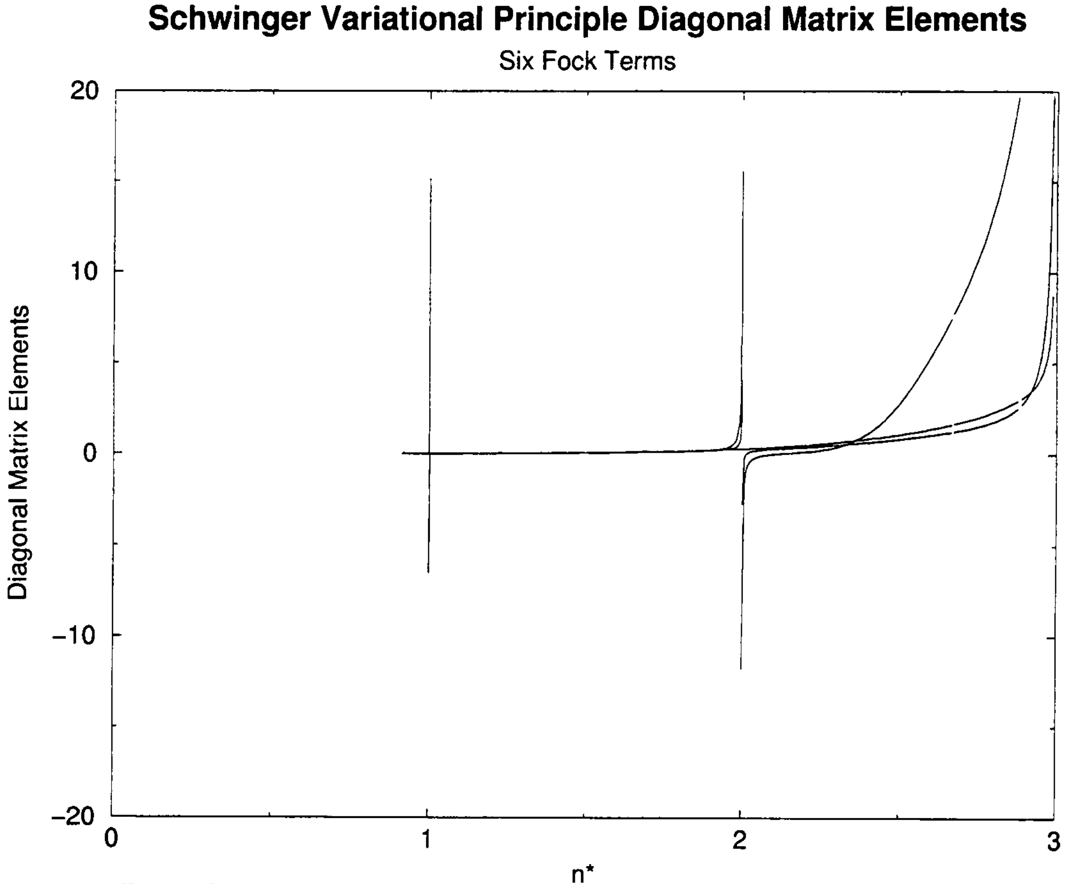

Figure 5.4: Plot of the Diagonal Matrix elements for the Schwinger variational principle matrix with six Fock terms: The diagonal matrix elements of the matrix which is to be diagonalized in the Schwinger variational principle is plotted here for an external field of $\beta = 0.05$ au. Because there are two diagonal terms, both are plotted on the same graph. In this plot, $n^* = \frac{n}{\sqrt{-2\epsilon}}$

when the excited states are calculated. The Schwinger variational principle does not have this disadvantage, however. As long as the condition for bound states in equation (4.33) is satisfied, bounds to the exact eigenvalues can be found. The behavior for excited states is exactly the same as that for the ground state. Once again, as the order of the Fock expansion increases, the calculation diverges, but it converges monotonically as the number of Fock functions is increased.

CHAPTER 6

Extensions

6.1 The high magnetic field case

In chapters two, three and four, a trial solution to the Schrödinger equation in terms of a Fock expansion was found. This expansion was substituted into the Raleigh-Ritz variational principle and find upper bounds to the eigenenergies for bound states were calculated. These Fock expansion solutions were also substituted into the Schwinger variational principle which produced lower bounds to the eigenenergies. Both of these calculations were done for relatively small magnetic field. Although the trial function in the previous chapters should work for large magnetic fields as well as small ones, the change in the natural geometry of the system makes them inefficient. This is because a large number of terms in each Fock solution ψ_ν, as well as a large number of different solutions are required in order to represent wavefunctions with a geometry significantly different from spherical geometry.

Other calculations have been made to obtain accurate upper bounds to the eigenenergies for the bound states of hydrogen in constant magnetic fields[21, 22]. Some of these calculations treated high fields, however no convergent lower bounds for high fields have been reported. Therefore a more efficient method for obtaining lower bounds using the Schwinger variational principle will be proposed here.

A small adjustment in the interaction potential makes the Schwinger variational principle more efficient for the high field case. In the previous calculation the potential

$$U = V_{\mathrm{C}} + V_{\mathrm{I}}$$

was used, where V_{C} is the Coulomb potential and V_{I} is the interaction potential which contained the magnetic interaction. This interaction potential contained the quadratic magnetic term. For the high magnetic field case, it makes sense to let the magnetic potential be the "main" part of the potential and let the Coulomb potential become the interaction. This is because the the magnetic field has a stronger effect on the the electron than the Coulomb potential in this case. If the magnetic field is aligned in the $\hat{z}$ direction, as it has been throughout this work, the magnetic field does not act on the electron in the $\hat{z}$ direction. Because of this, the $\hat{z}$ component can also be absorbed into the "main" part of the potential.

The potential can be written

$$U = V + V_{\mathrm{I}} \tag{6.1}$$

where

$$V = \frac{1}{2}\beta^2 r^2 \sin^2\theta - \frac{Z}{r_z} \tag{6.2}$$

and

$$V_{\mathrm{I}} = -\frac{Z}{r} + \frac{Z}{r_z} \tag{6.3}$$

Here, r_z represents the $\hat{z}$ component of r and Z represents the charge. The radial vector $\vec{r}$ can be written in Cartesian coordinates as

$$\vec{r} = r_x\hat{x} + r_y\hat{y} + r_z\hat{z} \tag{6.4}$$

The magnitude of this vector is

$$r = \sqrt{r_x^2 + r_y^2 + r_z^2} \tag{6.5}$$

Therefore $r \geq r_z$ since $r_x^2 \geq 0$ and $r_y^2 \geq 0$.

In section (4.2) it was shown that if the interaction potential V_{I} was greater than or equal to zero that the Schwinger potential always produces lower bounds to the the exact eigenenergies. Since $r \geq r_z$, it is easy to see that

$$V_{\mathrm{I}} = -\frac{Z}{r} + \frac{Z}{r_z} \geq 0 \tag{6.6}$$

Therefore, this interaction potential will also produce lower bounds to the eigenenergies when used with the Schwinger variational principle.

Although numerical calculation of the strong field case is beyond the scope of this work, the procedure for using this new interaction potential is similar to that of the weak field case. The "main" part of the potential is no longer the Coulomb potential. Therefore the Greens function is no longer the well known hydrogenic Greens function. In the high field case, the Hamiltonian without the interaction potential is written

$$\hat{h} = -\frac{1}{2}\nabla^2 + \frac{1}{2}\beta^2 r^2 \sin^2\theta - \frac{Z}{r_z} \tag{6.7}$$

In this case the Hamiltonian is separable and can be written in the form

$$\hat{h} = \hat{h}_\rho + \hat{h}_z. \tag{6.8}$$

The Greens functions corresponding to $\hat{h}_\rho$ and $\hat{h}_z$ are well known and correspond to the harmonic oscillator and one dimensional Coulomb Greens functions. The G_ρ corresponds to the Greens function for $\hat{h}_\rho$ and G_z corresponds to the Greens function for the Hamiltonian $\hat{h}_z$, then the total Greens function can be written in the form of a convolution integral

$$G = \int_c G_\rho(E-u)\, G_z(u)\, du \tag{6.9}$$

where c represents some contour. This new Greens function can be calculated in closed form. The Greens function operating on a function can be calculated numerically. It can be expanded in terms of hydrogenic Sturmian functions as it was in the weak field case. One consequence of the strong field separation of the potential is that all of the sums are unlikely to collapse to a finite number as they did in the weak field case. Therefore, further approximations must be made by truncating these sums.

6.2 Extension to the Continuum

One use for the strong field separation of the potential is for calculating phase shifts for continuum states. Although the solution proposed for weak fields is a complete solution to the problem, it has the disadvantage that the solutions are not asymptotically correct. In order to use this solution for the continuum, a very large number of terms would need to be included in the Fock expansion and extremely large matrices would need to be diagonalized. The strong field separation, however is asymptotically correct. Accurate, convergent methods for calculating lower bounds to the phase shifts in the continuum case have been proposed in the past[30]. The Schwinger variational principle allows convergent upper bounds to the phase shifts to be calculated also. In the continuum case, the Feynman theorem states that

$$\frac{\partial \delta}{\partial \lambda} = -\left\langle \psi\left(\lambda\right) \left| \frac{\partial V}{\partial \lambda} \right| \psi\left(\lambda\right) \right\rangle. \tag{6.10}$$

One significant difference between this expression and the one given for bound states is that the right hand side of the equation contains a negative sign. If this negative sign is propagated through the derivation it is seen that for phase shifts a positive interaction potential produces upper bounds. Therefore, by using previous methods to calculate lower bounds to the phase shifts and the Schwinger variational principle to calculate the upper bounds the phase shifts too can be bracketed from both above and below.

6.3 Hydrogenic Sturmian basis functions as trial functions

In all of the previous chapters the Fock expansion was used as a trial wavefunction. It was shown that the Fock expansion is able to produce solutions to the Schrödinger equation. These solutions can be used in both the Raleigh-Ritz and Schwinger variational principles to produce upper and lower bounds to the exact eigenenergies. The Fock expansion has the disadvantage that it is not written in a conventional orthonormal basis set. The hydrogenic Sturmian functions which were used as a basis to expand the Greens function in chapter four are closely related to the Fock expansion. Linear combinations of these hydrogenic Sturmian functions can also be used as trial solutions. Indeed the Fock expansion truncated at a power of r, say N, can be expressed exactly as a finite linear combination of Sturmian functions. It follows that the Raleigh-Ritz and Schwinger variational principle calculations using the Fock expansion are completely equivalent to using Sturmian basis functions in the same variational procedures. This is assuming that both expansions are truncated to the same power in r. For that reason, this section outlines how one would employ

Sturmian functions to bypass the Fock expansion, yet obtain equivalent results.

In equation (4.19) the hydrogenic Sturmian functions were shown to be of the form

$$S^{\varepsilon}_{nlm}\left(r,\theta,\phi,\varepsilon\right)=r^{l}e^{-\sqrt{-2\varepsilon}r}L^{2l+1}_{n-l-1}\left(2\sqrt{-2\varepsilon r}\right)Y_{lm}\left(\theta,\phi\right) \tag{6.11}$$

These Sturmian functions can be slightly redefined as

$$S^{\varepsilon}_{nlm}\left(r,\theta,\phi,\varepsilon\right)=(2\sqrt{-2\varepsilon r})^{l}e^{-\sqrt{-2\varepsilon}r}L^{2l+1}_{n-l-1}\left(2\sqrt{-2\varepsilon r}\right)Y_{lm}\left(\theta,\phi\right). \tag{6.12}$$

If the Sturmian functions are redefined as in equation (6.12), then the normalization factor $\beta^{\varepsilon}_{nlm}$ becomes

$$\beta^{\varepsilon}_{nlm}\equiv\left\langle S^{\varepsilon}_{nlm}\left|-\frac{Z}{r}\right|S^{\varepsilon}_{nlm}\right\rangle=-\frac{Z}{(2\sqrt{-2\varepsilon})^{2}}\frac{\Gamma(l+n+1)}{(n-l-1)!} \tag{6.13}$$

One benefit of using the Sturmian basis as defined in equation (6.12) instead of the Fock basis is that the Sturmian basis allows all of the matrix elements to be calculated independently of the physical parameters of the system (Z and β), and one variational parameter ε. Therefore, the matrix elements need only to be calculated once. The physical parameters are separated from the matrix elements and simply become multiplicative factors in front of the constant matrix elements. This was not the case for the Fock expansion. When the Fock expansion is used to calculate the matrices corresponding to the Raleigh-Ritz and Schwinger variational principles, the matrix must be recalculated and re-diagonalized for each value of the magnetic field B and for each value of the variational parameter ε.

If a Sturmian basis set is used instead of the Fock expansion basis set, the the condition for bound states in the Schwinger variational principle becomes

$$F(\varepsilon)=\det\left(\langle S^{\varepsilon}_{nlm}\left|V_{\mathrm{I}}-V_{\mathrm{I}}GV_{\mathrm{I}}\right|S^{\varepsilon}_{n'l'm'}\rangle\right)=0. \tag{6.14}$$

The Greens function is expanded in terms of the same Sturmian functions so that the determinant of

$$\langle S^{\varepsilon}_{nlm}\left|V_{\mathrm{I}}-V_{\mathrm{I}}GV_{\mathrm{I}}\right|S^{\varepsilon}_{n'l'm'}\rangle=\langle S^{\varepsilon}_{nlm}\left|V_{\mathrm{I}}\right|S^{\varepsilon}_{n'l'm'}\rangle-\frac{\left\langle S^{\varepsilon}_{nlm}\left|V_{\mathrm{I}}\right|S^{\varepsilon}_{qrs}\right\rangle\left\langle S^{\varepsilon}_{qrs}\left|V_{\mathrm{I}}\right|S^{\varepsilon}_{n'l'm'}\right\rangle}{\beta^{\varepsilon}_{qrs}\left(\lambda_{qrs}-1\right)} \tag{6.15}$$

must vanish. As one can see in equation (6.15), only one matrix needs to be calculated in this case. This matrix has elements

$$M^m_{nl,n'l'}\left(\beta,\varepsilon\right)\delta_{m,m'} = \langle S^\varepsilon_{nlm}\left|V_{\mathrm{I}}\right| S^\varepsilon_{n'l'm'}\rangle \tag{6.16}$$

where V_{I} is the quadratic magnetic potential

$$V_{\mathrm{I}} = \frac{\beta}{2}r^2\sin^2\theta \tag{6.17}$$

and we indicate by superscripts that M is diagonal in the magnetic quantum number m.

The matrix is

$$M^m_{nl,n'l'}\delta_{m,m'} = \frac{\beta^2}{2}\int_0^\infty\int_0^{2\pi}\int_0^\pi\left(2\sqrt{-2\varepsilon}\right)^l e^{-\sqrt{-2\varepsilon}r}L^{2l+1}_{n-l-1}\left(2\sqrt{-2\varepsilon}r\right)r^2\sin^2\theta$$

$$\left(2\sqrt{-2\varepsilon}r\right)^{l'}e^{-\sqrt{-2\varepsilon}r}L^{2l'+1}_{n'-l'-1}\left(2\sqrt{-2\varepsilon}r\right)Y_{lm}(\theta,\phi)Y_{l'm'}(\theta,\phi)r^2\sin\theta drd\theta d\phi \tag{6.18}$$

If the substitution $u = 2\sqrt{-2\varepsilon}r$ is made, then $du = 2\sqrt{-2\varepsilon}dr$ and $r = \frac{u}{2\sqrt{-2\varepsilon}}$, and the matrix element becomes

$$M^m_{nl,n'l'}\left(\beta,\varepsilon\right) = \frac{\beta^2}{2}\frac{1}{\left(2\sqrt{-2\varepsilon}\right)^5}\int_0^\infty\int_0^{2\pi}\int_0^\pi u^{l-l'}e^{-u}$$

$$L^{2l+1}_{n-l-1}\left(u\right)L^{2l'+1}_{n'-l'-1}\left(u\right)Y_{lm}(\theta,\phi)Y_{l'm}(\theta,\phi)\sin^2\theta\sin\theta dud\theta d\phi. \tag{6.19}$$

One can see that the triple integral in equation (6.19) is independent of β, ε and Z. Indeed it is just a pure number which is denoted by $\mathcal{M}$. Then equation (6.19) becomes,

$$M^m_{nl,n'l'}\left(\beta,\varepsilon\right) = \frac{\beta^2}{2\left(2\sqrt{-2\varepsilon}\right)^5}\mathcal{M}^m_{nl,n'l'} \tag{6.20}$$

One can see from equation (6.20) that the physical parameters β and ε are separated from the rest of the matrix. Thus $\mathcal{M}^m_{nl,n'l'}$ is a matrix of pure numbers which only have to be calculated once. For practical calculations this matrix can be evaluated as the first step of a computer program. The physical parameters of the system are then simply multiplicative factors which are simple powers of β and

$2\sqrt{-2\varepsilon}$. Multiplying these factors by combinations of this simple matrix together with the closed form expression for β_{nlm} in equation (6.13) and λ given in equation (4.2) creates a new matrix which is diagonalized to obtain the eigenvalues used for the Schwinger variational principle.

The Sturmian basis functions can also be used to separate the physical parameters from the matrix used for the Raleigh-Ritz method. In this case the matrix

$$\left\langle S^{\varepsilon}_{nlm} \middle| \hat{H} - \varepsilon \middle| S^{\varepsilon}_{n'l'm'} \right\rangle + \varepsilon \left\langle S^{\varepsilon}_{nlm} \mid S^{\varepsilon}_{n'l'm'} \right\rangle \tag{6.21}$$

must be diagonalized. In the above equation

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{\beta^2}{2} r^2 \sin^2\theta \tag{6.22}$$

It is recognized from the definition of the Sturmian function in equation (4.18) that

$$\left(-\frac{1}{2}\nabla^2 - \lambda_{nlm}\frac{1}{r} - \varepsilon\right) \left|S^{\varepsilon}_{nlm}\right\rangle = 0 \tag{6.23}$$

Therefore

$$\left(-\frac{1}{2}\nabla^2 - \varepsilon\right) \left|S^{\varepsilon}_{nlm}\right\rangle = \lambda_{nlm}\frac{1}{r} \left|S^{\varepsilon}_{nlm}\right\rangle \tag{6.24}$$

If equation (6.24) is substituted into the Raleigh-Ritz matrix, the Raleigh-Ritz matrix then becomes

$$R^{m}_{nl,n'l'}(\beta,\varepsilon) = \left\langle S^{\varepsilon}_{nlm} \middle| \lambda_{nlm}\frac{1}{r} - \frac{Z}{r} + \frac{\beta^2}{2}\sin^2\theta \middle| S_{n'l'm} \right\rangle - \varepsilon \left\langle S^{\varepsilon}_{nlm} \mid S^{\varepsilon}_{n'l'm} \right\rangle \tag{6.25}$$

The quadratic magnetic term was already calculated before in the discussion of the Schwinger variational principle and is seen in equation (6.20). This leaves two other matrices to be calculated. The matrices with a factor of $\left\langle S^{\varepsilon}_{nlm} \middle| \frac{1}{r} \middle| S_{n'l'm'} \right\rangle$ are equivalent to the normalization factor found in equation (6.13). This leaves the overlap integral found in the last term on the right hand side of equation (6.25).

This overlap integral is

$$O^{lm}_{n,n'}(\varepsilon) = \langle S^{\varepsilon}_{nlm} \mid S^{\varepsilon}_{n'l'm'}\rangle \, \delta_{l,l'}\delta_{m,m'} = \int_0^\infty \int_0^{2\pi} \int_0^{\pi} \left(2\sqrt{-2\varepsilon}\right)^l e^{-\sqrt{-2\varepsilon r}}$$

$$L^{2l+1}_{n-l-1}\left(2\sqrt{-2\varepsilon r}\right) \left(2\sqrt{-2\varepsilon r}\right)^{l'} e^{-\sqrt{-2\varepsilon r}} L^{2l'+1}_{n'-l'-1}\left(2\sqrt{-2\varepsilon r}\right) \tag{6.26}$$

$$Y_{lm}(\theta,\phi)\, Y_{l'm'}(\theta,\phi)\, r^2 \sin\theta dr d\theta d\phi$$

Once again, by making the substitution $u = 2\sqrt{-2\varepsilon r}$ the variational parameter ε can be removed from the integral. After integrating the angular terms this substitution yields

$$O^{lm}_{n,n'}(\varepsilon) = \frac{1}{(2\sqrt{-2\varepsilon})^3} \int_0^\infty u^{2l} e^{-u} L^{2l+1}_{n-l-1}(u)\, L^{2l+1}_{n'-l-1}(u)\, du \tag{6.27}$$

Therefore, the matrix above can be written as

$$O^{lm}_{n,n'}(\varepsilon) = \frac{1}{(2\sqrt{-2\varepsilon})^3} \mathcal{O}^{lm}_{n,n'}, \tag{6.28}$$

where $\mathcal{O}$ is a pure numerical matrix which is independent of any physical parameters. Once again, the matrices $\mathcal{M}$, β_{nlm} and $\mathcal{O}$ need to be calculated only once. The physical parameters are simple multiplicative factors. Therefore, the Raleigh-Ritz matrix can also be calculated quite efficiently if the Sturmian basis is used.

The ability to use the hydrogenic Sturmian expansion to remove all physical parameters from the matrix elements of $\mathcal{M}$, β_{nlm} and $\mathcal{O}$ leads to a method for improving the efficiency of the Raleigh-Ritz and Schwinger variational calculations. The only parameter on which these matrices are dependent is the size of the matrix (the number of Sturmians used). Because these matrices need only to be calculated once, Therefore, with only a little time investment these matrices can be found exactly with the integer arithmetic routines in a package such as $Mathematica^{TM}$. They can then be stored in a file and used any time they are needed. If the Fock expansion was employed these matrices would need to be calculated each time they are used. This is quite slow with integer arithmetic and would become very cumbersome if more than a few terms in the expansion were used.

Another very important advantage of using Sturmian basis functions is that unlike the case of the Fock expansion, there are no remainder terms. Each Sturmian function is used individually and no recurrence relation is solved. Therefore, one would expect that the convergence properties of these calculations will be much better behaved when performed on a Sturmian basis. This and the separability of physical parameters makes the Sturmian basis more desirable than the Fock basis for practical calculations.

6.4 The Fano-Bohn R-matrix method

At this time the best calculations of the bound states of hydrogen in a constant magnetic field are those of Kravchenko et al.[15]. They have the advantages of being extremely accurate even for excited states. They do not give bounds to the energies. Because the error is unknown they do not obtain exact solutions in the strict mathematical sense. Out calculations of upper and lower bounds confirm that the results of Kravchenko et al. are extremely accurate, however.

The method used by Kravchenko et al. writes the wavefunction in terms of the Fock expansion as is done in this dissertation. Instead of using variational methods, the boundary condition

$$\frac{g'(R)}{g(R)} = -\kappa \tag{6.29}$$

is solved using a rather complicated iterative method. In equation (6.29), $g(R)$ is a modified form of the wavefunction and $\kappa = -\sqrt{2E_b}$.

This method is effectively the same as the Fano-Bohn R-matrix[6, 7] which solves the boundary conditions

$$\frac{f(R)}{f'(R)} = \tan\phi \tag{6.30}$$

by diagonalizing the R matrix. The Fano-Bohn R-matrix is a modified version of the standard R-matrix method. In the conventional R-matrix method the R-matrix is constructed the solutions are matched at a fixed, finite radius R to asymptotic solutions. The Fano-Bohn R-matrix method attempts to use the R-matrix without knowing the asymptotic form of the solutions. The R-matrix is constructed at a variable radius. The behavior of the R-matrix solutions as a function of radius then indicates the existence of bound states. The method of Kravchenko et al. effectively diagonalizes the R-matrix proposed by Fano and Bohn.

The Fano-Bohn R-matrix is not well known, and has only been used explicitly to calculate the bound states of helium[7]. This calculation was able to qualitatively describe the bound states of helium, but it was not quantitatively very accurate. This is because the wavefunctions used were not very accurate and because only a small number of elements in the R-matrix were diagonalized. In order to obtain accurate results many elements must be taken into account. This was effectively done in reference [15].

I have examined the R-matrix method using the Fock expansion and have applied it to the ground state of hydrogen in a constant magnetic field of $\beta = 0.05$. In order to implement the Fano-Bohn R-matrix method, first the Fock expansion solutions to the Schrödinger equation were constructed. These were calculated in exactly the same way as was done for the Raleigh-Ritz and Schwinger variational principle calculations. These solutions were then projected onto the spherical harmonic functions $Y_{lm}(\theta, \phi)$. This yields,

$$\psi_{\nu,l}(r) = \langle \psi_\nu(r, \theta, \phi) \mid Y_{lm}(\theta, \phi) \rangle . \tag{6.31}$$

In equation (6.31), ψ_ν are the Fock expansion solutions. The same is done for the derivatives of the Fock expansion solutions with respect to r. The derivative matrix is

$$\psi'_{\nu,l} = \langle \psi'_\nu(r, \theta, \phi) \mid Y_{lm}(\theta, \phi) \rangle \tag{6.32}$$

where the prime indicates a derivative with respect to r. The inverse of $\psi_{\nu,l}(r)$ is calculated using the `LAPACK` inverse routines `dgetrf()` and `dgetri()`. This inverse is indicated by $\psi^{-1}_{l,\nu}(r)$. The Fano-Bohn R-matrix is then formed by matrix multiplication so that

$$R_{\nu,\nu'}(r) = \sum \left[\psi'_{\nu,l}(r)\right]^{-1} \psi'_{l,\nu'}(r) \tag{6.33}$$

Equation (6.33) defines the Fano-Bohn R-matrix. This matrix is diagonalized. In the Fano-Bohn R-matrix theory, the eigenvalues of this matrix behave as $\tan\phi$, where ϕ is a phase. If the phase goes through a factor of π, this indicates a bound state.

For practical calculations, if an eigenvalue's phase goes through a factor of π, a large negative number is produced near this discontinuity. Therefore, the lowest eigenvalue of the diagonalized R-matrix is examined. These discontinuities are readily seen in this eigenvalue. In figure (6.1) the lowest eigenvalue of $R_{\nu,\nu'}(r)$ is plotted.

Here eight terms were taken in the Fock expansion. In Bohn's notation, this should have the form of a tangent of some phase ϕ. For a bound state, the phase ϕ should go through a factor of π at some radius R[7]. In Figure (6.1) we can see this behavior for an energy of $\varepsilon = -0.497524$ au. This behavior vanishes for $\varepsilon = -0.497525$ au. Therefore, according to the R-matrix method there should be a bound state between these two values. Previous calculations have shown that the bound state lies at approximately $\varepsilon = -0.497526$ au which is lower than predicted by the R-matrix method. Therefore we can conclude that the R-matrix method in the form used in this calculation is the least accurate of the methods tried.

Kravchenko et al. have been able to effectively use the R-matrix method to achieve very accurate results. Their success was achieved by using rather advanced numerical methods. First, the R-matrix was not diagonalized directly, instead an iterative method was used. Although the iterative method is conceptually cumbersome, it is much more effective for performing R-matrix calculations with large numbers of terms. The direct method, on the other hand, must diagonalize a non-sparse matrix. This becomes computationally intensive as the dimensions of the matrix increase.

The other numerical innovation used by Kravchenko et al. is to use extended precision mathematical libraries. The iterative method for diagonalizing the R-matrix produces large numbers of canceling terms. Furthermore, because these terms have magnitudes of the order of R^n, these terms can become quite large. Therefore it is easy to lose all numerical accuracy. The numerical libraries developed by Kravchenko et al. are able keep hundreds of digits and can therefore overcome this numerical difficulty. This is probably a key step in employing the Fano-Bohn method generally. That is, for negative energies the solutions grow exponentially. This growth is reflected in the R-matrix and extensive cancellations are always required to obtain physical bound states. A similar cancellation of terms occurs in calculations involving the Fock expansion. Although all integrals are evaluated in closed form so that the large

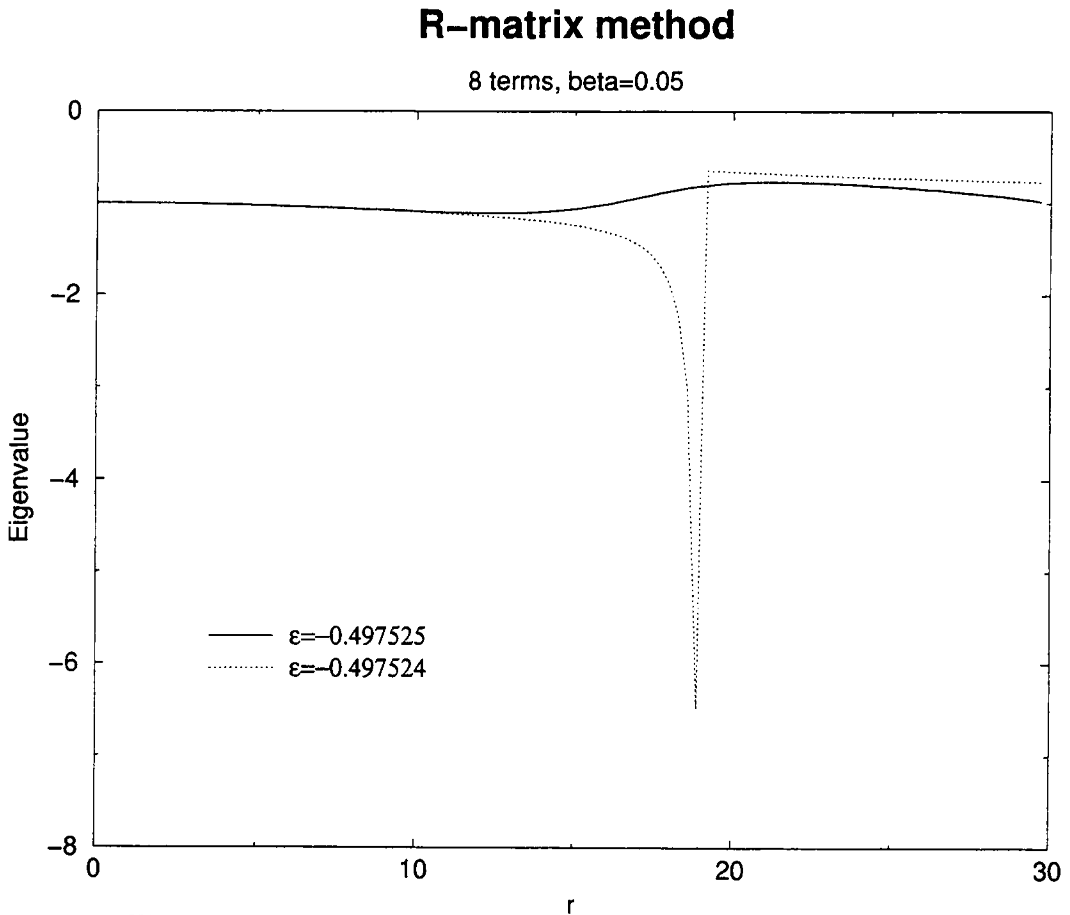

Figure 6.1: The behavior of the eigenvalues of the Fano-Bohn R-matrix are plotted with two different values of the parameter ε. One can see that the behavior of the eigenvalues change as ε crosses an eigenenergy.

powers in r are eliminated, these integrals invariably lead to sums containing gamma functions. These sums produce both large positive and large negative terms. The terms must cancel to become either a small negative number in the case of the Raleigh-Ritz variational principle, or become zero in the case of the Schwinger variational principle. For this reason, more advanced calculations using these variational principles with the Fock expansion should contain extended precision mathematical libraries similar to those of Kravchenko et al. Such libraries would enable these calculations to be pushed to much larger magnetic fields.

CHAPTER 7

Conclusions

In this thesis we have examined the variational aspects of the Fock expansion when applied to the system of a hydrogenic atom in a constant magnetic field. To do this a trial solution in the form of the Fock expansion was substituted into the Schrödinger equation and a three term recurrence relation was found which yields the coefficients of each Fock expansion term. In this way we showed that the Fock expansion can solve the Schrödinger equation. These coefficients can easily be found algorithmically on a computer. The physical problem, however, requires linear combinations of these Fock terms which satisfy the physical boundary conditions. Variational methods are used to satisfy these boundary conditions, and at the same time find bounds to the eigenenergies.

The Raleigh-Ritz variational principle is the most well-known of all variational methods, and it always produces upper bounds to the exact bound state eigenenergies. It was found that for the ground state and small magnetic fields that the Raleigh-Ritz principle can find linear combinations of the Fock functions which satisfy the boundary conditions even when the Fock solutions are truncated to a particular power of r. For larger fields, however, the Fock expansion can not be truncated because such a truncation scheme couples the number of Fock functions which are used with the order of the Fock functions. This does not produce accurate results because when the recurrence relation was solved to find solutions to the Schrödinger equation in terms of the Fock expansion, the solutions were found for an infinite order expansion. For practical calculations, the Fock expansion must be truncated at some order. Doing this leaves remainder terms which tend to become large as the order of the Fock expansion increases.

For these larger fields it was found that the results become worse as the order of the Fock expansion was increased because of the large contribution of the remainder terms. The results converge monotonically as the number of Fock functions is increased, however. This leads to a method of finding convergent upper bounds to the eigenenergies of the system even for large fields. As long as the number of Fock functions is increased, the energies become better, and therefore in principle upper bounds that are ΔE higher than the exact energy can be found to any desired tolerance.

For excited states, the Raleigh-Ritz principle does not work without modification. Although the Raleigh-Ritz principle produces upper bounds to the ground and excited states, the energies for the excited states are not very accurate. This is because the trial wavefunctions involve the variational parameter ε and are minimized on this parameter. The optimum value of ε is not the same for the ground state and each of the excited states, however. Therefore these states will not be orthogonal to each other, which is a requirement for the physical system. This problem can be rectified by a re-orhtogonalization routine. In this routine, first the optimal ground state is calculated. In the process of doing this a set of eigenvectors are produced. The eigenvector which corresponds to the ground state is removed from the manifold of eigenvectors and the remaining eigenvectors become a new basis in which the excited states are calculated. Any excited states calculated in this basis are automatically orthogonal to the ground state. This routine can be repeated for more highly excited states. Therefore, in principle convergent upper bounds to the excited states can be calculated.

The Schwinger variational principle was shown to be applicable to bound states, and it was shown that for the hydrogen atom in a constant magnetic field, the Schwinger principle produces lower bounds to the exact eigenenergies. Once again, for the case of the ground state and a small magnetic field, the Schwinger variational principle was able to produce linear combinations of the Fock solutions which approximately solve the Schrödinger equation and lower bounds to the exact eigenenergies were produced. In this case, even when the order and number of the Fock functions were coupled, the energies converged to machine precision.

When this result was combined with that of the Raleigh-Ritz principle, the exact energy was squeezed both from above and below. Therefore, this is an exact solution to the problem in the sense that convergent, "bounded" energies were found. This is the first time that such a calculation has been made for this system. Although there have recently been calculations which find the energies for hydrogen in a constant magnetic field to any desired precision, there is not guarantee that the results are above or below the exact energy.

For larger fields, it was once again shown that a truncation scheme in which the order and number of Fock terms are coupled does not produce convergent results. Just as in the Raleigh-Ritz case, the remainder terms from solving the recurrence relation for the Fock expansion cause the results to become worse as the order of the Fock expansion is increased. The results converge monotonically as the number of Fock functions is increased, however. This allows convergent lower bounds to the exact energies to be calculated from hydrogen in any magnetic field, although an efficient way of doing this has not been discovered.

One problem with using the Fock expansion is that remainder terms exist when solving the Schrödinger equation with a recurrence relation. We propose that this limitation can be removed by using a Sturmian basis rather than a Fock expansion basis. The Sturmian basis can represent all of the functions of the Fock expansion. In the case of Sturmian functions, a recurrence relation is not solved and there are no remainder terms. The Sturmian basis also has the advantage that all of the physical parameters, such as charge and external field can be removed from the calculation for both the Raleigh-Ritz and Schwinger variational principles. This allows one to calculate several matrices of pure numbers at the beginning of the calculation. The physical parameters can be added later, and most of the calculation is performed only once.

Finally, the Fock expansion was investigated in Fano-Bohn R-matrix theory. It was shown that this theory can produce approximate energies to the hydrogen atom in a constant magnetic field very quickly. It was shown that this is equivalent to the method used by Kravchenko et. al[15]. At this time, this method is probably the fastest and most accurate way to find energies for a very wide range of applied magnetic fields. It has the disadvantage that special numerical techniques are required such as arbitrary precision mathematical libraries. The method has already been used to produce very accurate results, however.

The work in this thesis has concentrated on "proof of principle" rather than extensive calculations for the purpose of data compilation. The lower bounds method is essentially new, but when taken with the standard upper bound calculations gives an essentially "exact" solution for the non-relativistic magnetic field problem. Future work would concentrate on developing efficient computer programs to implement the methods developed in this work. A number of improvements have been indicated here which would be implemented.

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APPENDICES

Appendix A

Wigner 3-j Symbols

$$\begin{pmatrix} 2 & l & l-2 \\ 0 & 0 & 0 \end{pmatrix} = \frac{(-1)^l \sqrt{3l}\,(l-1)}{\sqrt{(2l-3)\,(2l-2)\,(2l-1)\,(2l+1)}} \tag{A.1}$$

$$\begin{pmatrix} 2 & l & l \\ 0 & 0 & 0 \end{pmatrix} = \frac{(-1)^l \sqrt{2l}\,(l+1)}{\sqrt{(2l-1)\,(2l+1)\,(2l+2)\,(2l+3)}} \tag{A.2}$$

$$\begin{pmatrix} 2 & l & l+2 \\ 0 & 0 & 0 \end{pmatrix} = \frac{(-1)^l \sqrt{6}\,(l+1)\,(l+2)}{\sqrt{(2l+1)\,(2l+2)\,(2l+3)\,(2l+4)\,(2l+5)}} \tag{A.3}$$

$$\begin{pmatrix} 2 & l & l \\ 0 & -m & m \end{pmatrix} = \frac{(-1)^{l+m} \sqrt{2}\,(l^2-3m^2+1)}{\sqrt{(2l-1)\,(2l+1)\,(2l+2)\,(2l+3)}} \tag{A.4}$$

$$\begin{pmatrix} 2 & l & l-2 \\ 0 & -m & m \end{pmatrix} = \frac{(-1)^{l+m} \sqrt{3\,(l-m-1)\,(l+m)\,(l+m-1)\,(l+m)}}{\sqrt{(2l-3)\,(2l-2)\,(2l-1)\,(2l+1)}} \tag{A.5}$$

$$\begin{pmatrix} 2 & l & l+2 \\ 0 & -m & m \end{pmatrix} = \frac{(-1)^{l+m} \sqrt{6\,(l-m+1)\,(l-m+2)\,(l+m+1)\,(l+m+2)}}{\sqrt{(2l+1)\,(2l+2)\,(2l+3)\,(2l+4)\,(2l+5)}} \tag{A.6}$$

Appendix B

Proof of the Feynman Theorem

The Feynman theorem[29] states that

$$\frac{\partial E}{\partial \lambda} = \int \psi^* \frac{\partial U}{\partial \lambda} \psi d\lambda \tag{B.1}$$

The average energy is defined quantum mechanically as

$$E = \int \psi^* (\lambda) \, H (\lambda) \, \psi (\lambda) \, d\lambda \tag{B.2}$$

Taking the partial derivative with respect to λ on both sides yields

$$\frac{\partial E}{\partial \lambda} = \int \frac{\partial \psi^*(\lambda)}{\partial \lambda} H(\lambda)\psi(\lambda)d\lambda + \int \psi^*(\lambda)\frac{\partial H(\lambda)}{\partial \lambda}\psi(\lambda)d\lambda + \int \psi^*(\lambda)H(\lambda)\frac{\partial \psi(\lambda)}{\partial \lambda}d\lambda \tag{B.3}$$

H is a Hermitian operator, however. Therefore it can operate to both the left and the right, and it can operate on both ψ and ψ^*. Since $H\psi = E\psi$, equation (B.3) becomes

$$\frac{\partial E}{\partial \lambda} = E\int \frac{\partial \psi^*(\lambda)}{\partial \lambda}\psi(\lambda)d\lambda + \int \psi^*(\lambda)\frac{\partial H(\lambda)}{\partial \lambda}\psi(\lambda)d\lambda + E\int \psi^*(\lambda)\frac{\partial \psi(\lambda)}{\partial \lambda}d\lambda \tag{B.4}$$

It is recognized, however, that

$$\int \frac{\partial \psi^*}{\partial \lambda}\psi d\lambda + \int \psi^* \frac{\partial \psi}{\partial \lambda} d\lambda = \frac{\partial}{\partial \lambda}\int \psi^* \psi d\lambda = 0 \tag{B.5}$$

Therefore,

$$\frac{\partial E}{\partial \lambda} = \int \psi^*(\lambda)\frac{\partial H(\lambda)}{\partial \lambda}\psi(\lambda)d\lambda \tag{B.6}$$

The Hamiltonian is $H(\lambda) = T_l + U(\lambda)$. The kinetic terms is not a function of λ. Therefore,

$$\frac{\partial H(\lambda)}{\partial \lambda} = \frac{\partial U(\lambda)}{\partial \lambda} \tag{B.7}$$

Therefore, it is proven that

$$\frac{\partial E}{\partial \lambda} = \int \psi^*(\lambda)\frac{\partial U(\lambda)}{\partial \lambda}\psi(\lambda)d\lambda \tag{B.8}$$

Appendix C

Proof of the Schwartz Inequality

Let a vector be defined as $\vec{v} = \vec{A} + \lambda\vec{B}$ where λ is an arbitrary scalar. We can therefore write

$$v^2 = \vec{v}^*\vec{v} = \left(\vec{A}^* + \lambda^*\vec{B}^*\right)\left(\vec{A} + \lambda\vec{B}\right) \geq 0 \tag{C.1}$$

Because λ is an arbitrary constant we can define it as

$$\lambda \equiv \frac{-\vec{B}^* \cdot \vec{A}}{B^2}. \tag{C.2}$$

Therefore

$$\left(\vec{A}^* - \frac{\vec{B} \cdot \vec{A}^*}{B^2}\vec{B}^*\right)\left(\vec{A} - \frac{\vec{B}^* \cdot \vec{A}}{B^2}\vec{B}\right) \geq 0. \tag{C.3}$$

Expanding this yields

$$\left(A^2 - \frac{\vec{B}^* \cdot \vec{A}}{B^2}\vec{A}^* \cdot \vec{B} - \frac{\vec{B} \cdot \vec{A}^*}{B^2}\vec{B}^* \cdot \vec{A} + \frac{\left(\vec{B} \cdot \vec{A}^*\right)\left(\vec{B}^* \cdot \vec{A}\right)}{B^2}\right) \geq 0. \tag{C.4}$$

Multiplying both sides by B^2 yields the Schwartz inequality

$$A^2B^2 - \left(\vec{B}^* \cdot \vec{A}\right)^2 \geq 0. \tag{C.5}$$

This can be written in Hilbert space as

$$\langle A|A\rangle \langle B|B\rangle - |\langle A|B\rangle|^2 \geq 0. \tag{C.6}$$

Let us define $|A\rangle = \sqrt{V_I}\,|\phi_t\rangle$ and $|B\rangle = \sqrt{V_I}\,|\psi\rangle$. Then,

$$\langle\phi_t||V_I||\phi_t\rangle \langle\psi||V_I||\psi\rangle - \langle\psi||V_I||\phi_t\rangle \langle\phi_t||V_I||\phi\rangle \geq 0. \tag{C.7}$$

In our case, V_I has definite sign. Therefore,

$$\langle\phi_t|V_I|\phi_t\rangle \langle\psi|V_I|\psi\rangle - \langle\psi|V_I|\phi_t\rangle \langle\phi_t|V_I|\phi\rangle \geq 0. \tag{C.8}$$

Vita

James Sternberg was born in St. Petersburg, Florida on May 10, 1969. He graduated from Notre Dame High School in Chattanooga, Tennessee in 1987 and received a Bachelors of Science degree in Physics from Valparaiso University in the spring of 1992. He has published on the topic of generalized Ramsaur-Townsend minima. In the summer of 1997 he received a Mombusho fellowship to study in Japan. James Sternberg earned his Doctor of Philosophy degree in physics in December, 1999.