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Excitation and Ionization of $^6\text{Li}$ ions Following $\beta^-$ decay of $^6\text{He}$

by

Eva E. Schulhoff

A Thesis
Submitted to the Faculty of Graduate Studies and Research through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Masters of Science at the University of Windsor

Windsor, Ontario, Canada
2010
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Abstract

The ability of $^6$He to undergo $\beta^-$ decay into $^6$Li$^+$ ($^6$He$\rightarrow^6$Li$^+$ + $\beta^-$ + $\bar{\nu}_e$) makes it an interesting isotope. Due to the sudden increase in nuclear charge, this decay causes an electronic rearrangement of the final $^6$Li$^+$ atom. The method of calculation involves expanding the initial state of $^6$He in terms of a complete set of final states of $^6$Li$^+$. Correlated Hylleraas-like wave functions were used to create a pseudospectrum, (44 - 441 states), which span both the bound and continuum states of $^6$Li$^+$. The sudden approximation with neglected recoil ($p \rightarrow 0$) was used. Starting from both the 1 $^1S_1$ and 2 $^3S_1$ initial configurations of $^6$He, the excitation probabilities to the final $^6$Li$^+$ bound states, as well as the total probabilities of single and double ionization were calculated. The transition probabilities to bound states were compared with those of Wauters and Vaeck for the singlet configuration [1]. The dependence of energy and probability on the nonlinear variational parameter $\beta_1$ was also examined, and found that both show “special” behaviour near $\beta_1 \approx 1/n_2$. Finally, the total probabilities of ionization were compared with other theoretical and experimental values [1, 2, 3].
For my dad, Gabriel Schulhoff, a true physicist at heart!
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Chapter 1

Introduction

One of the greatest achievements of the twentieth century is the understanding of matter at an atomic level. From the beginning, scientists such as Schrödinger, Heisenberg, and Bohr developed mathematical descriptions of the quantum world. These mathematical techniques were successful in solving simple systems. After extensive studies on hydrogen, researchers turned their interests to the second lightest element in the universe, helium.

1.1 PARA AND ORTHO HELIUM

Before any mathematical explanations were given, it was already known that helium exhibited some strange properties. Through spectroscopy, researchers found that there were two characteristic spectral lines associated with this element, green and yellow. Electrons have an intrinsic spin of $\frac{1}{2}$, therefore, the two electrons of helium can either be parallel ($S = 1$) or anti-parallel ($S = 0$). When the two electrons have the same spin, the atom is in a triplet state and is known as orthohelium. When the two electrons have opposite spins, the atom is in a singlet state and referred to as parahelium. It is interesting to note that the orthohelium states are lower in energy (See Appendix 6.1). $^{6}$He can be in either state, and still undergo $\beta^{-}$- decay. The results from this
research deal with helium in both a triplet or singlet initial state.

1.2 ISOTOPES

There are eight known and studied isotopes of helium. The most common isotope here on Earth is $^4\text{He}$, and consists of a nucleus, made of two protons and two neutrons, and two orbiting electrons. Out of the remaining seven, only $^3\text{He}$ is stable. The instability of the other isotopes, $^5\text{He}$, $^6\text{He}$, $^7\text{He}$ and $^8\text{He}$, is not dependent on the size of the nucleus. For example, $^5\text{He}$ has a shorter half-life than $^6\text{He}$ [5]. Helium-6 and helium-8 contain what are known as halo nuclei. $^6\text{He}$ has the most rudimentary halo nucleus, where two loosely bound neutrons orbit around the compact alpha core particle, as seen in Figure (1.1). In 2004, researchers at Argonne National Laboratories, in collaboration with our group at the University of Windsor, found that these two extra neutrons are actually located asymmetrically on one side of the nucleus. Recently, however, the same researchers found that the four extra neutrons of $^8\text{He}$ arrange themselves less asymmetrically than those of $^6\text{He}$, causing the nucleus of $^8\text{He}$ to behave differently [4].

![Figure 1.1: Diagrammatic representations of the nuclei of (a) $^4\text{He}$, (b) $^6\text{He}$, and (c) $^8\text{He}$ [4].](image)

1.3 BETA-DECAY

Beta particles are electrons or positrons which are released during the radioactive decay of the nucleus of an atom. There are two types of beta-decay. Beta minus
decay, \((\beta^-)\), is when a neutron emits an electron.

\[ n \rightarrow p + e^- + \bar{\nu}_e \quad (1.1) \]

In beta plus decomposition, \((\beta^+)\), a positron and neutrino is emitted converting a proton into a neutron, with the aid of some external energy:

\[ \text{Energy} + p \rightarrow n + e^+ + \nu_e \quad (1.2) \]

The emitted electron in Equation (1.1) and positron in Equation (1.2) has a continuous energy spectrum. When either form of beta-decay occurs, it causes one chemical element to be converted into another, as a product of a sudden change in nuclear charge [6].

The halo nucleus of \(^6\text{He}\) is not stable and decays with a half-life of 0.8 seconds [7]. During this \(\beta^-\) decay of the parent \(^6\text{He}\) atom, the weak interaction converts a neutron into a proton while emitting an electron and an electron antineutrino. This leaves behind a lithium-6 daughter ion.

\[ ^6\text{He} \rightarrow ^6\text{Li}^+ + \beta^- + \bar{\nu}_e \quad (1.3) \]

### 1.4 SUDDEN APPROXIMATION

In 1926, Schrödinger discovered the solution to the wave equation which contains all the physical information about a system. The Hamiltonian of the time dependent Schrödinger equation consists of two parts, a kinetic term and a potential term. It describes how the wave function describing the quantum state of a physical system changes in time.

\[
i\hbar \frac{\partial}{\partial t} \Psi(r, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r, t) + V(r)\Psi(r, t) \quad (1.4)\]

The time dependence adds a dimension which makes the equation more difficult to solve. Although the transformation of the nucleus from \(^6\text{He}\) to \(^6\text{Li}^+\) is gradual over a short time scale, the calculations are simplified by the use of the sudden approximation.

A common problem in quantum mechanics is trying to determine the change in the state of a system after making small modifications to its Hamiltonian. Sometimes
perturbations on a system can be characterized as either a diabatic or adiabatic process. This classification depends critically on \( t \), the time during which the modification to the Hamiltonian takes place. According to the Adiabatic Theorem (Max Born and Vladimir Fock, 1928), if a disturbance acting on a Hamiltonian is gradual enough, the system will adapt its configuration accordingly [8]. This means for a truly adiabatic process, the initial state transforms continuously into a unique, corresponding final state. In contrast, in a diabatic process, the conditions change so rapidly that the electron distribution does not have time to adjust. The eigenstate of the initial system (i.e. He) relaxes into a linear combination of all possible eigenstates of the final system (i.e. Li\(^+\)) [9]. As a result, the state probability density transforms from a Dirac delta function to a distribution over all eigenstates.

In order to use the sudden approximation for a diabatic process, the ratio of \( t \), \((t = t_1 - t_0)\), to the characteristic time it takes the system to change from one state to the other is used as a criterion of validity. This criterion can be expressed as the inequality

\[
t \ll \frac{\hbar}{\Delta \bar{H}}
\]

where \( \Delta \bar{H} \) is the root mean square deviation of the system Hamiltonian (See Appendix 6.2 for derivation details). Note that Equation (1.5) is nearly the opposite of the Heisenberg, time-energy, uncertainty relation, \( \Delta t \gg \frac{\hbar}{\Delta E} \). Since the decay of \(^6\)He has an energy of 3.508 MeV, the velocity of the \( \beta^- \) particle emitted from the nucleus is quasirelativistic, and the time scale for emission is much shorter than that of the electronic redistribution of the orbiting electrons [1, 3]. Comparing this energy to the energies of the orbital electrons, which are of the eV order of magnitude, the ratio of the velocities is \( \left(\frac{v_{e^-}}{v_{\beta^-}}\right) \propto (1/10^3) \). This means that the time spent by the emitted particle traveling across the electron shells is much shorter than the electron orbital period. This justifies the use of the sudden approximation, and the assumption that the beta-decay happens instantaneously in time. In reality, the nuclear potential changes gradually over time. With the use of the sudden approximation, the assumption is made that the potential changes instantly from \( Z = 2 \) to \( Z = 3 \). This is illustrated in Figure (1.2). Finally, it is also assumed that the ejected particle does not directly
interact with the orbital electrons [10, 3].

Figure 1.2: Graphical representation of the change in nuclear potential (a) without sudden approximation and (b) with sudden approximation.

1.5 SHAKE UP - SHAKE OFF

There has been a wide range of experimental and theoretical research done on the outcome of beta-decay. Beta-decay is often accompanied by excitations of the orbital electrons into higher lying energy states (shake up), or ionization into continuum states (shake off). Subsequent to single $\beta^-$ decay, the nucleus is left with an extra positive charge, transmuting the atom into the next chemical element. As a result, atomic electrons can be excited or lost through two mechanisms. In the case of $^6$He, the first mechanism is due to the sudden change in nuclear charge, from $Z = 2$ to $Z = 3$, and is the dominant effect of “Coulombic shaking”. Since the $\beta^-$ particle is ejected from the atom so quickly, the electrons do not have enough time to adjust adiabatically to their new surroundings. They suddenly find themselves in a $^6$Li$^+$ like environment. This change in nuclear charge causes an instantaneous transfer of energy to the resulting system, exciting or ionizing the electrons [3]. The second mechanism is a result of the sudden gain of momentum of the nucleus due to the recoil from the emitted particles. The momentum carried away by the ejected $\beta^-$ particle is counterbalanced by the recoil momentum of the nucleus. This is known as “recoil ionization”, and is considered to be a secondary effect [11, 6]. Due to the the simplicity of having only two electrons,
and easy accessibility to accurate wave functions, helium is often used for beta-decay research [12].

1.6 ANALYTICAL TREATMENT

In calculations of atomic excitation and ionization processes, it has always been difficult to include all the bound states, but even more difficult to account for the infinite number of continuum states. Since the nuclear transmutation is accompanied by a redistribution of the atomic electrons, any calculations involving the daughter atom require a complete description of both the bound and continuum spectra.

For any time-independent problem, the solution can be expanded in terms of the complete set of solutions to the time-independent Schrödinger equation.

$$E\psi(r) = -\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) \tag{1.6}$$

This equation still contains a kinetic and potential term, however the time dependence has now been eliminated by the method of separation of variables. Because the Schrödinger equation for a three body system is not separable, different techniques are used to create approximate multi-electron atomic wave functions.

It was earlier established that $\beta^-$- decay of $^6$He is a diabatic process and the system does not have enough time to change its configuration. As a result, the initial state of $^6$He can be expanded as a complete sum over all final states of $^6$Li$^+$, including the continuum. This is a simple and elegant solution for the problem of infinite number of continuum states.

$$\psi(^6\text{He}) = \sum_{k=1}^{N} a_k \psi(^6\text{Li}^+) \tag{1.7}$$

The linear combination of states in Equation (1.7), forms a pseudospectrum, and allows the entire energy spectrum of an atom to be replaced by a finite number of discrete states, that becomes complete in the limit $N \to \infty$. Given that the initial $^6$He state is discrete, and singlet or triplet, there are two possible outcomes of the remaining lithium system. As mentioned previously, the lithium atom can either be excited into a final discrete state or ionized into the continuum.
In order to determine the most probable final state of the daughter atom, the transition amplitude matrix element must be calculated. This is given by Equation (1.8) [13]

\[ b_{if} = \int dr_1 \int dr_2 \psi_i(6\text{He}) e^{i\mathbf{p} \cdot \mathbf{r}_1} e^{i\mathbf{p} \cdot \mathbf{r}_2} \psi_f(6\text{Li}^+) \] (1.8)

where \( \psi_i(6\text{He}) \) and \( \psi_f(6\text{Li}^+) \) are the wave functions of the initial and final states respectively. Sandwiched between the two states, \( \hat{R} = e^{i\mathbf{p} (\mathbf{r}_1 + \mathbf{r}_2)} \) is the recoil momentum operator. This operator is what accounts for the recoil ionization. To simplify the calculations further, for this study the momentum was eliminated by assuming \( \mathbf{p} = 0 \). This gives rise to the new expression for the transition amplitude.

\[ b_{if} = \int dr_1 \int dr_2 \psi_i(6\text{He}) \psi_f(6\text{Li}^+) \] (1.9)

This simplification only slightly alters the results since recoil ionization is a secondary effect. Finally, in the framework of the sudden approximation, and neglecting the recoil momentum of the daughter nucleus, the probability of a specific final state is given by the Born rule [13]:

\[ P_{if} = |b_{if}|^2 = |\langle \psi_i | \psi_f \rangle|^2 \] (1.10)

Hylleraas-like wave functions, obtained through the variational principle (matrix diagonalization), were used in Equation (1.10) to calculate the full probability distribution to all the possible states of the daughter lithium atom, as well as the total probability of ionization.
Chapter 2

Theory and Method of Calculations

Expressions for helium and lithium ion wave functions had to be computed in order for the probability amplitude to be calculated. To get these states, and their corresponding energies, the Hamiltonian for a two electron system must first be discussed. Unfortunately, the Hamiltonian is not analytically solvable for a three body system. It is encouraging however, that the variational method with a Hylleraas basis set can be used to calculate results of arbitrary accuracy.

2.1 THE HAMILTONIAN

The nonrelativistic Schrödinger equation for a general three body system can be written as:

\[
\begin{align*}
-\frac{\hbar^2}{2m_1} \nabla^2_1 - \frac{\hbar^2}{2m_2} \nabla^2_2 - \frac{\hbar^2}{2m_3} \nabla^2_3 + \frac{q_1 q_3}{|\vec{R}_1 - \vec{R}_3|} + \frac{q_2 q_3}{|\vec{R}_2 - \vec{R}_3|} + \frac{q_1 q_2}{|\vec{R}_1 - \vec{R}_2|} \end{align*}
\]

\[
\psi = E_{NR} \psi \quad (2.1)
\]

The particle masses, charges, and positions relative to the origin of the coordinate system are given by \(m_i\), \(q_i\) and \(R_i\) respectively, where \(i = 1, 2, 3\). The transformation
to center-of-mass frame and relative coordinates is defined by:

\[ \vec{r}_1 = \vec{R}_1 - \vec{R}_3 \]
\[ \vec{r}_2 = \vec{R}_2 - \vec{R}_3 \]
\[ \vec{R}_{CM} = \frac{m_1 \vec{R}_1 + m_2 \vec{R}_2 + m_3 \vec{R}_3}{m_1 + m_2 + m_3} \]  

(2.2)

where \( \vec{r}_1 \) and \( \vec{r}_2 \) are the position vectors from the nucleus to the two electrons, and \( \vec{R}_{CM} \) is the position of the center-of-mass from the origin. Taking this into consideration for helium means that \( m_3 = M \), the mass of the nucleus, \( m_1 = m_2 = m_e = m \), the mass of an electron, and \( q_i = eZ_i \). The differential operators can then be written as:

\[ \nabla_1 = \frac{m}{2m + M} \nabla \vec{R}_{CM} - \nabla \vec{r}_1 \]
\[ \nabla_2 = \frac{m}{2m + M} \nabla \vec{R}_{CM} - \nabla \vec{r}_1 \]
\[ \nabla_3 = \frac{M}{2m + M} \nabla \vec{R}_{CM} - \nabla \vec{r}_1 - \nabla \vec{r}_2 \]  

(2.3)

Scaling the distances, using reduced mass \( \mu = \frac{mM}{m + M} \), and applying the above changes, gives rise to Equation (2.4), the Schrödinger equation in atomic units.

\[ \left[ -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{\mu}{M} \nabla_1 \cdot \nabla_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right] \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2) \]  

(2.4)

where \( r_{12} = |r_2 - r_1| \) is the distance between the two electrons. Due to this electron-electron repulsion term, the Schrödinger equation for helium is not separable. The new term, \( \frac{\mu}{M} \nabla_1 \cdot \nabla_2 \), is known as the mass polarization term. Because \( \frac{\mu}{M} \ll 1 \), this cross term can be ignored, and the dimensionless Schrödinger equation for infinite nuclear mass is becomes

\[ \left[ -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right] \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2). \]  

(2.5)

Further details on the derivations can be found in Appendix 6.3.

### 2.2 THE VARIATIONAL PRINCIPLE

The variational principle is often applied to problems in classical and quantum mechanics when exact solutions cannot be found. The first step in explaining this principle
is the Euler-Lagrange problem. Take for example two set end points, where the path \( q(t) \) between these end points may vary. The problem is to find the function \( q(t) \), such that the time integral of the Lagrangian describing the system is minimized. This time integral is also known as the action, and is defined by [14]:

\[
J = \int_{t_1}^{t_2} dt \; f(t, q, \dot{q}) \tag{2.6}
\]

Euler considered trying to make minuscule variations on the path, \( \delta q(t) \), such that the resulting change in the action vanishes. This required \( \delta J = 0 \). Euler realized that another, more logical way to find the preferred path, is to simply minimize the action integral. The great result of this procedure was that the derived \( q(t) \), is the actual path taken by a particle in nature.

### 2.2.1 Stationary States

The variational principle can be applied to obtain accurate eigenvalues and eigenfunctions for many atomic systems. When using it for a two body system such as hydrogen, it reproduces the exact results. Although exact solutions do not yet exist for multi-electron atoms, high precision and accuracy data can be calculated using this technique.

For a Hamiltonian \( H \), the exact eigenfunction \( \Psi \) may be used to obtain the energy eigenvalue \( E \) of a system through the expression

\[
H \ket{\Psi} = E \ket{\Psi}. \tag{2.7}
\]

Multiplying through by \( \bra{\Psi} \), and rearranging, gives the variational equation for energy,

\[
\bra{\Psi} H \ket{\Psi} = E \bra{\Psi} \ket{\Psi}
\]

\[
E = \frac{\bra{\Psi} H \ket{\Psi}}{\bra{\Psi} \ket{\Psi}} \tag{2.8}
\]

where the denominator is just a normalization factor. This equation can also be written in its integral form,

\[
E = \frac{\int \Psi^* H \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \tag{2.9}
\]
and minimized in much the same way as the action integral $J$ [Equation (2.6)], to get the best approximation for the energy eigenvalue. If $\Psi$ is not known exactly, then varying an assumed functional form of $\Psi(\vec{r})$ in either Equation (2.8) or (2.9) until it is a minimum will give the most accurate variational approximation for the energy. This gives a means for getting approximate solutions for unsolvable Schrödinger equations [15, 16].

### 2.2.2 Matrix Equivalency

Since we have a well established three body Hamiltonian, the main obstacle in applying of Equation (2.8) is the lack of an exact eigenfunction, $\Psi$. For this reason, the exact wave function is replaced with an approximate trial function, $\Psi_{tr}$.

$$E_{tr} = \frac{\langle \Psi_{tr} | H | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle}$$  \hspace{1cm} (2.10)

The trial wave function is written as a linear combination of a finite number of basis functions.

$$\psi_{tr} = \sum_{i=0}^{N} c_i \phi_i$$  \hspace{1cm} (2.11)

The linear coefficients are then determined by minimizing Equation (2.10), $\frac{\partial E_{tr}}{\partial c_i} = 0$, for $i = 0, ..., N$. This results in a system of N homogeneous linear equations. Expanding the equation for the trial energy makes it easier to apply the partial differential. In the following derivations, the index $i$ will refer to the left hand function, and $j$ to the right hand function.

$$E_{tr} = \frac{\langle \Psi_{tr} | H | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle} = \sum_{ij} c_i^* c_j \langle \phi_i | H | \phi_j \rangle \frac{1}{\sum_{ij} c_i^* c_j \langle \phi_i | \phi_j \rangle} = \sum_{ij} c_i^* c_j \langle \phi_i | H | \phi_j \rangle \frac{1}{\sum_{ij} c_i^* c_j O_{ij}}$$  \hspace{1cm} (2.12)

The above term is minimized by deriving it with respect to a given coefficient $c_k$. Only terms which contain $c_k$ will remain, the rest are zero. This is accounted for by $\delta_{jk} = 1$. 

when \( j = k \) and \( \delta_{jk} = 0 \) when \( j \neq k \). Inserting Equation (2.12) gives [17]

\[
\frac{\partial E_{tr}}{\partial c_i} = \left[ \sum_{ij} c_i^* c_j O_{ij} \right] \left[ \sum_{ij} c_i^* c_j H_{ij} \delta_{jk} \right] - \left[ \sum_{ij} c_i^* c_j H_{ij} \right] \left[ \sum_{ij} c_i^* O_{ij} \delta_{jk} \right] \left[ \sum_{ij} c_i^* c_j O_{ij} \right]^{-2}
\]

\[
= \frac{\sum_{ij} c_i^* H_{ij}}{\sum_{ij} c_i^* c_j O_{ij}} - \frac{\left[ \sum_{ij} c_i^* c_j H_{ij} \right] \left[ \sum_{ij} c_i^* O_{ij} \right]}{\left[ \sum_{ij} c_i^* c_j O_{ij} \right]^2}
\]

\[
= \frac{\sum_{ij} c_i^* H_{ij} - E_{tr} \sum_{ij} c_i^* O_{ij}}{\sum_{ij} c_i^* c_j O_{ij}}.
\]

(2.13)

Setting Equation (2.13) to zero to make the derivatives vanish results in

\[
\sum_{ij} c_i^* H_{ij} - E_{tr} \sum_{ij} c_i^* O_{ij} = 0
\]

\[
\sum_{ij} c_i^* H_{ij} - E_{tr} \sum_{ij} c_i^* O_{ij} = 0
\]

\[
\sum_{ij} c_i^* H_{ij} = E_{tr} \sum_{ij} c_i^* O_{ij}.
\]

(2.14)

Keeping in mind that the magnetic quantum number is factored out of the radial component making the states nondegenerate, and the wave function can be taken to be real for nondegenerate states, the process of complex conjugation can be ignored. Equation (2.14) can be then written in the following generalized eigenvalue equation

\[
H c = E_{tr} O c
\]

where \( H \) is the Hamiltonian matrix with elements, \( H_{ij} = \langle \phi_i | H | \phi_j \rangle \), \( O \) is the overlap matrix with elements, \( O_{ij} = \langle \phi_i | \phi_j \rangle \), and \( c \) is the column vector of linear coefficients \( c_i \).

\[
\begin{bmatrix}
H_{11} & H_{12} & \cdots & H_{1N} \\
H_{21} & H_{22} & \cdots & H_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
H_{N1} & H_{N2} & \cdots & H_{NN}
\end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
\vdots \\
c_N
\end{bmatrix}
= E_{tr}
\begin{bmatrix}
O_{11} & O_{12} & \cdots & O_{1N} \\
O_{21} & O_{22} & \cdots & O_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
O_{N1} & O_{N2} & \cdots & O_{NN}
\end{bmatrix}
\begin{bmatrix}
c_1 \\
c_2 \\
\vdots \\
c_N
\end{bmatrix}
\]

Diagonalizing \( H \) gives rise to \( N \) eigenvalues and eigenvectors. Eigenvalue \( E_N \) corresponds to the estimated energy of the \( N^{th} \) state. Furthermore, the corresponding column eigenvector \( c \), represents the optimum linear coefficients of the wave function for the \( N^{th} \) state.
2. Theory and Method of Calculations

2.2.3 Rayleigh-Ritz Variational Principle: Proof of Bounded Solution

The Rayleigh-Ritz variational principle states that the expectation value of a Hamiltonian, calculated with a trial wave function, always gives a trial energy that is higher than the true ground state energy. To prove this, let's first look at the format of the trial wave function. $\Psi_{tr}$ can always be expanded in terms of the complete set of exact eigenfunctions.

$$|\Psi_{tr}\rangle = \sum_{i=0}^{\infty} c_i |\phi_i\rangle \quad (2.16)$$

Introducing this trial function into Equation (2.10) and manipulating it gives [17]

$$E_{tr} = \frac{\langle \Psi_{tr} | H | \Psi_{tr} \rangle}{\langle \Psi_{tr} | \Psi_{tr} \rangle} = \sum_{ij} \langle c_i \phi_i | H | c_j \phi_j \rangle \sum_{ij} \langle c_i \phi_i | c_j \phi_j \rangle = \sum_{i} \left[ \langle c_i \phi_i | H | c_0 \phi_0 \rangle + \langle c_i \phi_i | H | c_1 \phi_1 \rangle + \cdots \right] \sum_{ij} c_i^* c_j \langle \phi_i | \phi_f \rangle \sum_{ij} c_i^* c_j \delta_{ij} = \sum_{i} c_i^* \left[ c_0 E_0 \langle \phi_i | \phi_0 \rangle + c_1 E_1 \langle \phi_i | \phi_1 \rangle + \cdots \right] \sum_{i} c_i^* c_i = \sum_{i} c_i^* \left[ c_0 E_0 \delta_{0i} + c_1 E_1 \delta_{1i} + \cdots \right] \sum_{i} |c_i|^2 \quad (2.17)$$

Assuming that the trial function is normalized to unity, so that $\sum_{i} |c_i|^2 = 1$, the denominator is unity. Continuing with the derivation results in

$$E_{tr} = \sum_{i} c_i^* \left[ c_0 E_0 \delta_{0i} + c_1 E_1 \delta_{1i} + \cdots \right] = c_0^* c_0 E_0 + c_1^* c_1 E_1 + c_2^* c_2 E_2 + \cdots = |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \cdots \quad (2.18)$$

Again, keeping in mind that $\sum_{i} |c_i|^2 = 1$, $|c_0|^2$ can be expanded as $|c_0|^2 = 1 - |c_1|^2 - |c_2|^2 - \cdots$. Finally, inserting this expansion into the previous equation proves that the eigenvalues are bounded from below.

$$E_{tr} = \left[ 1 - |c_1|^2 - |c_2|^2 - \cdots \right] E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \cdots = E_0 + |c_1|^2 (E_1 - E_0) + |c_2|^2 (E_2 - E_0) + \cdots \quad (2.19)$$
2. THEORY AND METHOD OF CALCULATIONS

It is clear that the trial energy is always higher than the exact ground state energy.

\[ E_{\text{tr}} \geq E_0 \]  

(2.20)

Although the true energy for a multi-electron system cannot be reached, increasing the accuracy of the trial wave function gives closer approximation to the actual answer. There are several ways to increase the accuracy of the wave functions, including optimizing the nonlinear parameters, and enlarging the size of the basis set. In the latter case, increasing the basis set results in adding new rows and columns to the Hamiltonian \(H\) and overlap \(O\) matrices mentioned earlier. For each new row and column added to the matrix, the basis set becomes more complete, and the old eigenvalues will interleave the new eigenvalues. This means that the new eigenvalues will fall between the old ones, pushing the old ones inexorably downward toward the exact eigenvalue, but never quite reaching them. This is known as the Hylleraas-Undheim theorem, and applies to all the variational eigenvalues, not just the ground state [18].

2.3 THE TRIAL WAVE FUNCTION

The pioneering variational work on the ground state energy of helium was started by E.A. Hylleraas in 1929. Hylleraas suggested to write a trial function with clear electron correlation terms. Although his initial basis functions were written in perimetric coordinates, present day calculations use wave functions which are written in inter-particle coordinates [19, 20]. For an S state, such a wave function with \(Z\)-scaled atomic units has the form

\[ \Psi_{\text{tr}}(r_1, r_2) = \sum_{ijk} a_{ijk} r_1^i r_2^j e^{-\alpha r_1 - \beta r_2} \pm \text{exchange} \]  

(2.21)

where \(a_{ijk}\) are linear coefficients and \(\alpha\) and \(\beta\) are nonlinear parameters scaling the distances to each electron. The exchange term has the same functional form as the first term, but the roles of \(r_1\) and \(r_2\) are interchanged. To include other states of higher angular momentum, the vector coupled products of spherical harmonics must
be included. The spherical harmonics have the form

\[ Y_{l_1 l_2 L}^{M}(\hat{r}_1, \hat{r}_2) = \sum_{m_1 m_2} Y_{l_1}^{m_1}(\hat{r}_1)Y_{l_2}^{m_2}(\hat{r}_2)\langle l_1 l_2 m_1 m_2 \mid LM \rangle. \]  

(2.22)

In recent years, there has been much progress in the calculation of a variety of states in both helium and lithium-like ions. Much of the achievement was due to the efforts of Drake, by the introduction of a second set of Hylleraas basis functions [21].

The addition of a different set of exponential parameters, \( \alpha_2 \) and \( \beta_2 \), not only increases the accuracy by orders of magnitude, but also simplifies the calculations by allowing for much smaller basis sets. The importance of fewer basis functions is that large basis sets with a single pair of parameters tend to become linearly dependent, resulting in numerical cancellations. Today, it is even possible to triple or quadruple the basis set, to create very large wave functions with extreme accuracy.

Besides the mathematical benefits, doubling the basis set also allows for a physical interpretation of the wave function. The optimization of the four nonlinear parameters produces two distinct regions. The first pair are close to their screened hydrogenic values, \( \alpha_1 \simeq Z \) and \( \beta_1 \simeq (Z - 1)n \), where \( n \) is the principal quantum number describing the electron shell of the outer electron. This pair describes the asymptotic form of the wave function. It is these parameters that represent the independent particle model picture of an atom. The second pair of coefficients naturally optimize to larger values, and describe the region close to the nucleus where complex correlation effects are most significant [21].

In this study, the trial function will contain a double basis set with Hylleraas functions, similar to Equation (2.23), with one small modification. Since the \( \beta^- \)-decay of \(^6\text{He}\) results in the transformation of the parent nucleus into the daughter, \(^6\text{Li}\) nucleus, it is important to include the atomic charge, \( Z \). When \( Z \) is factored back
into the radial function, the new \( \Psi_{tr}(r_1, r_2) \) has the form

\[
\Psi_{tr}(r_1, r_2) = \sum_{ijk} (Z^i + j + k) a_{ijk}^{(1)} r_1^i r_2^j r_{12}^k e^{-\alpha_1 Z r_1 - \beta_1 Z r_2} Y_{L_{12}^M}^{l_1 l_2}
\]

\[
+ \sum_{ijk} (Z^i + j + k) a_{ijk}^{(2)} r_1^i r_2^j r_{12}^k e^{-\alpha_2 Z r_1 - \beta_2 Z r_2} Y_{L_{12}^M}^{l_1 l_2} \pm \text{exchange.}
\]

Before any calculations were done, the first step was to account for this modification in the programs. Luckily, the programs which created the initial \(^6\)He wave function and the final \(^6\)Li\(^+\) pseudospectra, incorporated the nuclear charge \((Z)\) dependence in the calculations. Unfortunately, the program which computed the probability amplitudes did not. The second program was originally written to calculate transitions from one atomic state to another. This meant \(Z\) did not change, so it was simpler for previous calculations to work with the \(Z\)-scaled wave functions. Since \(\beta^-\) decay of \(^6\)He requires that the nucleus transform from \(Z = 2\) to \(Z = 3\), it was necessary to factor the nuclear charge back into the second program. Once this was completed, the program was then ready to calculate the state probability distributions of \(^6\)Li\(^+\).

Finally, to control the size of the basis set, Accad, Pekeris and Schiff [22] developed a truncation criterion depending on the powers \(i, j,\) and \(k,\)

\[
i + j + k \leq \Omega
\]

where \(\Omega\) is an integer constant that is gradually increased. The total number of basis functions is then given by

\[
N = \frac{1}{6}(\Omega + 1)(\Omega + 2)(\Omega + 3)
\]

and are called a “Pekeris Shell” [21]. For large basis sets, including all \(N\) terms often causes problems with linear dependence. As a solution to this problem, further truncation conditions were developed by Drake, and by Kono and Hattori [23]. In this research \(\Omega\) was varied from five to twelve, resulting in basis sets which ranged from 44 to 441 terms.
2.4 INTEGRALS

In order to construct the overlap (O) and Hamiltonian (H) matrices it is first necessary to evaluate general integrals of the form

\[ I = \int \nu \, d\tau \Psi_{tr}^*(r_1, r_2)\Psi_{tr}(r_1, r_2) \]  
\[ I = \int \nu \, d\tau R_{nl}(r_1, r_2, r_{12})Y_{M_1}Y_{M_2}R_{nl}(r_1, r_2, r_{12})Y_{M_1}Y_{M_2}. \]

The wave function, \(\Psi\), is comprised of a radial and an angular part. The radial component is based on the before mentioned Hylleraas basis function, and the angular component depends on the angular momentum of the state.

2.4.1 The Volume Element

The simplest factor in Equation (2.27) is \(d\tau\), the volume component. In Cartesian coordinates, the volume element would be determined by the position of the electrons, so \(d\tau = dx_1dy_1dz_1dx_2dy_2dz_2\). Because the wave function contains explicitly the \(r_{12}\) coordinate, it is convenient to convert the volume element to the six independent variables \(r_1, r_2, r_{12}, \theta_1, \phi_1, \) and \(\chi\) shown in Figure (2.1). The variables \(\theta_1\) and \(\phi_1\) are the spherical polar angles of the electron coordinate \(r_1\), and \(\chi\) is the angle of rotation about \(r_1\), of the rigid triangle formed by \(r_1, r_2,\) and \(r_{12}\). With this transformation,

![Figure 2.1: Hylleraas Coordinates](image)
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the new volume element is given by [24]

\[ d\tau = r_1 dr_1 r_2 dr_2 r_{12} dr_{12} \sin\theta_1 d\theta_1 d\phi_1 d\chi \] (2.29)

Integrating over Equation (2.29) results in

\[ \int_\nu d\tau = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12} dr_{12} \int_0^\pi \sin\theta_1 d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\chi \] (2.30)

This is the integral expression for the new volume element.

2.4.2 The Radial Integrals

The simplest atomic calculations involve the overlap integral between two states.

\[ \int_\nu d\tau \Psi_{tr}^* \Psi_{tr} = \int_\nu d\tau R^* Y^* R Y \] (2.31)

\( R \) is the radial component and \( \mathcal{Y} \) is the angular component of each wave function. This section focuses on the integrals of only the radial components.

There are several radial integrals which are calculated in this project, but the basic form of all of them is

\[ I_0(a, b, c; \alpha, \beta) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12} dr_{12} r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \] (2.32)

where \( a = i' + i, \ b = j' + j, \) and \( c = k' + k, \) are the summed exponent integers of the two states. In order to evaluate the integrals, \( I_0 \) must first be separated into two parts. This is because of the modulus in the lower limit of the \( r_{12} \) integral.

\[ I_0(a, b, c; \alpha, \beta) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{r_2 - r_1}^{r_2 + r_1} r_{12} dr_{12} r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} + \int_0^\infty r_2 dr_2 \int_0^\infty r_1 dr_1 \int_{r_1 - r_2}^{r_1 + r_2} r_{12} dr_{12} r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \] (2.33)

Integrating over \( r_{12} \) results in Equation (2.34),

\[ I_0 = \int_0^\infty dr_1 \int_{r_1}^\infty dr_2 \frac{1}{c+2} \left[ (r_2 + r_1)^{c+2} - (r_2 - r_1)^{c+2} \right] r_1^{a+1} r_2^{b+1} e^{-\alpha r_1 - \beta r_2} + \int_0^\infty dr_2 \int_{r_2}^\infty dr_1 \frac{1}{c+2} \left[ (r_1 + r_2)^{c+2} - (r_1 - r_2)^{c+2} \right] r_1^{a+1} r_2^{b+1} e^{-\alpha r_1 - \beta r_2} \] (2.34)

which can be rewritten using the binomial expansion. The general definition of the binomial theorem is

\[ (A + B)^n = \sum_{m=0}^{n} \binom{n}{m} A^{n-m} B^m, \quad \text{where} \quad \binom{n}{m} = \frac{n!}{m!(n-m)!} \] (2.35)
2. THEORY AND METHOD OF CALCULATIONS

Incorporating this definition into the basic radial integral gives

\[
I_0 = \frac{2}{c + 2} \left[ \sum_{s=0}^{[[c+1/2]]} \left( \frac{c + 2}{2s + 1} \right) \left[ \int_0^\infty dr_1 \int_0^\infty dr_2 r_1^p r_2^q e^{-\alpha r_1 - \beta r_2} \right. \\
\left. + \int_0^\infty dr_2 \int_0^\infty dr_1 r_1^p r_2^q e^{-\alpha r_1 - \beta r_2} \right] \right]
\]

(2.36)

where \( s \) is an index, \( p = a + 2s, p' = b + 2s, q = b + c - 2s, q' = a + c - 2s - 2, \) and \([x]\) means the greatest integer in \( x \) [25]. The final step is to rewrite the integrals in terms of the following Gamma and Incomplete Gamma function, \( \Gamma \) [26]:

\[
\Gamma(a, x) = \int_x^\infty t^{a-1} e^{-t} dt
\]

(2.37)

\[
\Gamma(n, x) = \frac{(n - 1)!}{e^{-x} x^{n-1} \sum_{s=0}^{\infty} x^s s!}, \quad n = 1, 2, 3, ...
\]

(2.38)

\[
\Gamma(n) = \int_0^\infty t^{n-1} e^{-t} dt, \quad n = 1, 2, 3, ...
\]

(2.39)

Introducing the Gamma functions gives the final expression for the basic integral [27, 28].

\[
I_0 = \frac{2}{c + 2} \left[ \sum_{s=0}^{[[c+1/2]]} \left( \frac{c + 2}{2s + 1} \right) \left[ F_{p,q}^{\alpha,\beta} + F_{p',q'}^{\alpha,\beta} \right] \right], \quad \text{where} \quad F_{p,q}^{\alpha,\beta} = \begin{cases} \\
\frac{q!}{(\alpha+\beta)^{p+q+\alpha+\beta}} \sum_{l=0}^{q} \frac{(p+l)!}{l!} \left( \frac{\beta}{\alpha+\beta} \right)^l, & q \geq 0, p \geq 0 \\
\frac{p!}{\alpha^{p+q+\alpha}} \sum_{l=p+q+1}^{\infty} \frac{n!}{(l-q)!} \left( \frac{\alpha}{\alpha+\beta} \right)^l, & q < 0, p \geq 0 \\
0 & p < 0
\end{cases}
\]

(2.40)

Equation (2.40) is valid for \( a, b \geq -1 \) and \( c \geq 1 \). Some special cases of \( I_0(a, b, c; \alpha, \beta) \) are

\[
I_0(-1, -1, -1; \alpha, \beta) = \frac{2}{\alpha \beta (\alpha + \beta)} \quad \text{and} \quad (2.42)
\]

\[
I_0(0, 0, 0; \alpha, \beta) = \frac{4}{\alpha^2 \beta^2} \]  

(2.43)

Table 11.1 in the *Atomic, Molecular, and Optical Physics Handbook* [27] has an extensive list of radial integrals.
2.4.3 The Angular Integrals

As mentioned previously, the starting point of most atomic calculations is the overlap integral. For convenience, Equation (2.31) is stated again.

\[ \int d\tau \Psi^*_t \Psi_t = \int d\tau R^*Y^* \]  

(2.44)

In this section, the integrals over the angular components, \( Y \), will be studied. For a detailed derivation see Appendix 6.4.

One of the consequences of converting to Hylleraas coordinates is that the polar angles \( \theta_2 \) and \( \phi_2 \) of \( r_2 \) are no longer independent. To allow for this, the spherical harmonic of the second electron can be written in terms of a rotation matrix [28]

\[ Y_{m_2}^{l_2}(\theta_2, \phi_2) = \sum_M D_{m_2,M}^{l_2*}(\phi_1, \chi) Y_{l_2}^M(\theta, \phi) \]  

(2.45)

where \( \theta \) and \( \phi \) are the polar angles of \( r_2 \) relative to \( r_1 \). This makes the direction \( r_1 \) as the origin of the new polar coordinate system. The spherical harmonic of the first electron is written as

\[ Y_{l_1}^{m_1*}(\theta_1, \phi_1) = \sqrt{\frac{2l_1+1}{4\pi}} D_{m_1,0}^{l_1}(\phi_1, \chi). \]  

(2.46)

The expression for the two electrons, along with the Legendre polynomial,

\[ P_l(\cos \theta) = \sqrt{\frac{4\pi}{2l+1}} Y_l^0(\theta, \phi) \] where

\[ \cos \theta = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2} \]  

(2.47)

(2.48)

is needed to find an equation for the basic angular integral. Because \( P_l(\cos \theta) \) is a purely radial function, it can be considered part of the radial integral,

\[ I_{l_2}(R'R) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} dr_{12} r_1^a r_2^b \gamma_{12} e^{-\alpha r_1 - \beta r_2} P_{l_2}(\cos \theta) \]  

(2.49)

which was discussed in the previous section. The basic angular integral is then

\[ \langle Y_{l_1}^{m_1*}(\theta_1, \phi_1) Y_{l_2}^{m_2}(\theta_2, \phi_2) \rangle_{\text{ang}} = 2\pi \delta_{l_1 l_2} \delta_{m_1 m_2} P_{l_2}(\cos \theta). \]  

(2.50)

The equivalent integral over vector coupled spherical harmonics is

\[ \langle Y_{l_1 l_2 L}^{M_1*}(\hat{r_1}, \hat{r_2}) Y_{l_2 l_2 L}^{M}(\hat{r_1}, \hat{r_2}) \rangle_{\text{ang}} = \delta_{\Lambda M} \delta_{M M'} \sum_{\Lambda} C_{\Lambda} P_{\Lambda}(\cos \theta) \]  

(2.51)
where $C_{\Lambda}$ is a constant given by [28]
\[
C_{\Lambda} = \frac{1}{2} \left[ \frac{(2l_1' + 1)(2l_1 + 1)(2l_2 + 1)(2l_2' + 1)}{4\pi} \right]^{1/2} (-1)^{L+\Lambda}(2\Lambda + 1)
\times \left( \begin{array}{ccc} l_1' & l_1 & \Lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_2' & l_2 & \Lambda \\ 0 & 0 & 0 \end{array} \right) \left\{ \begin{array}{ccc} L & l_1 & l_2 \\ \Lambda & l_2' & l_1' \end{array} \right\}.
\] (2.52)

The general integral can be conveniently expressed as
\[
I = \sum_{\Lambda} C_{\Lambda} I_{\Lambda}(R'R).
\] (2.53)

Since the initial configuration of $^6\text{He}$ is either $^1S_1$ or $^2S_1$, and the recoil momentum is neglected, the selection rules dictate that the daughter $^6\text{Li}$ must also be in and S state. This means the angular integrals are not used in this study.

### 2.5 THE HAMILTONIAN MATRIX ELEMENTS FOR S STATES

The two electron Hamiltonian for infinite nuclear mass is given by
\[
H = \frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}
\]  
(2.54)

where the Laplacian operator $\nabla_1^2$ in Hylleraas coordinates is [20]

\[
\nabla_1^2 = \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( \frac{r_1^2}{\partial r_1} \right) + \frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left( \frac{r_{12}^2}{\partial r_{12}} \right) + \frac{2(r_1 - r_2 \cos \theta)}{r_{12}} \frac{\partial}{\partial r_{12}} \left( \frac{(Y_1^2)^2}{r_1^2} - 2(r_2 \cdot \nabla_1 Y) \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} \right).
\]  
(2.55)

The second operator, $\nabla_2^2$, has the same form as the first but the indeces 1 and 2 are interchanged. The superscripts $R$ or $Y$ refer to operations acting only on the radial or angular components, respectively. The operators act on wave functions of the type
\[
\Psi(r_1, r_2) = \sum_{ijk} a_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} Y_{l_1 l_2 L}^M (r_1, r_2).
\]  
(2.56)

After $\nabla_1^2$ acts on $\Psi(r_1, r_2)$, the following expression is obtained [25],
\[
\nabla_1^2 \Psi(r_1, r_2) = \left\{ \frac{i(i+1) - l_1(l_1 + 1)}{r_1^2} + \frac{k(k + 1)}{r_{12}^2} + \frac{2\alpha(i + 1)}{r_1} \right\} \Psi(r_1, r_2)
\]
\[
+ \frac{2(r_1 - r_2 \cos \theta)}{r_{12}} \frac{2k}{r_{12}} (r_2 \cdot \nabla_1 Y) \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} \Psi(r_1, r_2)
\]
where \( i, j, \) and \( k \) are the powers of \( r_1, r_2, \) and \( r_{12} \) respectively. Since S states have no angular contributions \( (l = 0) \), this can be reduced to

\[
\nabla^2_r \psi(r_1, r_2) = \left\{ \frac{i(i+1)}{r_1^2} + \frac{k(k+1)}{r_{12}^2} + \alpha - \frac{2\alpha (i+1)}{r_1} + \frac{2(r_1 - r_2 \cos \theta)}{r_{12}} k(i - \alpha r_1) \right\} \psi(r_1, r_2).
\]

When \( \nabla^2_\frac{3}{2} \) acts on the wave function, essentially the same result is achieved, except \( \{\alpha, \beta\} \) and \( \{i, j\} \) are interchanged. The remaining operators in the Hamiltonian can be easily integrated for S states.

### 2.6 COMPUTATIONAL METHODS

The majority of integral functions calculated have the root form of those mentioned in Section 2.4. For this reason, it is very efficient to compute and store these integrals, and simply access their results whenever they are required. This process reduces the calculation time drastically.

In Section 2.2.2 it was concluded that the eigenvalue equation can be written in a matrix equivalent form (Equation [2.15]). The first step in creating these matrices is to generate Hylleraas-like trial functions, after which the Hamiltonian overlap matrix elements can be generated. This leads to a generalized eigenvalue problem

\[
(H - EO)c = 0
\]

where \( c \) is a column vector of the corresponding linear coefficients, and the matrix elements \( H_{ij} = \langle \phi_i \mid H \mid \phi_j \rangle \) and \( O_{ij} = \langle \phi_i \mid \phi_j \rangle \). There are several techniques to solving this problem, each with its own benefits and downfalls.

#### 2.6.1 The Power Method

The first technique to be discussed is the power method, however it can only be used if one eigenvalue is strictly larger in magnitude than the others. A sample equation which can be solved by this method, might have the form

\[
(A - \lambda g B) \cdot c = x
\]
where $A$ and $B$ are square matrices, $x$ and $c$ are vectors, and $\lambda_g$ is a guess eigenvalue. A random vector, $x$, and a guessed eigenvalue are selected, and the equation is solved for $y$. This solution is then inserted as $x$ into Equation (2.59), producing a new $y$. This process is repeated until $y$ nears convergence.

In order to use this technique for Equation (2.58), the equation is actually solved for the inverse of the eigenvalue problem. By choosing a guess energy, $E_g$, which is close to the true energy of the state being calculated, $E_n$, it makes the terms $\frac{1}{E_n - E_g}$ dominant. Each iteration produces a new column vector, $c$. When the calculations converge to machine accuracy, the optimized linear coefficients of $c$ are used to create a wave function of closest approximation to the actual energy level. To solve the matrix equations, the square root method is applied. For a more detailed explanation of the Power Method see Appendix 6.5.

The input values of the nonlinear parameters $\alpha$ and $\beta$ are chosen based on the specifics of the system being studied, or previously calculated wave functions of similar states. These values will not always yield the lowest energy eigenvalue. For this reason, $\alpha$ and $\beta$ are optimized using Newton’s method. In this case, the expression for the energy is differentiated with respect to each parameter. The minimum of these derivatives is found by varying $\alpha$ and $\beta$ and recalculating the problem and the energy derivatives each time until they are zero. Luckily, if $E_g$ is close to $E_n$, the process converges fairly quickly after only a few iterations.

As previously mentioned, in this study the initial state of $^6$He needs to be expanded as a complete sum over all the $^6$Li$^+$ energy states. This means that the general eigenvalue equation, containing $N \times N$ dimensional matrices, needs to be solved for all $N$ eigenfunctions and eigenvalues simultaneously. Since the power method solves for only one eigenvalue at a time, unfortunately, it cannot be used to create the pseudospectrum for the final $^6$Li states. The power method was, however, previously used by Drake to compute the initial $1^1S_1$ and $2^3S_1$ states $^6$He.
2.6.2 The Brute Force Method

The second technique is the brute force method, and is more suited for this study because it diagonalizes the $N \times N$ Hamiltonian matrix in one iteration, giving all the $N$ eigenvalues and eigenvectors. The downfall of this method, however, is that it is relatively slow.

The first step is the orthonormalization of the basis set by finding the orthogonal transformation $T$, acting on the overlap matrix $O$, such that

$$T^T OT = I,$$

where

$$I = \begin{pmatrix} I_1 & 0 & \cdots & 0 \\ 0 & I_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & I_N \end{pmatrix}$$

This is done by diagonalizing matrix $O$ using the Jacobi method. $T$ is then the matrix which satisfies Equation (2.60). The superscript $T$ of a matrix represents its transpose.

To make a scale change

$$S = \begin{pmatrix} \frac{1}{\sqrt{I_1}} & 0 & \cdots & 0 \\ 0 & \frac{1}{\sqrt{I_2}} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \frac{1}{\sqrt{I_N}} \end{pmatrix} = S^T.$$  

(2.61)

This means $S^T T^T OT S = 1$. To simplify the equation, and because $S$ is diagonal, the variable change $S^T T^T = R^T$ and $ST = R$ is made.

Before the Hamiltonian matrix $H$ can be diagonalized, it must first be expressed in the new orthonormal basis. To do this, the matrix $H'$ is created, such that

$$H' = R^T HR.$$  

(2.62)

Finally, finding the orthogonal transformation

$$W^T H' W = \Lambda = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_N \end{pmatrix}$$

(2.63)
2. THEORY AND METHOD OF CALCULATIONS

gives the eigenvalues $\lambda_1, \lambda_2, \cdots, \lambda_N$. The orthogonal transformation is actually found by diagonalizing the $H'$ matrix using the Jacobi method. For details on this method see Appendix 6.6. Since the matrices are symmetric, they are stored as triangular matrices in an array.

As previously discussed, the diagonalization of the $N \times N$ $H'$ matrix gives all the eigenvalues and eigenvectors simultaneously. All the eigenvectors together form a pseudospectrum. The pseudospectra created in this study contain $N$ pseudostates, each with a corresponding eigenenergy $E_N$. These pseudostates span both the bound and continuum regions of the energy spectrum of the daughter $^6$Li atom.

To conclude this section, now that the computational methods of the initial and final states have been discussed, the state probability distributions can be calculated. The probability amplitude between the initial $^6$He state and one of the final $^6$Li pseudostates is given by Equation (1.9)

$$b_{if} = \int dr_1 \int dr_2 \psi_i( ^6 \text{He} ) \psi_f( ^6 \text{Li}^+ )$$

$$= \langle \Psi_i | \Psi_f \rangle$$

$$= \sum_{ij} c_i \langle \phi_i | \phi_f \rangle c_f.$$

From the above expression it can be inferred that the $\sum_{ij} c_i \langle \phi_i | \phi_f \rangle$ part of Equation (2.64) remains constant while the coefficients $c_f$ change for each pseudostate. The program calculates the constants and stores them in an array TRB(i), where $i$ is the index corresponding to $c_i$. TRB(i) is then multiplied by each linear coefficient, $c_f$ of the wave function $\Psi_f$. Keeping in mind that $\Psi_f$ is just one pseudostate of the whole pseudospectrum, this array of constants then needs to be multiplied to the rest of the linear coefficients in the remaining $N - 1$ pseudostates. This means it is multiplied $N^N$ times. The state probability is then given by Born’s Rule, Equation (1.10).
Chapter 3

Results and Discussion

This section is broken up into three subsections: Stieltjes Imaging Graphs, Probability and Energy Dependence on $\beta_1$, and Total Probability of Ionization. Each subsection contains an introduction, corresponding graphs and tables, and a discussion of the resulting data.

3.1 STIELTJES IMAGING GRAPHS

The first data to be examined were the dependence of probability on the size of the basis set. These calculations were done with an initial $1\,^1S_1$ singlet configuration of $^6$He, requiring the final state to be the pseudospectrum spanning all possible singlet S states of $^6$Li$^+$, as well as the continuum. This means the orbital angular momentum quantum number describing is always zero ($l_i = 0, \ i = 1, 2$). The following graphs are probabilities of specific final configurations of $^6$Li$^+$ plotted against the number of terms in the basis set. The naming convention for the states is $n_1s\,n_2s$, where $n_i, \ i = 1, 2$ are the principal quantum numbers of the two electrons.
Figure 3.1: Dependence of probability on the size of the basis set for the singlet $1s^2$ configuration of $^6\text{Li}^+$.
Figure 3.2: Dependence of probability on the size of the basis set for the singlet $1s2s$ and $1s3s$ configurations of $^6\text{Li}^+$
Figure 3.3: Dependence of probability on the size of the basis set for the singlet 1s3s and 1s4s configurations of $^6\text{Li}^+$
Figure 3.4: Dependence of probability on the size of the basis set for singlet 1s5s, 1s6s, and 1s7s configurations of $^6\text{Li}^+$
The probability curves for the first four configurations looked promising. As predicted, the probability smoothly approached the expected values, those of Wauters and Vaeck [1], when the basis size (accuracy) of the wave functions was increased. The graphs of the last three configurations of $^6\text{Li}^+$, however, oscillated with no specific pattern. It was hypothesized that these oscillations occur because a pseudospectrum is used to represent the final states and the nonlinear parameters had not been optimized for the higher excited states. In such a pseudospectrum, the lower lying bound states of the real spectrum are represented quite accurately by the low lying pseudostates, with the remainder of the pseudostates representing the rest of the bound and continuum spectrum [Figure (3.5)].

Figure 3.5: Pseudospectrum

A pseudospectrum generated by diagonalizing the Hamiltonian $\mathbf{H}$ in an $N$-dimensional basis set. The $\lambda_p, p = 1, \ldots, N$ are the variational eigenvalues, and the $E_i$ are the exact eigenvalues of $\mathbf{H}$. The highest $\lambda_p$ lie in the continuum [27].

This means that the higher lying states, like those in the continuum, do not represent an exact state, but actually represent an average over a range of states. The probability is therefore an average probability over a specific energy range. This is illustrated well in Figure (3.6).

To account for this representation, the Stieltjes imagining technique was used. In this method, the average probability per unit energy is plotted against the average
3. RESULTS AND DISCUSSION

![Diagram showing pseudostates lying in the continuum]

The variational energy eigenvalues $\lambda_1$ and $\lambda_2$ are not the exact eigenvalues, but represent the range of energies $E_1$ and $E_2$ respectively.

\[ \frac{1}{2} (P_{i+1} + P_i) \quad \text{vs.} \quad \frac{1}{2} (E_{i+1} + E_i) \]  

(3.1)

It was hoped that using this technique would stabilize the data so that the features in the graphs are reproducible and random fluctuations are suppressed. This stabilization was previously seen in the photoionization calculations by Goldman and Drake [29]. The following are Stieltjes imaging graphs for different size basis sets for both the singlet and triplet data. It is important to keep in mind that these graphs focus on all the pseudostates, and do not focus on a specific configuration.
Figure 3.7: Singlet configuration Stieltjes imaging graph for 135 and 182 term basis sets.
Figure 3.8: Singlet configuration Stieltjes imaging graph for 236 and 302 term basis sets.
Figure 3.9: Singlet configuration Stieltjes imaging graph for 376, 464 and 561 term basis sets.
Figure 3.10: Triplet configuration Stieltjes imaging graph for 135 and 182 term basis sets.
Figure 3.11: Triplet configuration Stieltjes imaging graph for 236 and 302 term basis sets.
Figure 3.12: Triplet configuration Stieltjes imaging graph for 376, 464 and 561 term basis sets.

\[ \frac{PRB_{i+1} + PRB_i}{E_{i+1} - E_i} \text{ vs. } \frac{1}{2}(E_{i+1} + E_i) \]

\[ \frac{PRB_{i+1} + PRB_i}{E_{i+1} - E_i} \text{ vs. } \frac{1}{2}(E_{i+1} + E_i) \text{ a.u.} \]
It can be concluded from examining the graphs that this technique does in fact stabilize the data. However, there were still a few prevalent peaks recurring in all the graphs, which are believed to have physical meanings. In both the singlet and triplet graphs, the first peak at approximately $-4.5$ a.u, represents the first ionization threshold for $^{6}\text{Li}^+$. It is important to note that the original two electron helium system is transformed into a two electron lithium system. Given that neutral lithium has three electrons, even without any shake off, the daughter system is in an ionic state ($^{6}\text{Li}^+$). The first ionization threshold refers to the limit between $^{6}\text{Li}^+$ and $^{6}\text{Li}^{2+}$ and the second ionization threshold refers to $^{6}\text{Li}^{2+}$ to $^{6}\text{Li}^{3+}$. In the screened hydrogenic approximation, the energies of the ionic states are given by

$$E(\text{a.u.}) = -\frac{Z^2}{2n_1^2} - \frac{(Z-1)^2}{2n_2^2}$$  \hspace{1cm} (3.2)

where $Z = 3$, and $n_1$ and $n_2$ are the primary quantum numbers of electron one and two respectively [31]. Because the second electron is ionized into the continuum, $n_2 \rightarrow \infty$ at the series limit and consequently, the second term approaches zero. For singly excited states, such as most of the states dealt with in this study, the first electron is assumed to remain in the ground state ($n_1 = 1$). This leaves

$$E = -\frac{Z^2}{2n_1^2} = -\frac{3^2}{2(1)^2} = -4.5 \text{ a.u.}$$  \hspace{1cm} (3.3)

The two dominant peaks between $-2.0$ a.u. and 0 a.u. in the singlet Stieltjes imaging graphs are believed to be a result of autoionizing, doubly excited states. When comparing these energies to the calculated values of Şakir Erkoç [32] [Table (3.1)], there is a clear correlation between the two. The first peak from the left is believed to be the $(2, 2a)^1S$ doubly excited state and the second peak is the $(3, 3a, b, c)^1S$ configuration, where the states follow the classification scheme of Bruch et al. $(n_1, n_2, \alpha)$; $\alpha$ specifies the Rydberg series [31]. The triplet graphs have only one major prevailing peak, resulting from the $(2, 3, a, b)$ doubly excited state. While there are still some small oscillations at higher energies, the most important observation is that these fluctuations slowly fade away with increasing basis set size.
3. RESULTS AND DISCUSSION

Table 3.1: S autoionizing states of Li$^+$.  

<table>
<thead>
<tr>
<th>State $(n_1, n_2, \alpha)$</th>
<th>$E_{\text{rel.}}$ (eV)</th>
<th>$E_{\text{rel.}}$ (a.u.)</th>
<th>$E$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Singlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(2,2a) , ^1S$</td>
<td>70.5809</td>
<td>2.59380</td>
<td>-1.90620</td>
</tr>
<tr>
<td>$(2,2b) , ^1S$</td>
<td>78.0853</td>
<td>2.86958</td>
<td>-1.63042</td>
</tr>
<tr>
<td>$(2,3a) , ^1S$</td>
<td>83.9503</td>
<td>3.08512</td>
<td>-1.41488</td>
</tr>
<tr>
<td>$(2,3b) , ^1S$</td>
<td>86.6002</td>
<td>3.18250</td>
<td>-1.31750</td>
</tr>
<tr>
<td>$(3,3a) , ^1S$</td>
<td>99.0256</td>
<td>3.63912</td>
<td>-0.86088</td>
</tr>
<tr>
<td>$(3,3b) , ^1S$</td>
<td>100.7600</td>
<td>3.70286</td>
<td>-0.79714</td>
</tr>
<tr>
<td>$(3,3c) , ^1S$</td>
<td>103.8518</td>
<td>3.81648</td>
<td>-0.68352</td>
</tr>
<tr>
<td><strong>Triplet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(2,3a) , ^3S$</td>
<td>83.2643</td>
<td>3.05991</td>
<td>-1.44009</td>
</tr>
<tr>
<td>$(2,3b) , ^3S$</td>
<td>85.4418</td>
<td>3.13993</td>
<td>-1.36007</td>
</tr>
<tr>
<td>$(3,4a) , ^3S$</td>
<td>103.7250</td>
<td>3.81182</td>
<td>-0.68818</td>
</tr>
<tr>
<td>$(3,4b) , ^3S$</td>
<td>104.4979</td>
<td>3.84023</td>
<td>-0.65977</td>
</tr>
</tbody>
</table>

Energies are relative to the first ionization threshold (−4.5a.u.) of $^6$Li$^+$, the ground state of Li$^{2+}$.

3.2 PROBABILITY AND ENERGY DEPENDENCE ON $\beta_1$

As previously discussed, the nonlinear parameters $\alpha$ and $\beta$ scale the wave function as a function of distances $r_1$ and $r_2$ — the distances of the two electrons from the nucleus. Seeing as $\beta_1$ is a parameter which corresponds to the second electron’s orbit, it is expected that the graphs would show “special” behaviour around $\beta \approx 1/n_2$. In previous studies by Drake [33], it was ascertained that the energy minimized at roughly this value of $\beta_1$. Based on those results, it was hypothesized that the same would be true for the probabilities in this research. The following graphs pertain to two specific final configurations of $^6$Li$^+$, the $1s3s$ and $1s6s$ in the singlet case, and the $1s3s$ and $1s5s$ in the triplet case. There were other similar singlet plots for $1s^2$, $1s2s$, $1s4s$, $1s5s$, $1s7s$, and triplet plots for $1s2s$, $1s4s$, $1s6s$, and $1s7s$, which are not included. These graphs focus on the dependence of energy and probability on $\beta_1$. The
detailed shape of the graphs beyond the minimum regions, where $\beta_1$ is very large, is not meaningful. The region of stabilization has been extrapolated by increasing the number of data points. The probability corresponding to the local minimum of the region of stabilization for each configuration was tabulated.

<table>
<thead>
<tr>
<th>$n_1s$ $n_2s$</th>
<th>SINGLET</th>
<th>TRIPLET</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>State</strong></td>
<td><strong>Probability</strong></td>
<td><strong>Probability</strong></td>
</tr>
<tr>
<td>$1s^2$</td>
<td>70.85980(1)</td>
<td>70.85</td>
</tr>
<tr>
<td>$1s2s$</td>
<td>14.93789(1)</td>
<td>14.94</td>
</tr>
<tr>
<td>$1s3s$</td>
<td>1.85780(2)</td>
<td>1.86</td>
</tr>
<tr>
<td>$1s4s$</td>
<td>0.62266(2)</td>
<td>0.62</td>
</tr>
<tr>
<td>$1s5s$</td>
<td>0.28847(1)</td>
<td>0.29</td>
</tr>
<tr>
<td>$1s6s$</td>
<td>0.15823(1)</td>
<td>0.16</td>
</tr>
<tr>
<td>$1s7s$</td>
<td>0.09647(2)</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Transition probabilities are to discrete $^6\text{Li}^+$ states. Comparison values were provided by Wauters and Vaeck [1].
Figure 3.13: Dependence of probability on $\beta_1$ for the singlet $1s3s$ configuration of $^6\text{Li}^+$
Figure 3.14: Dependence of probability on $\beta_1$ for the singlet $1s3s$ configuration of $^6\text{Li}^+$, extrapolated near the minimum
Figure 3.15: Dependence of energy on $\beta_1$ for the singlet 1s3s configuration of $^6\text{Li}^+$.
Figure 3.16: Dependence of energy on $\beta_1$ for the singlet 1s3s configuration of $^6\text{Li}^+$, extrapolated near the minimum.
Figure 3.17: Dependence of probability on $\beta_1$ for the singlet $1s6s$ configuration of $^6\text{Li}^+$
Figure 3.18: Dependence of probability on $\beta_1$ for the singlet $1s6s$ configuration of $^6\text{Li}^+$, extrapolated near the minimum.
Figure 3.19: Dependence of energy on $\beta_1$ for the singlet 1s6s configuration of $^6\text{Li}^+$, extrapolated near the minimum.
Figure 3.20: Dependence of probability on $\beta_1$ for the triplet 1s3s configuration of $^6\text{Li}^+$
Figure 3.21: Dependence of probability on $\beta_1$ for the triplet 1s3s configuration of $^6\text{Li}^+$, extrapolated near the minimum.
Figure 3.22: Dependence of energy on $\beta_1$ for the triplet $1s3s$ configuration of $^6\text{Li}^+$.
Figure 3.23: Dependence of energy on $\beta_1$ for the triplet $1s3s$ configuration of $^6\text{Li}^+$, extrapolated near the minimum.
Figure 3.24: Dependence of probability on $\beta_1$ for the triplet 1s5s configuration of $^6\text{Li}^+$
Figure 3.25: Dependence of probability on $\beta_1$ for the triplet 1s5s configuration of $^6\text{Li}^+$, extrapolated near the minimum
Figure 3.26: Dependence of energy on $\beta_1$ for the triplet 1s5s configuration of $^6\text{Li}^+$.
Figure 3.27: Dependence of energy on $\beta_1$ for the triplet 1s5s configuration of $^6\text{Li}^+$, extrapolated near the minimum.
The parameters $\alpha_1$, $\alpha_2$, and $\beta_2$ had to be changed for each specific state of interest to obtain the starting values as input data for each calculation. This was done by looking at the nonlinear parameters of previously computed wave functions, and choosing the ones which best applied to the state. For example, if the purpose of the calculations was to find the probability of the atom being in the singlet, discrete $1s5s$ final configuration of $^6\text{Li}^+$, the nonlinear parameters of the previously created wave function describing the $1s5s$ final configuration of $^6\text{Li}^+$ were used. Once the three nonlinear parameters were chosen, they were written into the input file of the first program (DALLDVV.f). The remaining parameter, $\beta_1$, was then varied between 0.05 and 1.8. This meant that DALLDVV.f was run for every value $\beta_1$ took on, each time creating a pseudospectrum spanning all the possible bound and continuum states of $^6\text{Li}^+$. The closest representation to the real spectrum was near the fifth pseudostate, which approximates the true $1s5s$ configuration of the atom. The second program, OSC.f, then took the data from DALLDVV.f, and used it to calculate the state probability distribution. For every configuration, $\beta_1$ was divided into as many as 50 increments, with smaller incrementation in the regions near the minimum. Each time $\beta_1$ was changed, both programs needed to be run. In order to save time, a script file was created which automated the entire process.

Comparing the probability graphs to the energy graphs, it is evident that both stabilize around $\beta_1 \approx 1/n_2$. This was expected since these are singly excited states. The probability values corresponding to the local minima in the regions of stabilization are listed in Table 3.2. When rounded, the singlet values are the same as those of Wauters and Vaeck, which gives confidence that our values are not only correct, but also substantially more accurate. It can therefore be assumed that the triplet calculations are also correct. This is exciting because the triplet state calculations have never before been computed.

Comparing the singlet $1s3s$ and triplet $1s3s$ energy graphs shows that the triplet states do in fact lie lower in energy. The energies of the singlet and triplet $1s3s$ states are given by the minima, and are approximately $-4.733756(1)$ a.u. and $-4.7520764(1)$ a.u. respectively. As explained in Appendix 6.1, the triplet states are lower in energy due
to the antisymmetric spatial component of the wave function.

It is also interesting to note that the triplet graphs are less stable than the singlet graphs. It was more difficult to obtain data for the triplet states due to cancellation effects near $\alpha_1 \approx \beta_1$. This is again related to the antisymmetric spatial component of the wave function, given by Equation (6.2).

$$
\Psi^A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\Psi(\vec{r}_1, \vec{r}_2) - \Psi(\vec{r}_2, \vec{r}_1)].
$$

Since the overall wave function has to be antisymmetric, and the spin component of a triplet state is symmetric, the spatial part has to be antisymmetric. If $\alpha_1 \approx \beta_1$, $r_1$ and $r_2$ become interchangeable and the spatial component cancels itself out. To reduce cancellations in the calculations, only basis functions with $i \leq j$ are used, and terms which are symmetric under interchange can be divided out.

### 3.3 TOTAL PROBABILITY OF IONIZATION

The total probabilities of ionization are of great interest, especially to experimentalists at Argonne National Laboratories, who can observe this process in their experiments to measure the isotope shift for $^6$He. After $\beta^-$ decay, the daughter $^6$Li atom can undergo shake up and/or shake off. This means that the two orbital electrons can either be excited into higher bound states, or be ionized into the continuum. The state probability distributions can then be divided into the following three sections, with the energy thresholds given by Equation (3.3).

$$
^6\text{Li}^+, \quad E < -4.5 \text{ a.u.}
$$
$$
^6\text{Li}^{2+}, \quad -4.5 \text{ a.u.} \leq E \leq 0 \text{ a.u.}
$$
$$
^6\text{Li}^{3+}, \quad E > 0 \text{ a.u.}
$$

The total probability is calculated by simply summing over the probabilities in each section. These values are tabulated in Table 3.3 for both the singlet and triplet states. For a comparison, Table 3.4 contains other calculated and measured values.
### Table 3.3: Probabilities of ionization following $\beta^-$-decay from an initial state of $^6$He.

<table>
<thead>
<tr>
<th></th>
<th>He(1s$^2$ 1S) (%)</th>
<th>He(1s2s 3S) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>89.1 ± 0.2</td>
<td>88.72 ± 0.07</td>
</tr>
<tr>
<td>Li$^{2+}$</td>
<td>9.6 ± 0.3</td>
<td>Total 10.9 ± 0.5</td>
</tr>
<tr>
<td>Li$^{3+}$</td>
<td>1.3 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

Total probability of transition to bound discrete states, and probabilities of single or double ionization. Results for singlet and triplet configurations, without consideration of nuclear recoil ($p = 0$).

### Table 3.4: Comparison data for probabilities of ionization from the He(1s$^2$ 1S)

<table>
<thead>
<tr>
<th></th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Winther</td>
<td>Wauters and Vaeck</td>
</tr>
<tr>
<td></td>
<td>Without recoil (%)</td>
<td>Without recoil (%)</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>89.5 ± 1.5</td>
<td>89.09</td>
</tr>
<tr>
<td>Li$^{2+}$</td>
<td>10.5 ± 1.5</td>
<td>10.44*</td>
</tr>
<tr>
<td>Li$^{3+}$</td>
<td>0.32</td>
<td>0.018 ± 0.015</td>
</tr>
</tbody>
</table>

*autoionizing doubly excited states contribute 2.97% (7.47%+2.97%=10.44%)

These are the comparison values for the total probability of transitions to bound discrete states, and probabilities for single or double ionization. Theoretical values calculated by Winther [2], and Wauters and Vaeck [1] and do not include nuclear recoil. Experimental values were measured by Carlson et al, who managed to account for the nuclear recoil contribution [3].
Winther’s pioneering calculations of the transition probabilities resulting from the coulombic shaking of $^{6}\text{He}$ decaying into $^{6}\text{Li}^+$, were done using accurate Hylleraas ground state $(1s, 1s)$ and lowest singly excited state wave functions $(1s, n_2s)$, for both the initial and final systems. Hartree wave functions were then used for higher excited states of $^{6}\text{Li}^+$, up to $n_2 = 4$. The small contribution from the remaining $(1s, n_2s)$ excited states was estimated, to give the total probability of ionization [1, 3]. Wauters and Vaeck also calculated the electronic rearrangement resulting from the $\beta^-$- decay of $^{6}\text{He}$, using a numerical $B$-spline basis set approach. They tabulated results for excitation probabilities to specific discrete states of $^{6}\text{Li}^+$ (Table 3.2), as well as probabilities for single and double ionization. Finally, Carlson, Pleasonton, and Johnson measured the charge spectrum of $^{6}\text{Li}$ following the $\beta^-$- decay of $^{6}\text{He}$. The dependence of the charge spectrum on the recoil energy was measured by a specially designed mass spectrometer [3]. This method allowed for the measurement of the nuclear recoil contribution.

The total probability of the two electrons of the daughter $^{6}\text{Li}^+$ atom remaining bound was calculated to be $(89.1 \pm 0.2)\%$ for the singlet states, which is not within the range of Winther’s calculated value $(89.5 \pm 1.5)\%$, but is consistent with Wauters and Vaeck’s $(89.09)\%$. It is also not within range of the measured (without recoil) values of Carlson et al. $(89.9 \pm 0.2)\%$. The probabilities of single and double ionization were also not within range of any of the comparison values. In fact, the double ionization value $(1.3 \pm 0.2)\%$ was very inaccurate compared with the calculated value of $0.32\%$ (Wauters and Vaeck), and measured value of $(0.018 \pm 0.015)\%$. This indicates the calculations need some further improvements. However, it is encouraging that the total probability of ionization ($^{6}\text{Li}^{2+} + ^{6}\text{Li}^{3+}$) agreed with all three comparison values. Studying Tables 3.3 and 3.4, there are two interesting observations that can be made. First, the Li$^+$ and Li$^{2+}$ ionization probabilities are nearly independent of the initial state of helium. Second, even taking experimental recoil corrections into account, the calculated probabilities of Li$^{3+}$ disagree both with each other and none of the theories agree with the measured values. It is also important to note that all the triplet state calculations in this study have never been done. Therefore, any calculations involving
the triplet states are an excellent starting point for future research.

Finally, to determine the stability of the total probability of excitation to discrete states, and the probabilities of single and double ionization, the dependence of these probabilities on $\beta_1$ was plotted in Figures (28)-(38). The labels in the legend refer to different states of interest. The nonlinear parameters $\alpha_1$, $\alpha_2$, and $\beta_2$ used for these states were those which optimize the energy of that specific state.
Figure 3.28: Dependence of total probability of transitions to bound states on $\beta_1$ for the singlet configurations of $^6\text{Li}^+$. 
Figure 3.29: Dependence of total probability of transitions to bound states on $\beta_1$ for the singlet configurations of $^6\text{Li}^+$, zoomed in.
Figure 3.30: Dependence of first ionization probability on $\beta_1$ for the singlet configurations of $^6\text{Li}^{2+}$. 
Figure 3.31: Dependence of first ionization probability on $\beta_1$ for the singlet configurations of $^6\text{Li}^{2+}$, zoomed in.
Figure 3.32: Dependence of second ionization probability on $\beta_1$ for the singlet configurations of $^6\text{Li}^{3+}$.
Figure 3.33: Dependence of total probability of transitions to bound states on $\beta_1$ for the triplet configurations of $^6\text{Li}^+$. 
Figure 3.34: Dependence of total probability of transitions to bound states on $\beta_1$ for the triplet configurations of $^6\text{Li}^+$, zoomed in.
3. RESULTS AND DISCUSSION

Figure 3.35: Dependence of first ionization probability on $\beta_1$ for the triplet configurations of $^6\text{Li}^{2+}$.
Figure 3.36: Dependence of first ionization probability on $\beta_1$ for the triplet configurations of $^6\text{Li}^{2+}$, zoomed in.
Figure 3.37: Dependence of second ionization probability on $\beta_1$ for the triplet configurations of $^6\text{Li}^{3+}$. 
Figure 3.38: Dependence of second ionization probability on $\beta_1$ for the triplet configurations of $^{6}\text{Li}^{3+}$, zoomed in.
3. RESULTS AND DISCUSSION

Figures (28), (30), and (33) all show that as $\beta_1$ is incremented, the total probabilities follow an increasingly oscillating pattern. However, Figures (35), (37), and especially Figure (32), show a beat pattern. The oscillations start off large, and as $\beta_1$ is incremented they begin to decrease. After a certain point (a minimum in the oscillation pattern near a specific $\beta_1$), the oscillations begin to increase again. It is hypothesized that if $\beta_1$ is increased to larger values in the other graphs, the same pattern would appear. The oscillations can be used to determine an approximate error in the total probability values. In addition, since the oscillating pattern is similar for all states, it can be concluded that the results have no dependence on $\alpha_1$, $\alpha_2$, and $\beta_2$.

Each pseudospectrum was divided into three energy bins by the ionization thresholds given in Equation (3.4). All the pseudostates of a pseudospectrum fall within one of these bins. Each drop in the oscillating pattern in the graphs corresponds to a pseudostate falling through a threshold into another bin. In general, as $\beta_1$ increases the number of pseudostates in the Li$^+$ and Li$^{2+}$ bins decreases, and the number of pseudostates in the Li$^{3+}$ bin increases by the equivalent amount. This is because the total number of pseudostates remains constant, and is always equal to the number of terms in the basis set. The oscillating pattern of the Li$^+$ graphs are much cleaner than those of the other two bins. There are two reasons for this. First, there is only one ionization threshold which the pseudostates can cross ($E = -4.5$ a.u.). Each time $\beta_1$ is large enough, another pseudostate falls through this boundary, increasing the number of states in the Li$^{2+}$ bin. Since the Li$^{2+}$ bin has two thresholds ($E = -4.5$ a.u. and $E = 0$ a.u.), not only can the number of pseudostates increase, they can also decrease by falling through the second limit. In fact, the overall number of states in this bin decreases — there are more pseudostates being lost than gained. This results in a more random and unstructured oscillating pattern. The second reason the total probability of Li$^+$ graphs have a cleaner oscillating pattern is because this bin has the largest total probability and the most defined ionization threshold. The Li$^+$ bin contains roughly 15 pseudostates and represents as much as $(89.1 \pm 0.2)\%$ of the total probability, where as the Li$^{2+}$ and Li$^{3+}$ bins usually contain as many as 50 and 400 pseudostates respectively. Since the Li$^+$ bin has by far the lowest number of
pseudostates, each time a pseudostate falls into another bin it has a drastic effect on the total probability, causing a clear drop in the graphs.
Chapter 4

Conclusion

Hylleraas-like wave functions were used to create a pseudospectrum which spanned the real singlet and triplet energy spectrum of $^6$Li$^+$ following the $\beta^-$ decay of $^6$He, in the framework of the sudden approximation. The initial states were the $1^1S_1$ and $2^3S_1$ configurations of $^6$He. It is evident that this method can be used to obtain correct probabilities for transitions to bound states of $^6$Li$^+$ (Table 3.2). The Stieltjes imaging graphs had several peaks, representing the first ionization threshold, and numerous doubly excited autoionizing states. The dependence of energy and probability on the nonlinear parameter $\beta_1$ was also examined, and found that both stabilized around the same $\beta_1$ value ($\beta_1 \approx 1/n_2$). In addition, the total probabilities of transitions to bound states and the total probabilities of single and double ionization were also calculated (Table 3.3). It was observed that the total Li$^+$ and Li$^{2+}$ probabilities are nearly independent of the initial state of helium. It is also interesting that the calculated probability of Li$^{3+}$ disagrees with other theoretical values and none of the theories agree with experimental values. Finally, it was concluded that all three of the total probabilities were nearly independent of all the nonlinear parameters except $\beta_1$. 

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Chapter 5

Future Work

This research can be improved and extended in numerous ways. The results can be made more complete by including the recoil momentum operator, which should have a direct effect on the probabilities (Table 3.4). This opens the door for many research areas, such as incorporating transitions to states with higher angular momentum. Levinger accounted for nuclear recoil after $\beta^-$ decay with a first approximation general expression in terms of the atomic number $Z$. His calculations were simplified by the sudden approximation, and the use of nonrelativistic Coulomb wave functions [34]. Wauters et al. also included nuclear recoil in their studies of the electronic redistribution of one and two electron ions, however these involved only the emission or capture of a neutral particle by the nucleus. Thus, calculations for the $\beta^-$ decay specific to $^6$He incorporating nuclear recoil have never been done [11].

The overall accuracy can be increased by enlarging the basis set or adding a third set of nonlinear parameters. Since $\alpha_i$ and $\beta_i$, $i = 1, 2, 3$ set the distance scales along $r_1$ and $r_2$ respectively, the third set of nonlinear parameters would break up the representation of the wave function into three sections: the asymptotic, intermediate, and close range regions. This allows for a better approximation of the wave functions.

The probability values for each state were found by studying the dependence of
probability on $\beta_1$, and taking the value at the local minimum in the region of stabilization. This process is long and tedious. To reduce the amount of time and effort spent on finding the local minima of these graphs, $\beta_1$ can be optimized using Newton’s method over the regions of stabilization. This method was already used to optimize the nonlinear parameters (discussed in Section 2.6.1) to get the lowest energy. To determine the best probability, $\beta_1$ can be optimized by taking the analytical first derivative of the probability amplitude [Equation (1.9)] with respect to $\beta_1$ and applying Newton’s method until the change is smaller than the machine accuracy. This would also ensure greater accuracy in the probability results. It would also be interesting to see the resulting probabilities when using the already optimized minimum energy $\beta_1$ value. If this $\beta_1$ is sufficient for obtaining the minimum probability, it would not have to be optimized a second time with respect to probability.

More specifically, emphasis can be placed on increasing the accuracy in the single and double ionization probabilities. These total values were calculated by simply summing the probabilities of the pseudostates within each specific region of the energy spectrum [Equation (3.4)]. The pseudostates which lie very close to the thresholds can cause oscillations in the results. Fitting a polynomial function over this portion of the data may reduce some of the scattering and give greater consistency in the results. Ultimately, using the converged close coupling (CCC) method would give the most precise results [35]. Also, applying the Stieltjes imaging technique to the graphs which focus on the dependence of the total probabilities of Li$^+$, Li$^{2+}$, and Li$^{3+}$ on $\beta_1$, may significantly smooth the oscillations to provide more accurate total probabilities of ionization.

The calculations could also be done using different initial $^6$He states. Because of its long lifetime in comparison to other metastable states, the 1s2s singlet initial state is a good starting point [36]. It would be interesting to compare the results of such calculations with those of the 1s2s triplet initial state, to study the spin dependence. Finally, this research can also be extended to calculate transition probabilities of other two electron systems undergoing $\beta^-$, or even $\beta^+-$ decays, such as Ne$^{8+}$. 
6.1 Para and Ortho Helium

According to Pauli’s exclusion principle, helium, because it is a two electron system, must have an antisymmetric wave function. The overall wave function with spatial and spin components for the two electron configuration is given by

$$\Psi(1, 2) = \begin{cases} 
\Psi^S(r_1, r_2)\chi^A(1, 2) \\
\text{or} \\
\Psi^A(r_1, r_2)\chi^S(1, 2)
\end{cases}$$  \hspace{1cm} (6.1)

where $\Psi(r_1, r_2)$ and $\chi(1, 2)$ are the spatial and spin eigenfunctions respectively. The antisymmetric and symmetric forms of the spatial component are

$$\Psi^A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}[\Psi(\vec{r}_1, \vec{r}_2) - \Psi(\vec{r}_2, \vec{r}_1)].$$  \hspace{1cm} (6.2)

$$\Psi^S(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}[\Psi(\vec{r}_1, \vec{r}_2) + \Psi(\vec{r}_2, \vec{r}_1)].$$  \hspace{1cm} (6.3)
In contrast, the spin eigenfunctions have four possible configurations. One antisymmetric and three symmetric.

\[
\chi^A(1,2) = \frac{1}{\sqrt{2}} (\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2) \quad (6.4)
\]

\[
\chi^S(1,2) = \begin{cases} 
\uparrow_1 \uparrow_2 \\
\frac{1}{\sqrt{2}} (\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2) \\
\downarrow_1 \downarrow_2
\end{cases} \quad (6.5)
\]

The combination of spatial and spin eigenfunctions produce the singlet (parahelium) and triplet (orthohelium) configurations accordingly. Given that the overall wave function must be antisymmetric, a symmetric triplet spin function must be multiplied with an antisymmetric spatial eigenfunction, or an antisymmetric singlet spin function must be multiplied with a symmetric spatial eigenfunction.

While the ground state of helium can have only the singlet configuration, the excited states exist in both forms. It is a general feature that the triplet states always lie lower in energy than those of the singlet, as can be seen in Figure (6.1). This observation can be explained by the fact that the triplet state has an antisymmetric spatial function which vanishes if \( r_1 = r_2 \). Hence, the probability of finding the two electrons close together is very low. This extra separation between them allows the electrons to experience less coulomb repulsion and more attraction from the nucleus, thus, giving them a lower energy \([37]\).
6.2 Derivation of the Sudden Approximation Criterion

An adiabatic process is a slowly applied perturbation to a system. The time, $T$, during which the modification takes place is very large. The adiabatic theorem states:

*If the time $T$ is sufficiently large ($T \to \infty$), and the system is initially in an eigenstate of $H(t_0)$, it will have passed into a corresponding eigenstate of $H(t_1)$; i.e. is derived from it by continuity.*

The following is the calculation for the condition for the sudden approximation [9].

Given the initial state of the system at $t_0$, the evolved state at a later time $t_1$ will be derived using:

$$| \Psi(t) \rangle = \hat{U}(t, t_0) \, | \Psi(t_0) \rangle$$  \hspace{1cm} (6.6)
where
\[ \hat{U}(t, t_0) = 1 - \frac{i}{\hbar} T \int_0^s H(s) U_T(s) ds \quad \text{and} \quad s = \frac{(t - t_0)}{T}. \] (6.7)

\( \hat{U}(t, t_0) \) is the operator describing the evolution in time of the system and \( H(s) \) is the value of the Hamiltonian at time \( t = t_0 + sT \). It is obvious that as \( T \to 0 \), \( \hat{U}(t, t_0) = 1 \).

The sudden approximation assumes that
\[ \hat{U}(t, t_0) | \Psi(t_0) \rangle \approx | \Psi(t_0) \rangle. \] (6.8)

To find the validity of this approximation, the probability of finding the system in a state other than initial is calculated. The state vector at time \( t_0 \), \( | \Psi(t_0) \rangle \), will be from here on written as \( | 0 \rangle \).

\[ \tilde{\omega} = \langle 0 | \hat{U}^\dagger(t, t_0) \hat{U}(t, t_0) | 0 \rangle - \langle 0 | \hat{U}^\dagger(t, t_0) | 0 \rangle \langle 0 | \hat{U}(t, t_0) | 0 \rangle. \] (6.9)

Expanding the time evolution operator gives
\[ \hat{U}(t, t_0) = 1 + \frac{1}{i\hbar} \int_{t_0}^{t_1} \hat{H}(t) dt + \frac{1}{(1\hbar)^2} \int_{t_0}^{t_1} dt' \int_{t_0}^{t'} dt'' \hat{H}(t') \hat{H}(t'') \cdots. \] (6.10)

Using the equivalency
\[ \frac{1}{T} \int_{t_0}^{t_1} \hat{H} dt \equiv \tilde{H} \] (6.11)
and the first two terms of the time evolution operator expansion, and substituting them into \( \tilde{\omega} \) derives the expression
\[ \tilde{\omega} = \frac{T^2}{\hbar^2} (\langle 0 | \tilde{H}^2 | 0 \rangle - \langle 0 | \tilde{H} | 0 \rangle \langle 0 | \tilde{H} | 0 \rangle) \] (6.12)
\[ = \frac{T^2}{\hbar^2} \Delta \tilde{H}^2 \] (6.13)

\( \Delta \tilde{H} \) is the root mean square deviation of the observable \( \tilde{H} \) — the average time it takes the system to change from one state to another. The sudden approximation is then valid when \( \tilde{\omega} \ll 1 \). The outcome is the criterion for the diabatic process:
\[ T \ll \frac{\hbar}{\Delta \tilde{H}} \] (6.14)

This result shows that the state of the system cannot be appreciably changed until the time \( \frac{\hbar}{\Delta \tilde{H}} \) expires [9].
6. APPENDIX

6.3 Derivation of the Infinite Nuclear Mass Schrödinger Equation

Starting from the general Schrödinger equation for a three body system

\[
\left[ -\frac{\hbar^2}{2m_1}\nabla^2_1 - \frac{\hbar^2}{2m_2}\nabla^2_2 - \frac{\hbar^2}{2m_3}\nabla^2_3 + \frac{q_1q_2}{|R_1 - R_2|} + \frac{q_1q_3}{|R_1 - R_3|} + \frac{q_2q_3}{|R_2 - R_3|} \right] \Psi = E_{NR}\Psi
\]

and using the center of mass transformations defined in Equation (2.2)

\[
\begin{align*}
\mathbf{r}_1 &= \mathbf{R}_1 - \mathbf{R}_3 \\
\mathbf{r}_2 &= \mathbf{R}_2 - \mathbf{R}_3 \\
\mathbf{R}_{CM} &= \frac{m_1\mathbf{R}_1 + m_2\mathbf{R}_2 + m_3\mathbf{R}_3}{m_1 + m_2 + m_3}
\end{align*}
\]

the differential operators are [Equation (2.3)]

\[
\begin{align*}
\nabla_1 &= \frac{m}{2m + M} \nabla_{R_{CM}} - \nabla_{r_1} \\
\nabla_2 &= \frac{m}{2m + M} \nabla_{R_{CM}} - \nabla_{r_2} \\
\nabla_3 &= \frac{M}{2m + M} \nabla_{R_{CM}} - \nabla_{r_1} - \nabla_{r_2}
\end{align*}
\]

Substituting these into the Schrödinger equation above, and keeping in mind that that \(m_3 = M\), the mass of the nucleus, \(m_1 = m_2 = m_e = m\), the mass of an electron, \(q_i = eZ_i\), the charges, and \(r_{12} = |r_2 - r_1|\), is the distance between the electrons, results in

\[
\left\{ -\frac{\hbar^2}{2} \left[ \left( \frac{1}{m} + \frac{1}{M} \right) \nabla^2_{r_1} + \left( \frac{1}{m} + \frac{1}{M} \right) \nabla^2_{r_2} + \left( \frac{1}{2m + M} \right) \nabla^2_{R_{CM}} \right] - \frac{2}{M} \nabla_{r_1} \cdot \nabla_{r_2} \right\} \Psi = E_{NR}\Psi.
\]

Since there are no outside forces acting on the atom, the center of mass dependence can be ignored, eliminating the third term.

\[
-\frac{\hbar^2}{2} \left[ \frac{1}{\mu} \nabla^2_{r_1} + \frac{1}{\mu} \nabla^2_{r_2} - \frac{2}{M} \nabla_{r_1} \cdot \nabla_{r_2} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \right] \Psi = E_{NR}\Psi
\]

can be derived by using the inverse of the reduced mass, \(\mu = \frac{Mm}{M+m}\), and multiplying by \(\frac{\mu}{\hbar^2} \). Finally, reducing to atomic units with the distance conversion \(a_\mu = \frac{\hbar^2}{\mu e^2}\), and
dropping the mass polarization cross term, (because $\frac{\mu}{M} \ll 1$), gives the expression for the infinite nuclear mass Schrödinger equation.

$$\left( \frac{1}{2}\nabla^2_{r_1} - \frac{1}{2}\nabla^2_{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi(r_1, r_2) = E_{NR}\Psi(r_1, r_2) \quad (6.16)$$

The solution of this equation gives the nonrelativistic energy $E_{NR}$. The relationship $\epsilon = \frac{a_0}{\epsilon^2} E$ scales the energy back into laboratory units.

### 6.4 Derivation of Angular Integral

The general overlap integral of two states is given by

$$I(a, b, c; l_1, m_1, l_2, m_2; \alpha, \beta) = \int_\nu d\tau R(i', j', k') Y_{l_1}^{m_1*}(\theta_1, \phi_1) R(i, j, k) Y_{l_2}^{m_2*}(\theta_2, \phi_2). \quad (6.17)$$

where $\nu$ represents volume. Because of the conversion to Hylleraas coordinates, the position of the second electron must be expressed relative to the new direction, $r_1$. So the spherical harmonic of the second electron is then be represented in terms of the rotation matrix by the expression

$$Y_{l_2}^{m_2}(\theta_2, \phi_2) = \sum_M D_{m_2, M}^{l_2*}(\phi_1, \theta_1, \chi) Y_{l_2}^M(\theta, \phi)$$

Since $r_{12}$ is now an independent variable, the polar angles $\theta_2$ and $\phi_2$ of $r_2$ are dependent. The new angles $\theta$ and $\phi$ are the polar angles of $r_2$ with respect to $r_1$. The spherical harmonic of the first electron is a special case of the rotation matrix with $M = 0$. If Equations (2.46) and (2.47)

$$Y_{l_1}^{m_1*}(\theta_1, \phi_1) = \sqrt{\frac{2l_1 + 1}{4\pi}} D_{m_1, 0}^{l_1*}(\phi_1, \theta_1, \chi)$$

$$P_{l_2}(\cos\theta) = \sqrt{\frac{4\pi}{2l_1 + 1}} Y_{l_2}^0(\theta, \phi)$$

are inserted into Equation (6.17), it results in

$$I(a, b, c; l_1, m_1, l_2, m_2; \alpha, \beta) = 2\pi \delta_{l_1 l_2} \delta_{m_1 m_2} \int_\nu d\tau R I_{l_2}(R'R), \quad (6.18)$$

where the radial integral is defined by

$$I_{l_2}(R'R) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12} dr_{12} r_1^a r_2^b e^{-\alpha r_1 - \beta r_2} P_{l_2}(\cos\theta).$$
The next step is to apply the same principles to a more general situation, one which involves vector coupled spherical harmonics. The general integral under these circumstances has the form

\[ I(l_1, m_1, l_2, m_2; \alpha, \beta) = \int \nu \, d\tau R(i', j', k')(r_1, r_2) \mathcal{Y}^M_{l_1 l_2 L}(r_1, r_2) \mathcal{Y}^M_{l_1 l_2 L}(r_1, r_2). \] (6.19)

To evaluate this, one must keep in mind that [25]

\[ Y^M_L(\hat{r}) = (-1)^M Y^{-M}_L(\hat{r}), \] (6.20)

\[ \mathcal{Y}^M_{l_1 l_2 L}(r_1, r_2) = \sum_{m_1 m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle Y^{m_1}_{l_1}(r_1) Y^{m_2}_{l_2}(r_2), \] where (6.21)

\[ Y^{m_1'}_{l_1'}(r_1) Y^{m_1}_{l_1}(r_1) = \sum_{LM} \left[ \frac{(2l_1 + 1)(2l'_1 + 1)(2L + 1)}{4\pi} \right]^{1/2} Y^M_{l_1 l_2 L}(r_1) \times \left( \begin{array}{ccc} l & l' & L \\ m_1 & m_1' & M \end{array} \right) \left( \begin{array}{ccc} l & l' & L \\ 0 & 0 & 0 \end{array} \right). \] (6.22)
The integral can then be derived. [25]

\[
I = \int \sum_{l_1 m_1} \sum_{l_2 m_2} \langle l_1 l_2 m_1 m_2 | L'M' \rangle Y_{l_1}^{m_1} (\hat{r}_1) Y_{l_2}^{m_2} (\hat{r}_2)
\]

\[
= \int \sum_{l_1 m_1} \sum_{l_2 m_2} \langle l_1 l_2 m_1 m_2 | L'M' \rangle (l_1 l_2 m_1 m_2 | L'M)
\]

\[
= \sum_{\Lambda} \sum_{\Lambda'} \sum_{\Lambda M} \left[ \frac{(2l_1' + 1)(2l_1 + 1)(2l_2 + 1)(2l_2' + 1)(2\Lambda' + 1)}{4\pi} \right]^{1/2}
\]

\[
\times \left( \begin{array}{ccc} l_1' & l_1 & \Lambda \\ -m_1' & m_1 & 0 \end{array} \right) \left( \begin{array}{ccc} l_1' & l_1 & \Lambda \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_2' & l_2 & \Lambda' \\ -m_2' & m_2 & M' \end{array} \right) \left( \begin{array}{ccc} l_2' & l_2 & \Lambda' \\ 0 & 0 & 0 \end{array} \right)
\]

\[
= \int \sum_{\Lambda} \sum_{\Lambda M} \left[ \frac{2\Lambda + 1}{4\pi} D_{M,0}^{\Lambda,\Lambda'}(\theta_1, \phi_1, \chi) \sum_{\Lambda N} \right]
\]

\[
= \int \sum_{\Lambda} \sum_{\Lambda M} C_\Lambda P_\Lambda (\cos \theta)
\]

The constant then \(C_\Lambda\) simplifies to

\[
C_\Lambda = \frac{1}{2} \left[ \frac{(2l_1' + 1)(2l_1 + 1)(2l_2 + 1)(2l_2' + 1)}{4\pi} \right]^{1/2} \frac{\Lambda + \Lambda'}{2\Lambda + 1} \frac{1}{4\pi} \frac{2\Lambda + 1}{4\pi} \delta_{\Lambda M} \delta_{\Lambda N} P_\Lambda (\cos \theta)
\]

6.5 The Power Method

Let \(H\) be and \(N \times N\) matrix with \(N\), \(\vec{N}\) linearly independent eigenvectors, and \(E_N\) eigenvalues fitting the criterion \(|E_1| > |E_2| \geq |E_3| \geq \cdots \geq |E_N|\). Meaning, the magnitudes of the eigenvalues must increase in progression, and more importantly, the eigenvalue corresponding to the lowest eigenstate must be clearly bigger than all the
rest. Let \( x_0 \) be any starting vector

\[
x_0 = c_1 \phi_1 + c_2 \phi_2 + \cdots + c_N \phi_N. \tag{6.27}
\]

Allowing \( H \) to act on the \( x_0 \) repeatedly gives

\[
Hx_0 = c_1 E_1 \phi_1 + c_2 E_2 \phi_2 + \cdots + c_N E_N \phi_N
\]

\[
H^2 x_0 = c_1 E_1^2 \phi_1 + c_2 E_2^2 \phi_2 + \cdots + c_N E_N^2 \phi_N
\]

\[
\vdots
\]

\[
H^m x_0 = c_1 E_1^m \phi_1 + c_2 E_2^m \phi_2 + \cdots + c_N E_N^m \phi_N \tag{6.28}
\]

where \( m \) is an integer representing the iteration index [17]. This is equivalent to letting \( H \) act on each progressive eigenvector.

\[
Hx_0 = c_1 E_1 \phi_1 + c_2 E_2 \phi_2 + \cdots + c_N E_N \phi_N = x_1
\]

\[
Hx_1 = c_1 E_1^2 \phi_1 + c_2 E_2^2 \phi_2 + \cdots + c_N E_N^2 \phi_N = x_2
\]

\[
\vdots
\]

\[
Hx_{m-1} = c_1 E_1^m \phi_1 + c_2 E_2^m \phi_2 + \cdots + c_N E_N^m \phi_N = x_m \tag{6.30}
\]

The vector \( x_m \) approaches the true eigenvector of \( H \) as \( m \) becomes very large. Since \( |E_1| > |E_i|, m \to \infty \), and \((E_i/E_1)^m \to 0 \) (for \( i = 1, 2, 3, \cdots, N - 1 \)), dividing the last expression by \( E_1^m \) results in

\[
\frac{x_m}{E_1^m} = c_1 \left( \frac{E_1}{E_1} \right)^m \phi_1 + c_2 \left( \frac{E_2}{E_1} \right)^m \phi_2 + \cdots + c_N \left( \frac{E_N}{E_1} \right)^m \phi_N
\]

\[
\frac{x_m}{E_1^m} = c_1 \phi_1 + c_2 \left( \frac{E_2}{E_1} \right)^m \phi_2 + \cdots + c_N \left( \frac{E_N}{E_1} \right)^m \phi_N
\]

\[
x_m = c_1 E_1^m \phi_1. \tag{6.32}
\]

From Equation (6.32) it can be deduced that

\[
x_{m+1} = c_1 E_1^{m+1} \phi_1 = E_1 x_m = Hx_m. \tag{6.33}
\]
So far, this method can only be used to find the largest eigenvalue. Taking $E_i$ as the energy eigenvalue of the state of interest, and manipulating Equation (6.33) into an inverse eigenvalue problem

$$
\mathbf{H} x = E_i \mathbf{O} x
$$

$$(\mathbf{H} - E_g \mathbf{O}) x = (E_i - E_g) \mathbf{O} x$$

$$(\mathbf{H} - E_g \mathbf{O})^{-1} \mathbf{O} x = \frac{1}{(E_i - E_g)x}$$

$$\mathbf{G} x = E' x$$

(6.34)

where $\mathbf{G} = (\mathbf{H} - E_g \mathbf{O})^{-1} \mathbf{O}$ and $E' = 1/(E_i - E_g)$, will make it possible to solve for any of the $N$ eigenvalues. Choosing a guess energy $E_g$, close to the desired eigenvalue $E_i$, will make $E'$ dominant over all the rest. The upper triangular matrices resulting from the process are solved by the square root method, giving the coefficients for the eigenvector $x_i$.

### 6.6 The Jacobi Method

One of the most useful methods for finding solutions to matrix equations, and the method used to diagonalize the matrices for the final pseudostates of $^6$Li, is that of Jacobi. It consists of solving a matrix equation of the form

$$\mathbf{A} x = \mathbf{b}$$

(6.35)

with the convergence condition that each row is dominated by the diagonal element. Mathematically, this is expressed as

$$|a_{ii}| > \sum_{i \neq j} |a_{ij}| .$$

(6.36)

The process is started by breaking the matrix $\mathbf{A}$ into three parts, $\mathbf{D}$ the diagonal component, $\mathbf{M}$ the upper triangular part, and $\mathbf{N}$ the lower triangular part of $\mathbf{A}$.

$$\mathbf{A} = \mathbf{D} + \mathbf{M} + \mathbf{N}$$

(6.37)

$$
\begin{bmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{bmatrix} =
\begin{bmatrix}
a_{11} & 0 \\
0 & a_{22}
\end{bmatrix} +
\begin{bmatrix}
0 & a_{12} \\
0 & 0
\end{bmatrix} +
\begin{bmatrix}
0 & 0 \\
a_{21} & 0
\end{bmatrix}
$$
Substituting this back into Equation (6.35) gives

\[
\begin{align*}
Ax &= b \\
(D + M + N)x &= b \\
(D - 1)x &= b - (M + N)x \\
x &= D^{-1}b - D^{-1}(M + N)x \\
\end{align*}
\] (6.38)

With the careful choice of the initial guess for \( x_0 \), the iteration

\[
x_{k+1} = D^{-1}b - D^{-1}(M + N)x_k
\] (6.39)

is repeated until the convergence criteria

\[
\frac{\|b - Ax_k\|}{\|b\|} < \epsilon
\] (6.40)

is met, where \( \epsilon \) is a chosen precision value. Each time \( x \) is calculated, it is tested in Equation (6.35). When it fits the convergence criteria, the iteration process is stopped, and \( x_k \) is an eigenvector.
References


REFERENCES


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