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Nonrelativistic Operators for Relativistic Transition Rates

By

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Nonrelativistic Operators for Relativistic Transition Rates

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Declaration of Originality

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Abstract

The Dirac equation provides a fully relativistic covariant equation which can be used to calculate relativistic transition rates but only for one-electron systems. For the two-electron case, one can either use approximate relativistic wave functions or obtain equivalent nonrelativistic operators that can be used with Schrödinger wave functions; an approach that is preferred for low atomic number (Z) atoms. By using equivalent nonrelativistic operators obtained from the Foldy-Wouthuysen transformation and relativistically corrected Schrödinger wave functions, we show that we obtain the same transition amplitude as in Dirac Theory up to order α^2, where α is the fine structure constant. We show this for the one-electron case and provide a theoretical framework for the two-electron case. For the one-electron case we obtain analytic first order corrected wave functions for the $2p$ states which have not been published before. For the two-electron case we obtain first order corrected wave functions using a variational method and compare two different Sturmian basis sets, which we label triangular and linear basis sets. We show that the triangular basis set provides a significant advantage over the linear basis set, increasing the precision by two orders of magnitude. We also compare the wave functions obtained using pseudostates with those obtained analytically and give some suggestions to improve the agreement near zero.

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Chapter 1

Introduction

Transition probabilities give the probability that an atom will undergo a transition from one atomic state to another due to interactions with electromagnetic fields. These probabilities are used to calculate oscillator strengths and transition rates. They are used extensively to determine the brighteness of atomic spectral lines in spectroscopy.

Accurate relativistic transitions probabilities, which include relativistic corrections, are needed in astrophysics for the interpretation of radiation intensities to determine the temperature and density of the source [3], as well as relative chemical abundances [4]. Chemical abundances are important in determining both the structure and evolution of stars, enabling one to understand the internal structure of stars [5]. Space spectrometers such as those on the Hubble, FUSE and Spitzer space observatories, now have a much higher resolving power giving detailed spectra which demand accurate transition probabilities [6]. Also the observation of some spin-forbidden transitions in astrophysics [7] can only be explained by relativistic treatment [8]. Plasma physics also require reliable spectral data for plasma modelling and diagnostics [6]. The relativistic transition probabilities (along with thermodynamics) will also allow for measurements of the temperature in fusion plasmas [9].

These are of use for projects such as the ongoing international ITER project [10] in France, which hopes to make a reliable carbon-free energy source from the fusion of deuterium and tritium [11]. The plasma particles are heated, and fusion is achieved in a tokomak device that uses magnetic fields to contain and control the hot plasma. The tokomak uses tungsten in the divertor [12], which has a high atomic number, and thus relativistic corrections are once again important in analysing the light emitted by tungsten ions [13].

The Dirac theory provides a fully covariant relativistic theory which we can use to calculate relativistic transition rates for one-electron systems. Thus in order to calculate the relativistic transition probability we only need to evaluate:

$$\left\langle \Psi_j^D | \vec{\alpha} \cdot \mathbf{A} | \Psi_i^D \right\rangle \tag{1.1}$$

where $\mathbf{A}$ is the vector potential for the emitted or absorbed photons and $\left|\Psi^D\right\rangle$ represent Dirac wave functions.

However, it is a much more difficult problem for many-electron systems as there is no such thing as a two-electron Dirac equation [14]. For low atomic number (Z) helium-like ions, the approach that is often used is to start with a nonrelativistic Hamiltonian with relativistic and QED corrections added by successive orders of perturbation theory. Since the relativistic effects are of order $(\alpha Z)^2$ or higher, it is not appropriate to do a perturbation expansion for helium-like ions that have a large Z. On the other hand, due to the dominant Coulomb field in large Z atoms the electron correlation effects decrease in proportion to $\frac{1}{Z}$ relative to the energies [15].

The high Z region is therefore the region when the relativistic effects become larger than correlation effects; i.e, when $(\alpha Z)^2 > \frac{1}{Z}, \text{or}, \mathrm{Z} > 26$ [15]. For high Z, two approaches can be used. Since relativistic effects dominate one can start with the one-electron Dirac equation, which has relativistic effects included to all orders, and treat the electron correlation as a perturbation. One can also use the Multiconfigurational Dirac Fock Method (MCDF), which is a self-consistent procedure that uses a completely relativistic basis [16]. However, there are a number of difficulties. In relativity the total number of particles is not conserved rather only the charge is and it cannot be written in Hamiltonian form as it is not fully relativistically covariant. Thus, all practical calculations use an effective electron-electron interaction [17]. Additionally, due to the negative energy solutions of the Dirac Hamiltonian, the calculations of bound states must be restricted to the positive energy subspace through the use of projection operators to prevent the "Brown and Ravenhall Disease [18] in which a variational solution may collapse into the negative energy continuum.

It should be noted that in the nonrelativistic case approximations are added to reduce the complexity of the calculations, while in the relativistic case the lack of a fully covariant closed form of the Hamiltonian is a fundamental problem [19] and approximations are needed to formulate the mathematical model. In general, it is easier to perform accurate nonrelativistic calculations than accurate relativistic calculations [20], as the wave functions are less complex and we have a two-electron Schrödinger Hamiltonian. Starting with the nonrelativistic case and adding relativistic corrections may be an approach that will turn out to be both more practical and more accurate than *a priori* relativistic calculations for many- electron systems [20]. At least for low Z, where correlation effects are more important, a nonrelativistic approach would be preferred.

Relativisitic transition probabilities for hydrogen, and hydrogenlike ions have been calculated almost exactly, leaving only small quantum electrodynamic (QED) corrections to be included [21]. For helium and helium-like ions Drake [22] developed the "Unified Method" in 1988, which extended the high precision varational results valid at low Z to those at intermediate and high Z by merging the $\frac{1}{Z}$ expansions from nonrelativistic energies with the $(\alpha Z)^2$ expansions from Dirac energies. This was used for very accurate calculations for the helium isoelectronic sequence and isolectronic transition probabilities which included relativistic effects. Using the Foldy-Wouthuysen method, which is a canonical transformation used in relativistic quantum mechanics to decouple the positive energy states from the negative states to some desired order, Drake [23] developped a theory of relativistic magentic dipole transitions and also applied it to the length form of electric dipole transitions [7]. Lin[24] again used the Foldy-Wouthuysen transformation and presented an interaction Hamiltonian for electric dipole transitions in helium-like systems. The resulting interaction Hamiltonian, used with relativistically corrected wave functions, via the Breit interaction, should enable the evaluation of relativistic transition probabilities. Also, due to the Foldy-Wouthuysen transformation, the operators in the interaction Hamiltonian are nonrelativistic operators which enables us to use nonrelativistic wave functions and also fully take into account electron correlation effects.

1.1 Purpose

This work investigates the Foldy-Wouthuysen method as a technique to calculate relativistic corrections to electric dipole transitions. This method starts from the nonrelativistic case and relativistic corrections will have to be included in both the wave functions and the operator, up to order $(\alpha Z)^2$. We will consider especially spin allowed transitions. While the ultimate goal is to use the interaction Hamiltonian from Lin [24] to do calculations in two-electron systems, the present work investigates the validity of Lin's method by first testing it for one-electron systems, for which we have exact relativistic results to compare with. Furthermore, in order to calculate the relativistic corrections to the wave functions we will investigate two different Sturmian basis sets for the pseudospectral method, and compare them with calculated analytic wave function corrections.

The goal is to show that by using equivalent nonrelativistic operators and relativistically corrected Schrödinger wave functions we can obtain the same results as using relativistic operators and Dirac wave functions, correct up to some fixed order in powers of the fine structure constant $\alpha = \frac{e^2}{\hbar c}$ while $Z = 1$ as we are considering the hydrogenic case. Thus we would like to show that

$$\left\langle \Psi_j^D | \vec{\alpha} \cdot \mathbf{A} | \Psi_i^D \right\rangle = \left\langle \Psi_j^{(0)} + \alpha^2 \Psi_j^{(1)} | T^{(0)} + \alpha^2 T^{(1)} | \Psi_i^{(0)} + \alpha^2 \Psi_i^{(1)} \right\rangle \tag{1.2}$$

where $\left|\Psi^D\right\rangle$ are Dirac wave functions, $\left|\Psi^{(0)}\right\rangle$ are Schrödinger wave functions, $\left|\Psi^{(1)}\right\rangle$ are the first order relativistic correction to the Schrödinger wave function and $T^{(0)}$ is the usual nonrelativistic transition operator and $T^{(1)}$ are the equivalent nonrelativistic transition operators obtained from the Foldy-Wouthuysen transformation. The equality sign is valid up to order α^2. We prove this for the one-electron case and obtain the necessary operators and analytic wave functions. We also compare the analytic results with those obtained from variational methods (which will be required to extend this to the two-electron case).

Chapter 2 discusses the transition operator and the interaction Hamiltonian. Chapter 3 discusses the Foldy-Wouthuysen transformation and the corrections to the nonrelativistic transition operator, as well as the different terms needed to calculate the transition integral. Chapter 4 discusses the theory of the pseudospectral method. Chapter 5 focuses on corrections to the wave functions; we compare two different basis sets used for generating the wave functions and obtain analytic wave functions to use as a reference. Chapter 6 presents the results with discussion. And Chapter 7 presents the conclusion and suggestions for future work.

Chapter 2

Transition Operator

In this chapter, we will discuss the interaction of an atom with an electromagnetic radiation field. When discussing the emission or absorption of electromagnetic energy by an atom, we usually employ the method of quantum mechanical perturbation theory [25]. One assumes that the atom and electromagnetic field are loosely coupled, and that the atom is a separate entity [26, p.32]. In this approximation, we can separate the entire wave function describing the system into a product of two wave functions. Thus, we consider two quantum-mechanical systems, in our case the atom and the electromagnetic field, with an interaction energy [25]. This interaction is regarded as perturbation, which will cause transitions. These transitions are changes of the atom state which result in the emission or absorption of one or more photons.

In 1916, Einstein proposed three processes by which such transitions could occur, and gave them corresponding coefficients which are now called "Einstein Coefficients". Einstein Coefficients are related to the probability of absorption or emission of light by an atom. Einstein A coefficients are for spontaneous emission, they are related to the probability that an atom sponatenously emits a photon, and are in units of s^{-1} [26, p.43]

$$A_{ji} = \frac{1}{4\pi\epsilon_0}\frac{4}{3}\frac{\omega_{ji}^3}{\hbar c^3}\frac{e}{m}|\left\langle\Psi_j|H_{int}|\Psi_i\right\rangle|^2 \tag{2.1}$$

where i and j are two different states of the atom, H_{int} is the interaction hamiltonian between the two states of the atomic system and ω_{ij} corresponds to the frequency of the transition between the two states. The above expression is for an unpolarized field.

The two coefficients are related to each other by the relation [26, p.35]

$$A_{ji} = \frac{\omega_{ij}^2}{\pi^2 c^3}\hbar\omega_{ij}B_{ji} \tag{2.2}$$

Einstein B coefficients are for absorption (which is related to the probability that the atom absorbs a photon) and stimulated emission (which is related to the probability to emit a photon under the influence of an incoming photon).

In spectroscopy, oscillator strengths are more often used. These are dimensionless quantities that describe the probabaility of emission or absorption of radiation in transitions. These are related to the Einstein coefficients by [26, p.46]

$$A_{ji} = -3\gamma f_{ji} \tag{2.3}$$

In all these values, the main term to calculate is $\langle\Psi_j|H_{int}|\Psi_i\rangle$, which is the *interaction matrix* also called the *transition amplitude.*

We will show the resulting interaction matrix in nonrelativisitic theory, relativistic theory and using the Foldy-Wouthuysen transformation.

2.1 Interaction Matrix in Nonrelativistic Theory

We will now show the interaction matrix in the nonrelativisitc theory. As stated before, we are considering an atom in a classical radiation field. The theory is nonrelativistic since intrinsic spin is ommitted. [26, p.37]

An unperturbed atom has the following Schrödinger Hamiltonian

$$H_0 = \frac{\mathbf{p}^2}{2m} + V \tag{2.4}$$

where $V = e\phi$ is the scalar potential from the atom and $\mathbf{p}$ is the conjugate momentum, which becomes $-i\hbar\nabla$. This satisfies the Schrödinger equation

$$H_0 \left|\Psi\right\rangle = E_0 \left|\Psi\right\rangle \tag{2.5}$$

The total Hamiltonian for an atom in an electromagnetic field in the Schrödinger representation is

$$H = \frac{1}{2m}(\mathbf{p} - \frac{e\mathbf{A}}{c})^2 - e\phi_{\text{ext}} + V \tag{2.6}$$

where we made the change that $\mathbf{p} \longrightarrow \mathbf{p} - \frac{e\mathbf{A}}{c}$[27, p.582] and added $-e\phi_{\text{ext}}$ for static potentials. We can rewrite this as

$$H = H_0 + H_{int} \tag{2.7}$$

where H_0 was defined in Eq.(2.4) and

$$H_{int} = -\frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2mc^2}\mathbf{A}^2 - e\phi_{\text{ext}} \tag{2.8}$$

which describes the interaction with the electromagnetic field, and is treated as a perturbation.

We apply the coulomb gauge condition $\nabla \cdot \mathbf{A} = 0$, and let the scalar potential be 0 ($\phi_{\text{ext}} = 0$) [26, p.38]. We can also use the relationship that for any function $f(x)$ [28, p.287]

$$[f(x), p] = ih\frac{df(x)}{dx} \tag{2.9}$$

Thus

$$\mathbf{A} \cdot \mathbf{p} - \mathbf{p} \cdot \mathbf{A} = i\hbar\nabla \cdot \mathbf{A} = 0 \tag{2.10}$$

We thus obtain the interaction Hamiltonian

$$H_{int} = -\frac{e}{mc}\mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2mc^2}\mathbf{A}^2 \tag{2.11}$$

We will consider small fields and can therefore omit the A^2 term. Also we note that the A^2 term represents two-photon transitions, which could occur if there is more than one photon within a volume of a_0^3 ($a_0 = 5.29177 \times 10^{-9}$ cm is the Bohr radius); however, this would only occur if the photon density is about 10^{25} cm^{-3} or greater [29]. Since the density of photons at the sun's surface is only 10^{12} cm^{-3} it is reasonable to assume that the number of photons is sufficiently small and we can neglect the A^2 generally[29] but it might need to be included for high intensity laser fields. There can also be times when single photon transitions are forbidden and then two photon transitions need to be considered. In our case, we are only concerned with allowed single photon transitions so we will omit the A^2 term.

Moreover, suppose we consider $\mathbf{A}$ as a plane wave

$$\begin{aligned}\mathbf{A} &= 2\mathbf{A}_0 cos[\mathbf{k} \cdot \mathbf{r} - wt] \\ &= \mathbf{A}_0 e^{i\mathbf{k}\cdot\mathbf{r}} e^{-iwt} + \mathbf{A}_0 e^{-i\mathbf{k}\cdot\mathbf{r}} e^{iwt} \\ &= \mathbf{A}(\mathbf{r})_0 e^{-iwt} + \mathbf{A}(\mathbf{r})_0^* e^{iwt}\end{aligned}$$

Since the atomic states have wave functions that are well localized and have small wavelengths compared to the wavelengths of the incident photons [28, p.472], we can expand $e^{i\mathbf{k}\cdot\mathbf{r}}$ as a power series in the small quantity $\mathbf{k} \cdot \mathbf{r}$

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k} \cdot \mathbf{r} + \frac{1}{2}(i\mathbf{k} \cdot \mathbf{r})^2 + ... \approx 1 \tag{2.12}$$

this means that the amplitude of the wave is approximately constant over the size of the atom [26, p.42]. We also note that the the assumption that $k \cdot r$ is small also means that [29, p.272]

$$\mathbf{k} \cdot \mathbf{r} \approx k a_0 \approx \frac{a_0 \triangle E}{\hbar c} \approx \frac{Z\alpha}{2} \ll 1 \tag{2.13}$$

where α is the fine structure constant. For high Z atoms (≈ 100) the assumption that $Z\alpha$ is small is not valid, and we need to include the quadrupole and multipole terms. For our case, we are considering low Z atoms and need only the electric dipole term. Therefore the interaction Hamiltonian is now

$$H_{int} = -\frac{e}{mc}\hat{\mathbf{e}} \cdot \mathbf{p} \tag{2.14}$$

where $\hat{\mathbf{e}}$ is the polarization vector. which means the interaction matrix element is

$$\langle \Psi_j | H_{int} | \Psi_i \rangle = \left\langle \Psi_j \middle| -\frac{e}{mc}\hat{\mathbf{e}} \cdot \mathbf{p} \middle| \Psi_i \right\rangle \tag{2.15}$$

where $\mathbf{p} = -ih\nabla$ is an odd operator and the wave functions are Schrödinger wave functions. This is referred to as the“velocity form” of the interaction matrix. We can simplify it further by using [28, p.472]

$$[H_0, \mathbf{r}] = \frac{-ih\mathbf{p}}{m} \tag{2.16}$$

Thus we have

$$\begin{aligned}
\langle\Psi_j|H_{int}|\Psi_i\rangle &= -\frac{e}{mc}\hat{\mathbf{e}}\cdot\left\langle\Psi_j|\frac{mi}{\hbar}[H_0,\mathbf{r}]|\Psi_i\right\rangle \\
&= \frac{e}{i\hbar c}\hat{\mathbf{e}}\cdot\langle\Psi_j|H_0\mathbf{r}-\mathbf{r}H_0|\Psi_i\rangle \\
&= -\frac{ei}{\hbar c}\hat{\mathbf{e}}\cdot\langle\Psi_j|E_j\mathbf{r}-\mathbf{r}E_i|\Psi_i\rangle \\
&= -\frac{ei}{\hbar c}(E_j-E_i)\,\langle\Psi_j|\hat{\mathbf{e}}\cdot\ \mathbf{r}|\Psi_i\rangle
\end{aligned}$$

where the wave functions are Schrödinger wave functions. This is referred to as the "length form" of the interaction matrix.

2.2 Interaction Matrix in Dirac Theory

In relativistic theory, the total Hamiltonian for a particle in a field is [30]

$$H = \vec{\alpha}\cdot(c\mathbf{p}-e\mathbf{A})+\beta mc^2+e\phi, \tag{2.17}$$

where

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \tag{2.18}$$

where we have made the usual replacement $\mathbf{p}\rightarrow\mathbf{p}-\frac{e}{c}\mathbf{A}$ $[27, p.582]$ and assumed $\phi_{\text{ext}}=0$ in the Coulomb gauge. The Hamiltonian can be written as

$$H = H_0 + H_{int} \tag{2.19}$$

where

$$H_0 = c\vec{\alpha}\cdot(\mathbf{p})+\beta mc^2+e\phi \tag{2.20}$$

thus $H_{int} = \vec{\alpha} \cdot e\mathbf{A}$ and the interaction matrix is

$$\langle \Psi_j | \vec{\alpha} \cdot e\mathbf{A} | \Psi_i \rangle \tag{2.21}$$

$$\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c} = \frac{e^2}{\hbar c} = \frac{1}{c}$$

where the $|\Psi\rangle = \begin{bmatrix} \varphi \\ \chi \end{bmatrix}$, is a four-component Dirac wave function, where φ is the large component consisting of $\begin{bmatrix} \varphi^{\frac{1}{2}} \\ \varphi^{\frac{-1}{2}} \end{bmatrix}$ and χ is the small component consisting of $\begin{bmatrix} \chi^{\frac{1}{2}} \\ \chi^{\frac{-1}{2}} \end{bmatrix}$.

2.3 Interaction Matrix using Foldy-Wouthuysen Transformation

So far we have shown that the nonrelativistic transition operator is $\frac{e}{c}\mathbf{p} \cdot \mathbf{A}$ and the relativistic transition operator is $\vec{\alpha} \cdot e\mathbf{A}$. The next section will use the Foldy-Wouthuysen transformation [31] to determine the equivalent nonrelativistic transition operators. Thus, the interaction matrix will be of the form

$$\left\langle \Psi_j | -\frac{e\alpha}{m}\mathbf{A} \cdot \mathbf{p} + \alpha^3 H_{FW} | \Psi_i \right\rangle \tag{2.22}$$

where the $|\Psi_i\rangle$ are relativistically corrected, i.e Breit-corrected, wave functions. This means we can write the wave functions as

$$|\Psi_i\rangle = \left|\Psi_i^{(0)}\right\rangle + \alpha^2 \left|\Psi_i^{(1)}\right\rangle \tag{2.23}$$

where $\left|\Psi_i^{(0)}\right\rangle$ represents the Schrödinger wave functions and $\left|\Psi_i^{(1)}\right\rangle$ are the first order relativistically corrected wave functions, these will be discussed in Chapter 5. The

H_{FW} are the additional operators obtained from the Foldy-Wouthuysen transformation, which will be shown in Chapter 3.

This gives a total of four elements that need to be evaluated

$$\alpha \left\langle \Psi_j^{(0)} | \frac{e}{m} \mathbf{A} \cdot \mathbf{p} | \Psi_i^{(0)} \right\rangle \tag{2.24}$$

$$\alpha^3 \left\langle \Psi_j^{(1)} | \frac{e}{m} \mathbf{A} \cdot \mathbf{p} | \Psi_i^{(0)} \right\rangle \tag{2.25}$$

$$\alpha^3 \left\langle \Psi_j^{(0)} | \frac{e}{m} \mathbf{A} \cdot \mathbf{p} | \Psi_i^{(1)} \right\rangle \tag{2.26}$$

$$\alpha^3 \left\langle \Psi_j^{(0)} | H_{FW} | \Psi_i^{(0)} \right\rangle \tag{2.27}$$

The first term is simply the nonrelativistic interaction matrix element as shown in Section 2.1. The following two terms depend on the corrections to the wave functions and these will be discussed in Chapter 5. The last term depends on the operators obtained after the Foldy-Wouthuysen transformation and these are discussed in the next Chapter. The total interaction matrix thus consists of the nonrelativistic interaction matrix element plus three correction terms that are of order α^2 compared to the nonrelativistic term. Adding up all the terms should equal the relativistic interaction matrix (Eq.(2.21)) up to $O(\alpha^2)$.

Chapter 3

The Foldy-Wouthuysen Transformation

Relativistic effects are rigorously treated by using the four-component Dirac Hamiltonian, but this formulation has difficulties which arise both theoretically and computationally. Furthermore, the Dirac Equation has no true bound state for two or more electron systems [32] due to what is called the Brown-Ravenhall disease [18]. Foldy and Wouthuysen [31] developed a method by which we can approximate the four-component Dirac theory by a two-component theory to any given order in $\frac{v}{c}$. The Foldy-Wouthuysen transformation (FW) eliminates the odd operator in the Dirac Hamiltonian to some desired order, as the odd operators connect positive and negative energy states. By choosing a suitable unitary transformation which will act on both the wave functions and operator and using a series of canonical transformations, the odd operator is made smaller and eventually neglected [24]. In the Foldy-Wouthuysen representation, the Dirac Hamiltonian only contains even operators up to the desired order of $\frac{v}{c}$ and the small and large components are completely decoupled [33]. We can thus ignore the small components and we are left with a two-component theory.

This method was originally used for the one-electron case, which results in an exact transformed Hamiltonian for the free particle case. Some attempts to eliminate the odd operators were also made for the Breit equation in a two particle system [34]. The Foldy-Wouthuysen transformation was extended to two-particles by Chraplyvy [35] and Erikson used this method to get a two-electron Hamiltonian [36]. However, the treatment had to be different if the masses were equal [35]. About 20 years later, Dong L. Lin [24] obtained a Foldy-Wouthuysen transformation for the field theory of quantum electrodynamics which does not have such a difficulty, and gave the explicit expression for the operators in the interaction Hamiltonian for the two-electron system using which the relativistic corrections to transitions can be calculated with relativistically corrected wave functions.

We will apply the Foldy-Wouthuysen transformation and derive the terms needed in the interaction matrix element for the one-electron case. We will include both spin dependent and spin independent terms. In doing so, we follow closely to procedure adopted in the original Foldy and Wouthuysen paper [31] and in Messiah's book [33, p.945] however they considered only time-independent potentials. We will, however, consider time dependent potentials since the photon vector potential **A** is in fact time dependent [23] which our results also confirm.

3.1 Foldy-Wouthuysen Transformation for a Particle in a field

The fully relativistic quantum mechanical description of the electron is given by the Dirac equation but it is often difficult to calculate due to the four-components. The Foldy-Wouthuysen transformation transforms the four-component problem into a two-component problem by decoupling the positive and negative energy components of the wave-functions. This gives a nonrelativistic limit for the Dirac Theory.

However, when external fields are present the Foldy-Wouthuysen transformation can only be given up to a desired order in $\frac{v}{c}$; it cannot be precisely made. We will perform the Foldy-Wouthuysen transformation until all the odd terms are of an order smaller then $(\frac{v}{c})^2$. We will use atomic units so $\frac{v}{c} = \frac{1}{c}$, where $c = 137$, however we will still display the m and e for clarity even though they are equal to unity in these units. It should also be noted that we can consider an expansion in $\frac{v}{c}$ as an expansion in αZ where $\alpha = \frac{1}{c}$ is the fine structure constant, and Z is the atomic number, which depends linearly on v. Thus this expansion is valid only in the low Z limit.

The Dirac Hamiltonian for a particle in a central field is [33, p.945]

$$\begin{gathered} H = \vec{\alpha} \cdot (c\mathbf{p} - e\mathbf{A}) + \beta mc^2 + e\phi. \\ \vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \end{gathered} \tag{3.1}$$

We can split the Dirac Hamiltonian into even ($\mathcal{E}$) and odd ($\mathcal{O}$) operators.

$$H = \beta mc^2 + \mathcal{E} + \mathcal{O} \tag{3.2}$$

where

$$\mathcal{O} = \vec{\alpha} \cdot \vec{\pi} = \vec{\alpha} \cdot (c\mathbf{p} - e\mathbf{A}) \qquad \mathcal{E} = e\phi \tag{3.3}$$

with the following commuting properties:

$$\beta\mathcal{E} = \mathcal{E}\beta, \quad \beta\mathcal{O} = -\mathcal{O}\beta \tag{3.4}$$

Odd operators are those that are off-diagonal such as the $\vec{\alpha}$ matrix. And even operators are diagonal such as the β matrix. In the general case, we transform to the new representation by a unitary operator U according to

$$\Psi' = U\Psi = e^{iS}\Psi \tag{3.5}$$

where the Ψ are the four-component Dirac wave functions , $|\Psi\rangle = \begin{bmatrix} \varphi \\ \chi \end{bmatrix}$, where φ is the large component consisting of $\begin{bmatrix} \varphi^{\frac{1}{2}} \\ \varphi^{\frac{-1}{2}} \end{bmatrix}$ and χ is the small component consisting of $\begin{bmatrix} \chi^{\frac{1}{2}} \\ \chi^{\frac{-1}{2}} \end{bmatrix}$. The small component $\chi \propto \frac{\phi}{c}$. Now we have

$$H\Psi = i\frac{\partial}{\partial t}(e^{-iS}\Psi') = i\frac{\partial e^{-iS}}{\partial t}\Psi' + e^{-iS}i\frac{\partial \Psi'}{\partial t} \tag{3.6}$$

We can use the above to find an expression for the transformed Hamiltonian H'

$$e^{iS}(H\Psi - i\frac{\partial e^{-iS}}{\partial t}\Psi') = i\frac{\partial \Psi'}{\partial t} = H'\Psi' \tag{3.7}$$

therefore

$$H' = UHU^{\dagger} - iU\frac{\partial U^{\dagger}}{\partial t} \tag{3.8}$$

We can expand these terms in powers of $\frac{1}{c}$ by using the following operator identity:

$$e^{iS}He^{-iS} = H + i[S,H] + \frac{i^2}{2!}[S,[S,H]] + \frac{i^3}{3!}[S,[S,[S,H]]] + ... + \frac{i^n}{n!}[S,[S,...[S,H]]] \tag{3.9}$$

Therefore, to a desired order

$$\begin{aligned} H' =& H + i[S,H] - \frac{1}{2}[S,[S,H]] - \frac{i}{6}[S,[S,[S,H]]] + \frac{1}{24}[S,[S,[S,[S,\beta m]]]] \\ & - \dot{S} - \frac{i}{2}[S,\dot{S}] + \frac{1}{6}[S,[S,\dot{S}]] \end{aligned} \tag{3.10}$$

We can eliminate the odd operators by order $\frac{1}{c}$ successively, until the desired order is reached. For first order, we shall call it H':

$$H' = \beta mc^2 + \mathcal{E} + \mathcal{O} + i[S,\beta]mc^2 \tag{3.11}$$

To cancel $\mathcal{O}$, we let $S = \frac{-i\beta\mathcal{O}}{2mc^2}$ and substitute into Eq.(3.10). We will explicitly show the first term, and only the results for the other terms as one needs only to use the commutator rules and the properties in Eq.(3.4). The first term is

$$\begin{aligned}
i[S,H] &= -i\left[\frac{-i\beta\mathcal{O}}{2mc^2}, \beta mc^2 + \mathcal{E} + \mathcal{O}\right] = \left[\frac{\beta\mathcal{O}}{2mc^2}, \beta mc^2\right] + \left[\frac{\beta\mathcal{O}}{2mc^2}, \mathcal{E}\right] + \left[\frac{\beta\mathcal{O}}{2mc^2}, \mathcal{O}\right] \\
&= \frac{1}{2}\left[\beta\mathcal{O}, \beta\right] + \frac{1}{2mc^2}\left[\beta\mathcal{O}, \mathcal{E}\right] + \frac{1}{2mc^2}\left[\beta\mathcal{O}, \mathcal{O}\right] \\
&= \frac{1}{2}\Big(\beta[\mathcal{O},\beta] + [\beta,\beta]\mathcal{O}\Big) + \frac{1}{2mc^2}\Big(\beta[\mathcal{O},\mathcal{E}] + [\beta,\mathcal{E}]\mathcal{O}]\Big) + \frac{1}{2mc^2}\Big(\beta[\mathcal{O},\mathcal{O}] + [\beta,\mathcal{O}]\mathcal{O}\Big) \\
&= \frac{1}{2}\Big(\beta(\mathcal{O}\beta - \beta\mathcal{O})\Big) + \frac{1}{2mc^2}\Big(\beta[\mathcal{O},\mathcal{E}]\Big) + \frac{1}{2mc^2}\Big((\beta\mathcal{O} - \mathcal{O}\beta)\mathcal{O}\Big) \\
&= \frac{1}{2}\Big(-2\beta^2\mathcal{O}\Big) + \frac{1}{2mc^2}\Big(\beta[\mathcal{O},\mathcal{E}]\Big) + \frac{1}{2mc^2}\Big(2\beta\mathcal{O}^2\Big) \\
&= -\mathcal{O} + \frac{\beta}{2mc^2}\Big[\mathcal{O},\mathcal{E}\Big] + \frac{1}{mc^2}\beta\mathcal{O}^2
\end{aligned} \tag{3.12}$$

The rest of the terms are

$$\begin{aligned}
\frac{1}{2}[S,[S,H]] &= -\frac{\beta\mathcal{O}^2}{2mc^2} - \frac{1}{8(mc^2)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{\mathcal{O}^3}{2(mc^2)^2} \\
\frac{-1}{6}[S,[S,[S,H]]] &= \frac{\mathcal{O}^3}{6(mc^2)^2} - \frac{1}{6(mc^2)^3}\beta\mathcal{O}^4 \\
\frac{1}{24}[S,[S,[S,[S,H]]]] &= \frac{\beta\mathcal{O}^4}{24(mc^2)^3} \\
-\dot{S} &= \frac{i\beta\dot{\mathcal{O}}}{2mc^2} \\
-\frac{i}{2}[S,\dot{S}] &= -\frac{i}{8(mc^2)^2}[\mathcal{O},\dot{\mathcal{O}}]
\end{aligned} \tag{3.13}$$

Then Eq.(3.10) becomes

$$\begin{aligned} H' &= \beta\left(mc^2 + \frac{\mathcal{O}^2}{2mc^2} - \frac{\mathcal{O}^4}{8(mc^2)^3}\right) + \mathcal{E} - \frac{\mathcal{O}^3}{3(mc^2)^2} + \frac{\beta}{2mc^2}[\mathcal{O},\mathcal{E}] \\ &- \frac{1}{8(mc^2)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}] - \frac{i}{8(mc^2)^2}[\mathcal{O},\dot{\mathcal{O}}] + \frac{i\beta\dot{\mathcal{O}}}{2mc^2} \\ &= \beta m + \mathcal{O}' + \mathcal{E}' \end{aligned} \tag{3.14}$$

where

$$\begin{aligned} \mathcal{E}' &= \beta\left(mc^2 + \frac{\mathcal{O}^2}{2mc^2} - \frac{\mathcal{O}^4}{8(mc^2)^3}\right) + \mathcal{E} - \frac{1}{8(mc^2)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}] - \frac{i}{8(mc^2)^2}[\mathcal{O},\dot{\mathcal{O}}] \\ \mathcal{O}' &= \left(-\frac{\mathcal{O}^3}{3(mc^2)^2} + \frac{\beta}{2mc^2}[\mathcal{O},\mathcal{E}] + \frac{i\beta\dot{\mathcal{O}}}{2mc^2}\right) \end{aligned} \tag{3.15}$$

Now $\mathcal{O}'$ is of order $\frac{1}{c^2}$ smaller then $\mathcal{O}$. We can now repeat the process, and transform H' by S'

$$S' = \frac{-i\beta}{2mc^2}\mathcal{O}' = \frac{-i\beta}{2mc^2}\left(-\frac{\mathcal{O}^3}{3(mc)^2} + \frac{\beta}{2mc^2}[\mathcal{O},\mathcal{E}] + \frac{i\beta\dot{\mathcal{O}}}{2mc^2}\right) \tag{3.16}$$

Using this transformation we get the Hamiltonian

$$\begin{aligned} H'' = e^{iS'}\left(H' - i\frac{\partial}{\partial t}\right)e^{-iS'} &= \beta mc^2 + \mathcal{E}' + \frac{\beta}{2mc^2}[\mathcal{O}',\mathcal{E}'] + \frac{i\beta\dot{\mathcal{O}}'}{2mc^2} \\ &= \beta mc^2 + \mathcal{E}' + \mathcal{O}'' \end{aligned} \tag{3.17}$$

where $\mathcal{O}''$ is of order $\frac{1}{c^2}$ smaller then $\mathcal{O}'$, and thus it's an order of $\frac{1}{c^4}$ smaller than $\mathcal{O}$. We can repeat the process again and transform H'' by $S'' = \frac{i\beta\mathcal{O}''}{2mc^2}$. Following the same trend $\mathcal{O}'''$ would be an order of $\frac{1}{c^2}$ smaller than $\mathcal{O}''$, and an order of $\frac{1}{c^6}$ smaller than $\mathcal{O}$. Since $\mathcal{O}$ is of order c, therefore the $\mathcal{O}'''$ is of order $\frac{1}{c^5}$. As we are only calculating corrections up to $\alpha^2 = \frac{1}{c^4}$, we can ignore $\mathcal{O}'''$ as it is of a smaller order, so up to the desired order the Hamiltonian is

$$
\begin{aligned}
H''' &= \beta mc^2 + \mathcal{E}' \\
&= \beta\left(mc^2 + \frac{\mathcal{O}^2}{2mc^2} - \frac{\mathcal{O}^4}{8(mc^2)^3}\right) + \mathcal{E} - \frac{1}{8(mc^2)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i}{8(mc^2)^2}[\mathcal{O},\dot{\mathcal{O}}]
\end{aligned} \tag{3.18}
$$

Now we have all even terms up to the desired order (α^2), thus the large components ϕ' and small components χ' are completely decoupled. To within order of $\frac{1}{c^5}$ the positive energy solutions are represented by the large component wave functions ϕ' which obey

$$i\frac{\partial\phi'}{\partial t} = H'''\phi$$

We will now explicitly calculate H''', in which case we will replace the 4 x 4 $\vec{\alpha}$ by the 2 x 2 $\boldsymbol{\sigma}$ since we are now looking at only the large components. The first term is

$$
\begin{aligned}
\frac{\mathcal{O}^2}{2mc^2} &= \frac{1}{2mc^2}\boldsymbol{\sigma}\cdot(c\mathbf{p}-e\mathbf{A})\boldsymbol{\sigma}\cdot(c\mathbf{p}-e\mathbf{A}) \\
&= \frac{1}{2mc^2}(c\mathbf{p}-e\mathbf{A})^2 + \frac{i}{2m}\boldsymbol{\sigma}\cdot[(c\mathbf{p}-e\mathbf{A})\times(c\mathbf{p}-e\mathbf{A})] \\
&= \frac{1}{2mc^2}(c\mathbf{p}-e\mathbf{A})^2 + \frac{i}{2mc^2}\boldsymbol{\sigma}\cdot[c(\mathbf{p}\times\mathbf{p}) - ec(\mathbf{p}\times\mathbf{A}+\mathbf{A}\times\mathbf{p}) + e^2(\mathbf{A}\times\mathbf{A})] \\
&= \frac{1}{2mc^2}(c\mathbf{p}-e\mathbf{A})^2 - \frac{-ec\hbar}{2mc^2}\boldsymbol{\sigma}\cdot(\nabla\times\mathbf{A}+\mathbf{A}\times\nabla)
\end{aligned} \tag{3.19}
$$

where we used the identity [37, p.78]

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B}) = \mathbf{A}\cdot\mathbf{B} + i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B}) \tag{3.20}$$

Now we note that

$$\begin{aligned}(\nabla\times\mathbf{A}+\mathbf{A}\times\nabla)f &= \nabla\times(\mathbf{A}f)+\mathbf{A}\times\nabla f\\ &= \nabla\times\mathbf{A}-\mathbf{A}\times\nabla f+\mathbf{A}\times\nabla f\\ &= \nabla\times\mathbf{A}\end{aligned}\tag{3.21}$$

So we can now simplify the first term to obtain

$$\begin{aligned}\frac{\mathcal{O}^2}{2mc^2} &= \frac{1}{2mc^2}(c\mathbf{p}-e\mathbf{A})^2-\frac{-ec\hbar}{2mc^2}\boldsymbol{\sigma}\cdot(\nabla\times\mathbf{A}+\mathbf{A}\times\nabla)\\ &= \frac{1}{2mc^2}(c\mathbf{p}-e\mathbf{A})^2-\frac{-ec\hbar}{2mc^2}\boldsymbol{\sigma}\cdot(\nabla\times\mathbf{A})\\ &= \frac{1}{2mc^2}(c\mathbf{p}-e\mathbf{A})^2-\frac{-e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}\end{aligned}\tag{3.22}$$

The second term is

$$-\frac{\mathcal{O}^4}{8(mc^2)^3} = -\frac{1}{8(mc^2)^3}((c\mathbf{p}-e\mathbf{A})^2-e\hbar c(\boldsymbol{\sigma}\cdot\mathbf{B}))^2\tag{3.23}$$

The third term is

$$-\frac{1}{8(mc)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]]\tag{3.24}$$

We will first evaluate inner commutator

$$\begin{aligned}[\mathcal{O},\mathcal{E}] &= [\boldsymbol{\sigma}\cdot(c\mathbf{p}-e\mathbf{A}),e\phi]\\ &= [\boldsymbol{\sigma}\cdot c\mathbf{p},e\phi]-e^2[\boldsymbol{\sigma}\cdot\mathbf{A},\phi]\\ &= -i\hbar ec[\boldsymbol{\sigma}\cdot\nabla,\phi]\end{aligned}\tag{3.25}$$

where we have used the fact that $\mathbf{A}$ and ϕ are even operators thus $[\boldsymbol{\sigma}\cdot\mathbf{A},\phi]=0$ [38].

We can evaluate the remaining commutator by noting that

$$\begin{aligned}[\boldsymbol{\sigma}\cdot\nabla,\phi]f &= (\boldsymbol{\sigma}\cdot\nabla\phi-\phi\boldsymbol{\sigma}\cdot\nabla)f\\ &= \boldsymbol{\sigma}\cdot\nabla\phi f-\phi\boldsymbol{\sigma}\cdot\nabla f\\ &= (\boldsymbol{\sigma}\cdot\nabla\phi)f+(\boldsymbol{\sigma}\cdot\nabla f)\phi-\phi\boldsymbol{\sigma}\cdot\nabla f\\ &= (\boldsymbol{\sigma}\cdot\nabla\phi)f\end{aligned} \tag{3.26}$$

Thus

$$[\mathcal{O},\mathcal{E}] = -i\hbar ce(\boldsymbol{\sigma}\cdot\nabla\phi) \tag{3.27}$$

then the third term is

$$\begin{aligned}-\frac{1}{8(mc^2)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] &= -\frac{1}{8(mc^2)^2}[\boldsymbol{\sigma}\cdot(c\mathbf{p}-e\mathbf{A}),-i\hbar ce(\boldsymbol{\sigma}\cdot\nabla\phi)]\\ &= \frac{i\hbar ce}{8(mc^2)^2}\left([\boldsymbol{\sigma}\cdot c\mathbf{p},\boldsymbol{\sigma}\cdot\nabla\phi]-[\boldsymbol{\sigma}\cdot e\mathbf{A},\boldsymbol{\sigma}\cdot\nabla\phi]\ \right)\\ &= \frac{i\hbar e}{8m^2c^3}\left(c(\boldsymbol{\sigma}\cdot\mathbf{p}\boldsymbol{\sigma}\cdot\nabla\phi-\boldsymbol{\sigma}\cdot\nabla\phi\boldsymbol{\sigma}\cdot\mathbf{p})-e(\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\nabla\phi-\boldsymbol{\sigma}\cdot\nabla\phi\boldsymbol{\sigma}\cdot\mathbf{A})\right)\\ &= \frac{i\hbar e}{8m^2c^3}(c\left(\mathbf{p}\cdot\nabla\phi+i\boldsymbol{\sigma}\cdot(\mathbf{p}\times\nabla\phi)-\nabla\phi\cdot\mathbf{p}-i\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p}\right)\\ &-e\left(\mathbf{A}\cdot\nabla\phi+i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\nabla\phi)-\nabla\phi\cdot\mathbf{A}-i\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{A}\right))\\ &= \frac{i\hbar e}{8(mc)^2}(\mathbf{p}\cdot\nabla\phi+i\boldsymbol{\sigma}\cdot(\mathbf{p}\times\nabla\phi)-\nabla\phi\cdot\mathbf{p}-i\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p})\\ &+\frac{i\hbar e^2}{8m^2c^3}(2i\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))\end{aligned} \tag{3.28}$$

Once again, we need to be careful with the momentum operator as it contains ∇

$$\begin{aligned}\mathbf{p}\cdot\nabla\phi f = -i\hbar\nabla\cdot\nabla\phi f &= -i\hbar(\nabla\cdot\nabla\phi)f-i\hbar(\nabla\phi\cdot\nabla f)\\ &= \left[(-i\hbar\nabla\cdot\nabla\phi)+(\nabla\phi\cdot(-i\hbar\nabla))\right]f = \left[(\mathbf{p}\cdot\nabla\phi)+(\nabla\phi\cdot\mathbf{p})\right]f\end{aligned} \tag{3.29}$$

Therefore we have:

$$\mathbf{p}\cdot\nabla\phi = (\mathbf{p}\cdot\nabla\phi)+\nabla\phi\cdot\mathbf{p} \tag{3.30}$$

where the gradient operator in the first term on the right hand side does not go beyond the bracket. We thus have

$$
\begin{aligned}
&((\mathbf{p}\cdot\nabla\phi)+\nabla\phi\cdot\mathbf{p}+i\boldsymbol{\sigma}\cdot\mathbf{p}\times\nabla\phi-\nabla\phi\cdot\mathbf{p}-i\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p})\\
&=((\mathbf{p}\cdot\nabla\phi)+i\boldsymbol{\sigma}\cdot\mathbf{p}\times\nabla\phi-i\boldsymbol{\sigma}\cdot\times\mathbf{p})
\end{aligned}
\tag{3.31}
$$

As before, we need to be careful with the gradient term in the momentum operator. We note that:

$$
\mathbf{p}\times\nabla\phi=(\mathbf{p}\times\nabla\phi)-\nabla\phi\times\mathbf{p}
\tag{3.32}
$$

which means that $-\frac{1}{8(mc^2)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]]$ is

$$
\begin{aligned}
&=\frac{ie\hbar}{8(mc)^2}\left((\mathbf{p}\cdot\nabla\phi)+i\boldsymbol{\sigma}\cdot(\mathbf{p}\times\nabla\phi)-i\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p}-i\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p}\right)+\frac{i\hbar e^2}{8m^2c^3}(2i\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))\\
&=\frac{e\hbar}{8(mc)^2}\left((\mathbf{p}\cdot\nabla\phi)+i\boldsymbol{\sigma}\cdot(\mathbf{p}\times\nabla\phi)-2i\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p}\right)+\frac{i\hbar e^2}{8m^2c^3}(2i\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))\\
&=\frac{ie\hbar}{8(mc)^2}(\mathbf{p}\cdot\nabla\phi)-\frac{e\hbar}{8(mc)^2}\boldsymbol{\sigma}\cdot(\mathbf{p}\times\nabla\phi)+\frac{e\hbar}{4(mc)^2}\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p}-\frac{\hbar e^2}{4m^2c^3}(\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))\\
&=\frac{e\hbar^2}{8(mc)^2}(\nabla\cdot\nabla\phi)+\frac{ie\hbar^2}{8(mc)^2}\boldsymbol{\sigma}\cdot(\nabla\times\nabla\phi)+\frac{e\hbar}{4(mc)^2}\boldsymbol{\sigma}\cdot\nabla\phi\times\mathbf{p}-\frac{\hbar e^2}{4m^2c^3}(\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))
\end{aligned}
\tag{3.33}
$$

If we consider ϕ to be a spherically symmetric potential then we can make some further simplifications

$$
\begin{aligned}
&\nabla\phi=\nabla_r\phi=\frac{1}{r}\frac{\partial\phi}{\partial r}\vec{r}\\
&\nabla\times\nabla\phi=0\\
&\nabla\cdot\nabla\phi=\nabla_r^2(\phi)
\end{aligned}
\tag{3.34}
$$

Thus

$$-\frac{1}{8(mc^2)^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]]=\frac{e\hbar^2}{8(mc)^2}(\nabla_r^2(\phi))+\frac{e\hbar}{4(mc)^2}\frac{1}{r}\frac{\partial\phi}{\partial r}\boldsymbol{\sigma}\cdot\mathbf{L}-\frac{\hbar e^2}{4m^2c^3}(\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A})) \tag{3.35}$$

Now the fourth term is

$$\begin{aligned}-\frac{1}{8(mc^2)^2}[\mathcal{O},\dot{\mathcal{O}}]&=-\frac{1}{8(mc^2)^2}\left[\mathcal{O},\left[\mathcal{O},i\frac{\partial}{\partial t}\right]\right]\\&=-\frac{1}{8(mc^2)^2}\left[\mathcal{O},\omega\boldsymbol{\sigma}\cdot\mathbf{eA}\right]=-\frac{e\omega}{8(mc^2)^2}\left[\mathcal{O},\boldsymbol{\sigma}\cdot\mathbf{A}\right]\\&=\frac{-ce\omega}{8(mc^2)^2}\left[\boldsymbol{\sigma}\cdot\mathbf{p},\boldsymbol{\sigma}\cdot\mathbf{A}\right]\end{aligned} \tag{3.36}$$

Again, we need to be careful with the ∇

$$\begin{aligned}[\boldsymbol{\sigma}\cdot\mathbf{p},\,\boldsymbol{\sigma}\cdot\mathbf{A}]f&=-i\hbar\left(\boldsymbol{\sigma}\cdot\nabla\boldsymbol{\sigma}\cdot\mathbf{A}-\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\nabla\right)f\\&=-i\hbar\left(\boldsymbol{\sigma}\cdot\nabla f\boldsymbol{\sigma}\cdot\mathbf{A}+(\boldsymbol{\sigma}\cdot\nabla\boldsymbol{\sigma}\cdot\mathbf{A})f-\boldsymbol{\sigma}\cdot\mathbf{A}\boldsymbol{\sigma}\cdot\nabla f\right)\\&=-i\hbar\left(\nabla f\cdot\mathbf{A}+i\boldsymbol{\sigma}\cdot\nabla f\times\mathbf{A}+(\nabla\cdot\mathbf{A})f+(i\boldsymbol{\sigma}\cdot\nabla\times\mathbf{A})f-\mathbf{A}\cdot\nabla f-i\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla f\right)\\&=-i\hbar\left(-2i\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla f+(\nabla\cdot\mathbf{A})f+i\boldsymbol{\sigma}\cdot\nabla\times\mathbf{A}\right)f\\&=\hbar\left(-2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla f-i(\nabla\cdot\mathbf{A})f+\boldsymbol{\sigma}\cdot\nabla\times\mathbf{A}\right)f\\&=\hbar\left(-2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla f+\boldsymbol{\sigma}\cdot\mathbf{B}\right)f\end{aligned} \tag{3.37}$$

where we have used $\nabla\cdot\mathbf{A}=0$ since we are in the Coulomb guage, and once again let $\mathbf{B}=\nabla\times\mathbf{A}$. The fourth term is now

$$-\frac{1}{8(mc^2)^2}\left[\mathcal{O},\left[\mathcal{O},i\frac{\partial}{\partial t}\right]\right]=-\frac{\hbar ce\omega}{8(mc^2)^2}\left(-2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla+\boldsymbol{\sigma}\cdot\mathbf{B}\right) \tag{3.38}$$

we can make an equivalent operator out of the ω term, thus giving

$$\begin{aligned}
&\frac{-\hbar c e\omega}{8(mc^2)^2}(-2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla+\boldsymbol{\sigma}\cdot\mathbf{B})\\
&\qquad\qquad= \frac{\hbar c e}{8(mc^2)^2}\left[\frac{\mathbf{p}^2}{2m}+e\phi, -2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla+\boldsymbol{\sigma}\cdot\mathbf{B}\right]\\
&\qquad\qquad= \frac{\hbar e}{16m^3c^3}\left[\mathbf{p}^2, -2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla+\boldsymbol{\sigma}\cdot\mathbf{B}\right]+\frac{\hbar e^2}{4m^2c^3}\left[\phi, -\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla\right]\\
&\qquad\qquad= \frac{\hbar e}{16m^3c^3}\left[\mathbf{p}^2, -2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla+\boldsymbol{\sigma}\cdot\mathbf{B}\right]+\frac{\hbar e^2}{4m^2c^3}\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla\phi
\end{aligned} \tag{3.39}$$

Therefore the Hamiltonian in Eq.(3.18) is now:

$$\begin{aligned}
H''' &= \beta\left(mc^2+\frac{(c\mathbf{p}-e\mathbf{A})^2}{2mc^2}-\frac{-e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}-\frac{((c\mathbf{p}-e\mathbf{A})^2-e\hbar c(\boldsymbol{\sigma}\cdot\mathbf{B}))^2}{8(mc^2)^3}\right)+e\phi\\
&+\frac{e\hbar^2}{8(mc)^2}(\nabla_r^2(\phi))+\frac{e\hbar}{4(mc)^2}\frac{1}{r}\frac{\partial\phi}{\partial r}\boldsymbol{\sigma}\cdot\mathbf{L}-\frac{\hbar e^2}{2m^2c^3}(\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))\\
&-\frac{i\hbar c e}{16(mc^2)^3}\left[\mathbf{p}^2, -2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla+\boldsymbol{\sigma}\cdot\mathbf{B}\right]\\
&=\beta\left(mc^2+\frac{\mathbf{p}^2}{2m}-\frac{\mathbf{p}\cdot e\mathbf{A}}{mc}-\frac{\mathbf{p}^4}{8m^3c^2}+\frac{\{\mathbf{p}^2,\mathbf{p}\cdot e\mathbf{A}\}}{4mc^3}\right)+e\phi\\
&+\frac{e\hbar^2}{8(mc)^2}(\nabla_r^2(\phi))+\frac{e\hbar}{4(mc)^2}\frac{1}{r}\frac{\partial\phi}{\partial r}\boldsymbol{\sigma}\cdot\mathbf{L}-\frac{\hbar e^2}{2m^2c^3}(\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))\\
&+\frac{\hbar e}{16m^3c^3}\left[\mathbf{p}^2, -2\boldsymbol{\sigma}\cdot\mathbf{A}\times\nabla\right]
\end{aligned} \tag{3.40}$$

where we have used $\mathbf{B}=\nabla\times\mathbf{A}=0$ since we will consider $\mathbf{A}=\hat{\mathbf{z}}$, and omitted $\mathbf{A}^2$ terms (see Section 2.1 for details). We will convert to atomic units ($m=e=\hbar=1$), and use the fine structure constant $\alpha=\frac{1}{c}$. We will consider the transition from a $2p$ state to a $1s$ state thus the interaction matrix element is

$$\left\langle\Psi'_{1s}|H'''|\Psi'_{2p}\right\rangle=\left\langle\Psi'_{1s}|-\alpha\mathbf{p}\cdot\mathbf{A}+\alpha^3\frac{\{\mathbf{p}^2,\mathbf{p}\cdot\mathbf{A}\}}{4}-\frac{\alpha^3}{2}(\boldsymbol{\sigma}\cdot(\nabla\phi\times\mathbf{A}))|\Psi'_{2p}\right\rangle \tag{3.41}$$

where Ψ' is the large component part of $U''U'U\Psi = e^{iS''}e^{iS'}e^{iS}\Psi$, and Ψ is the four-component Dirac wave function. Only three terms contribute to the matrix element. The operators in Eq.(3.41) are nonrelativistic operators. The last term is the only spin dependent term.

3.2 Two-electron Foldy-Wouthuysen Result

The previous section considered a one-electron problem; for the two-electron problem Lin [24] determined the following interaction matrix Hamiltonian for spin allowed transitions between Breit-corrected wave functions.

$$\begin{aligned} H_{int} = &\Bigg(-\alpha \mathbf{A_1}\cdot\mathbf{p_1} + \alpha^3 \frac{\{\mathbf{p_1}^2, \mathbf{A_1}\cdot\mathbf{p_1}\}}{4} + \frac{e\alpha}{2m^2\mathbf{r_{12}}}[\mathbf{A_1}\cdot\mathbf{p_2} + \mathbf{A_1}\cdot\hat{\mathbf{r}}_{\mathbf{12}}\mathbf{p_2}\cdot\hat{\mathbf{r}}_{\mathbf{12}}] \\ &+ \frac{e\alpha}{2m}(\boldsymbol{\sigma_1}+\boldsymbol{\sigma_2})\cdot\frac{\hat{\mathbf{r}}_{\mathbf{12}}}{\mathbf{r_{12}}}\times\mathbf{A_1}\Bigg) + (1 \Longleftrightarrow 2) \end{aligned} \tag{3.42}$$

where the $(1 \Longleftrightarrow 2)$ means we add the same terms except wherever there is a subscript of 1 we replace it with 2. thus the interaction matrix element is

$$\left\langle \Psi'_{1s}|H_{int}|\Psi'_{2p}\right\rangle \tag{3.43}$$

where the wave functions are Breit-corrected wave functions

$$|\Psi'\rangle = \left|\Psi^{(0)}\right\rangle + \alpha^2\left|\Psi^{(1)}\right\rangle \tag{3.44}$$

The Breit-corrected wave functions (i.e relativistically corrected wave functions) are discussed in Chapter 5.

3.3 Evaluation of Foldy-Wouthuysen terms

We will now give the explicit expressions for every term to be evaluated for the one-electron case and we will use the long wavelength approximation and let $\mathbf{A} = \hat{\mathbf{z}}$ (see Eq.(2.12)). The spin independent terms are

$$-\alpha \left\langle \Psi_{1s}^{(0)} | \mathbf{p}_z | \Psi_{2p}^{(0)} \right\rangle \tag{3.45}$$

$$-\alpha^3 \left\langle \Psi_{1s}^{(1)} | \mathbf{p}_z | \Psi_{2p}^{(0)} \right\rangle \tag{3.46}$$

$$-\alpha^3 \left\langle \Psi_{2s}^{(0)} | \mathbf{p}_z | \Psi_{2p}^{(1)} \right\rangle \tag{3.47}$$

$$\frac{\alpha^3}{4} \left\langle \Psi_{1s}^{(0)} | (\mathbf{p}^2 \mathbf{p}_z + \mathbf{p}_z \mathbf{p}^2) | \Psi_{2p}^{(0)} \right\rangle \tag{3.48}$$

and the spin dependent term is

$$-\frac{\alpha^3}{2} \left\langle \Psi_{1s}^{(0)} | (\boldsymbol{\sigma} \cdot (\nabla\phi \times \hat{\mathbf{z}})) | \Psi_{2p}^{(0)} \right\rangle \tag{3.49}$$

Eq.(3.45) is the nonrelativistic term, its' evaluation is simple. Eq.(3.46) and Eq.(3.47) are due to the corrections from the wave functions. These terms will be discussed in Chapter 5. Eq.(3.48) and Eq.(3.49) are due to the corrections from the Foldy-Wouthuysen transformation, we will now refer to them as the Foldy term and the Foldy spin term respectively.

The Foldy term can be evaluated as

$$\frac{i\alpha^3}{4} \left\langle \Psi_{1s}^{(0)} | \nabla^2 \nabla_z + \nabla_z \nabla^2) | \Psi_{2p}^{(0)} \right\rangle = \frac{i\alpha^3}{2} \left\langle \Psi_{1s}^{(0)} | \nabla^2 \nabla_z) | \Psi_{2p}^{(0)} \right\rangle = -\alpha^3 \frac{2i\sqrt{2}}{27} \tag{3.50}$$

The Foldy spin term can be written as:

$$-\frac{\alpha^3}{2} \left\langle \Psi_{1s}^{(0)} | (\boldsymbol{\sigma} \cdot (\nabla\phi \times \hat{\mathbf{z}})) | \Psi_{2p}^{(0)} \right\rangle = -\alpha^3 \left\langle \Psi_{1s}^{(0)} | (\boldsymbol{S} \times \nabla\phi) \cdot \hat{z} | \Psi_{2p}^{(0)} \right\rangle \tag{3.51}$$

where we have used

$$\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b}) \tag{3.52}$$

and

$$\mathbf{S} = \frac{\boldsymbol{\sigma}}{2} \tag{3.53}$$

In order to calculate the matrix element, we use the following:

$$\begin{aligned}
\mathbf{E} = -\nabla\phi; &\quad \phi = -\frac{1}{r} \\
(\boldsymbol{S} \times \mathbf{E} \cdot \hat{\mathbf{z}}) &= \mathbf{S}_x\mathbf{E}_y - \mathbf{S}_y\mathbf{E}_y \\
\mathbf{E}_x &= -\frac{1}{r^2}\sin\theta\cos\phi \\
\mathbf{E}_y &= -\frac{1}{r^2}\sin\theta\sin\phi \\
\mathbf{S}_x &= \frac{S^+ + S^-}{2} \\
\mathbf{S}_y &= \frac{S^+ - S^-}{2}
\end{aligned} \tag{3.54}$$

We will also need to explicitely write the wave functions, using Clebsch-Gordon Coefficients.

$$\begin{aligned}
\left|2p_{\frac{1}{2},\frac{1}{2}}\right\rangle &= \left(-\sqrt{\frac{1}{3}}Y_1^0\alpha + \sqrt{\frac{2}{3}}Y_1^1\beta\right)R_{21} \\
\left|2p_{\frac{1}{2},-\frac{1}{2}}\right\rangle &= \left(-\sqrt{\frac{2}{3}}Y_1^{-1}\alpha + \sqrt{\frac{1}{3}}Y_1^0\beta\right)R_{21} \\
\left|2p_{\frac{3}{2},\frac{3}{2}}\right\rangle &= Y_1^{-1}\beta R_{21} \\
\left|2p_{\frac{3}{2},-\frac{1}{2}}\right\rangle &= \left(\sqrt{\frac{1}{3}}Y_1^{-1}\alpha + \sqrt{\frac{2}{3}}Y_1^0\beta\right)R_{21} \\
\left|2p_{\frac{3}{2},\frac{1}{2}}\right\rangle &= \left(\sqrt{\frac{2}{3}}Y_1^0\alpha + \sqrt{\frac{1}{3}}Y_1^0\beta\right)R_{21} \\
\left|2p_{\frac{3}{2},-\frac{3}{2}}\right\rangle &= Y_1^1\alpha R_{21}
\end{aligned} \tag{3.55}$$

where the notation used is $\left|2p_{j,m_j}\right\rangle$. The α and β represent the spin up and spin down states respectively, the Y_l^m represent the spherical harmonics and R_{nl} represent the radial wave function.

Then we get the following results:

$$-\frac{\alpha^3}{2}\left\langle \Psi_{1s}^{(0)}|(\boldsymbol{\sigma}\cdot(\nabla\phi\times\hat{\mathbf{z}}))|\Psi_{2p_{\frac{1}{2}}}^{(0)}\right\rangle = -\frac{2i\alpha^3}{27}\sqrt{\frac{2}{3}} \tag{3.56}$$

$$-\frac{\alpha^3}{2}\left\langle \Psi_{1s}^{(0)}|(\boldsymbol{\sigma}\cdot(\nabla\phi\times\hat{\mathbf{z}}))|\Psi_{2p_{\frac{3}{2}}}^{(0)}\right\rangle = \frac{2i\alpha^3}{27}\sqrt{\frac{1}{3}} \tag{3.57}$$

Here we have evaluated Eq.(3.49) analytically. For the two-electron case it would not be possible to evaluate the operator in this way, we would need to use angular momentum algebra. In order to evaluate the matrix element we can first convert it to the reduced matrix element form using [39, p.75]

$$\langle\gamma' j' m'|\mathbf{T}(k,q)|\gamma j m\rangle = (-1)^{j'-m'}\begin{pmatrix} j' & k & j \\ m' & q & m\end{pmatrix}\langle\gamma' j'||\mathbf{T}(k)||\gamma j\rangle \tag{3.58}$$

where $\mathbf{T}(k,q)$ is a the q component of a Tensor of order k. γ represents the additional values for the states, and the matrix represents a 3−j symbol. We will have two terms, one for the transition of $2p_{\frac{3}{2}}$ to $1s$ and one for $2p_{\frac{1}{2}}$ to $1s$. For the $2p_{\frac{1}{2}}$ to $1s$ transition we can write:

$$\begin{aligned}\left\langle 0\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \middle|(\boldsymbol{S}\times\mathbf{E}\cdot\hat{z})\middle| 1\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \right\rangle &= i\sqrt{2}\begin{pmatrix} \frac{1}{2} & 1 & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2}\end{pmatrix}\left\langle 0\ \frac{1}{2}\ \frac{1}{2}\ \middle|\middle|\boldsymbol{S}\times\mathbf{E}\middle|\middle|\ 1\ \frac{1}{2}\ \frac{1}{2}\ \right\rangle \\ &= \frac{1}{\sqrt{6}}\left\langle 0\ \frac{1}{2}\ \frac{1}{2}\ \middle|\middle|\boldsymbol{S}\times\mathbf{E}\middle|\middle|\ 1\ \frac{1}{2}\ \frac{1}{2}\ \right\rangle\end{aligned} \tag{3.59}$$

where we have used [39, p.70]

$$\mathbf{T}(1,m) = \frac{i}{\sqrt{2}}(\mathbf{x}\times\mathbf{y})_m \tag{3.60}$$

to evaluate the reduced tensor matrix we can use [39, p.110]

$$\langle \gamma' j_1' j_2' J' || \mathbf{X}(K) || \gamma j_1 j_2 J\rangle = \sum_{\gamma''} \langle \gamma' j_1' || \mathbf{T}(k_1) || \gamma'' j_1\rangle \langle \gamma'' j_2' || \mathbf{U}(k_2) || \gamma j_2\rangle \times \\ [(2J+1)(2J'+1)(2K+1)]^{\frac{1}{2}} \begin{Bmatrix} j_1' & j_1 & k_1 \\ j_2' & j_2 & k_2 \\ J' & J & K \end{Bmatrix} \tag{3.61}$$

where the matrix is a 9−j symbol. For the $2p_{\frac{1}{2}}$ to $1s$ transition we can write

$$\begin{aligned} \left\langle 0\ \frac{1}{2}\ \frac{1}{2}\ \middle|\middle| \boldsymbol{S}\times\mathbf{E} \middle|\middle|\ 1\ \frac{1}{2}\ \frac{1}{2}\ \right\rangle &= \langle 0||\mathbf{E}||1\rangle \left\langle \frac{1}{2} \middle|\middle| \mathbf{S} \middle|\middle| \frac{1}{2}\right\rangle \sqrt{12} \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ 0 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & 1 \end{Bmatrix} \\ &= \langle 0||\mathbf{E}||1\rangle \sqrt{\frac{3}{2}}\sqrt{12}\frac{1}{3}\sqrt{\frac{1}{6}} = \langle 0||\mathbf{E}||1\rangle \sqrt{\frac{1}{3}} \end{aligned} \tag{3.62}$$

where we have used [39, p.76]

$$\left\langle \frac{1}{2} \middle|\middle| \mathbf{S} \middle|\middle| \frac{1}{2}\right\rangle = \hbar\sqrt{\frac{3}{2}} \tag{3.63}$$

we now evaluate $\langle 0||\mathbf{E}||1\rangle$ using Eq.(3.58)

$$\langle 00|\mathbf{E}\cdot\hat{z}||10\rangle = \begin{pmatrix} 0 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} \langle 0||\mathbf{E}||1\rangle = -\sqrt{\frac{1}{3}}\langle 0||\mathbf{E}||1\rangle \tag{3.64}$$

Therefore

$$\begin{aligned} \left\langle 0\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \middle| (\boldsymbol{S}\times\mathbf{E}\cdot\hat{z}) \middle| 1\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \right\rangle &= -i\sqrt{2}\sqrt{\frac{1}{6}}\sqrt{\frac{1}{3}}\sqrt{3}\,\langle 00|\mathbf{E}\cdot\hat{z}||10\rangle \\ &= -i\sqrt{\frac{1}{3}}\,\langle 00|\mathbf{E}\cdot\hat{z}||10\rangle \\ &= -i\sqrt{\frac{1}{3}}\left\langle \Psi_{1s}|\frac{\cos\theta}{r^2}|\Psi_{2p}\right\rangle = -\frac{2i}{27}\sqrt{\frac{2}{3}} \end{aligned} \tag{3.65}$$

Similarly for the $2p_{\frac{3}{2}}$ to $1s$ we have

$$\begin{aligned}\left\langle 0\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\ \middle| (\boldsymbol{S}\times\mathbf{E}\cdot\hat{z}) \middle| 1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}\ \right\rangle &= \sqrt{\frac{1}{6}}\left\langle \Psi_{1s} \middle| \frac{\cos\theta}{r^2} \middle| \Psi_{2p} \right\rangle \\ &= \frac{2i}{27}\sqrt{\frac{1}{3}}\end{aligned} \tag{3.66}$$

which are the same results we obtained analytically.

Chapter 4

Psuedospectral Method

We have so far only discussed the corrections to the operator, we will now consider the corrections to the wave functions. For one-electron systems we can obtain the exact analytic form of the wave functions, as shown in the Appendix and in Chapter 5. This is not possible for the two-electron case, but we can make use of variational methods. Variational methods have the advantage that they can be used to solve the Schrödinger equation in cases where it cannot be solved analytically. This chapter discusses how variational methods can be applied to many-electron atoms or complicated systems. An expansion in a basis set essentially converts the differential equation into a matrix equation, making it into a linear algebra problem that can be solved by matrix diagonalization. We can thus create a discrete variational spectrum, called a pseudospectrum, which approximates the physical spectrum.

4.1 Rayleigh-Ritz Variational Method

The following sections are discussed in detail in [40], we present here a summary for the reader. Suppose we have a Hamiltonian that we cannot solve exactly. We know there exists a spectrum of exact solutions to the Schrödinger equation for this

Hamiltonian.

$$H\Psi_i = E_i\Psi_i, i = 1, 2, 3.. \tag{4.1}$$

Let us now define a trial wave function, Ψ_{trial}, that approximates one of the Ψ_i. Assume that Ψ_i and Ψ_{trial} are both normalized and ideally $\Psi_{\text{trial}} = \Psi_i$. Although we may not even know the Ψ_i, since we know they form a complete basis set we can expand the trial wave function, Ψ_{trial} in terms of the Ψ_i, as follows

$$\Psi_{\text{trial}} = \sum_i^{\infty} c_i\Psi_i \tag{4.2}$$

We can get the trial energy, E_{trial}, corresponding to the trial wave function using the Rayleigh Quotient [40]

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{4.3}$$

Using Eq.(4.1) and Eq.(4.2) and substituting into Eq.(4.3) gives

$$E = \frac{\sum_i^{\infty} E_i|c_i|^2}{\sum_i^{\infty} |c_i|^2} \tag{4.4}$$

Since we had made the assumption that all the Ψ_i and Ψ_{trial} are normalized, this means that

$$\sum_i^{\infty} |c_i|^2 = 1 \tag{4.5}$$

so that Eq.(4.3) becomes

$$\begin{aligned} E_{\text{trial}} &= |c_1|^2E_1 + |c_2|^2E_2 + |c_3|^2E_3 + ... \\ &= E_1 + |c_2|^2(E_2 - E_1) + |c_3|^2(E_3 - E_1) + ... \end{aligned}$$

If we let the eigenvalue spectrum be ordered such that $E_1 < E_2 < E_3...$, then E_{trial} is either greater or equal to E_1. Thus, E_{trial} is an upper bound to the lowest energy eigenvalue E_1.

The Rayleigh-Ritz Variational Method uses the fact that we can write an arbitrary function Ψ_{trial} with variational parameters that can be varied to minimize the energy E_{trial}, thus obtaining the closest value to E_1. Therefore any variation in the trial function, which leads to a smaller energy inevitably leads us to a wave function that is closer to the exact solution.

We can thus find the upper bound to the eigenvalue E_1 by minimizing E_{trial}, which means varying the variational parameters in ψ_{trial} until E_{trial} is minimized. Since E_{trial} can never fall below E_1, when we have minimized E_{trial} we would have a good approximation to both the energy eigenvalue and wave function for the first state [41].

In fact, as shown by Hylleraas, Undheim and MacDonald, this method can be used to find the remaining eigenvalues as well [1, 2]. Note that this is only true if the energy spectrum is bounded from below. This will be discussed further in the next section.

4.2 Linear Variational Method

Suppose one writes

$$\Psi_{\text{trial}} = \sum_{i}^{N} a_i \phi_i \tag{4.6}$$

where the ϕ_i are a normalizable set of arbitrary functions. We assume that ϕ_i form a complete basis set in the limit $N \longrightarrow \infty$. Note that these ϕ_i need not have anything to do with the exact wave functions, Ψ_i, discussed in Section 4.1. Again if we use the Rayeligh Quotient (Eq.(4.3)) we get the following expression for the energy

$$\begin{aligned} E_{\text{trial}} &= \frac{\langle \Psi_{\text{trial}} | H | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle} \\ &= \frac{\sum_{ij} a_i^* a_j \langle \phi_i | H | \phi_j \rangle}{\sum_{ij} a_i^* a_j \langle \phi_i | \phi_j \rangle} \end{aligned} \tag{4.7}$$

Then in order to satisfy the minimization condition

$$\frac{\partial E_{\text{trial}}}{\partial a_i} = 0, i = 1...N \tag{4.8}$$

the following must be satisfied

$$\sum_{i=1}^{N} (\langle \phi_i | H | \phi_k \rangle - E_{\text{trial}} \langle \phi_i | \phi_k \rangle) a_i = 0 \tag{4.9}$$

which can be expressed as a N-dimensional eigenvalue problem

$$\begin{bmatrix} \langle \phi_1 | H | \phi_1 \rangle & \dots & \langle \phi_1 | H | \phi_N \rangle \\ \vdots & \ddots & \vdots \\ \langle \phi_N | H | \phi_1 \rangle & \dots & \langle \phi_N | H | \phi_N \rangle \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_N \end{bmatrix} = \begin{bmatrix} \lambda_1 \\ \vdots \\ \lambda_N \end{bmatrix} \begin{bmatrix} \langle \phi_1 | \phi_1 \rangle & \dots & \langle \phi_1 | \phi_N \rangle \\ \vdots & \ddots & \vdots \\ \langle \phi_N | \phi_1 \rangle & \dots & \langle \phi_N | \phi_N \rangle \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_N \end{bmatrix} \tag{4.10}$$

The lowest of the N eigenvalues will be an upper bound to E_1 as discussed in Section 4.1 Note that Eq.(4.9) in the limit $N \longrightarrow \infty$ is equivalent to the Schrödinger Equation provided that the basis set is complete in the limit. Since this is a generalized eigenvalue problem, first the overlap matrix $\langle \phi_i | \phi_j \rangle$, is diagonalized followed by the Hamiltonian matrix. Any set of functions can form ϕ_i as long as they are a complete normalizable set.

The benefit of Eq.(4.9) is its computational usefulness. We need only increase N until the lowest eigenvalue converges to a sufficient degree of accuracy.

This method can be extended beyond the first eigenvalue also, if we use the Hylleraas-Unheim-MacDonald Theorem, which states that "the variational bound property applies not just to the lowest eigenvalue, but also to all the higher-lying variational eigenvalues" [41] provided that the spectrum is bounded from below. This means that not only is $\lambda_1 \geq E_1$, but $\lambda_2 \geq E_2$, and $\lambda_3 \geq E_3$ and so on.

As an extra row and column is added to the Hamiltonian, the N old eigenvalues lie

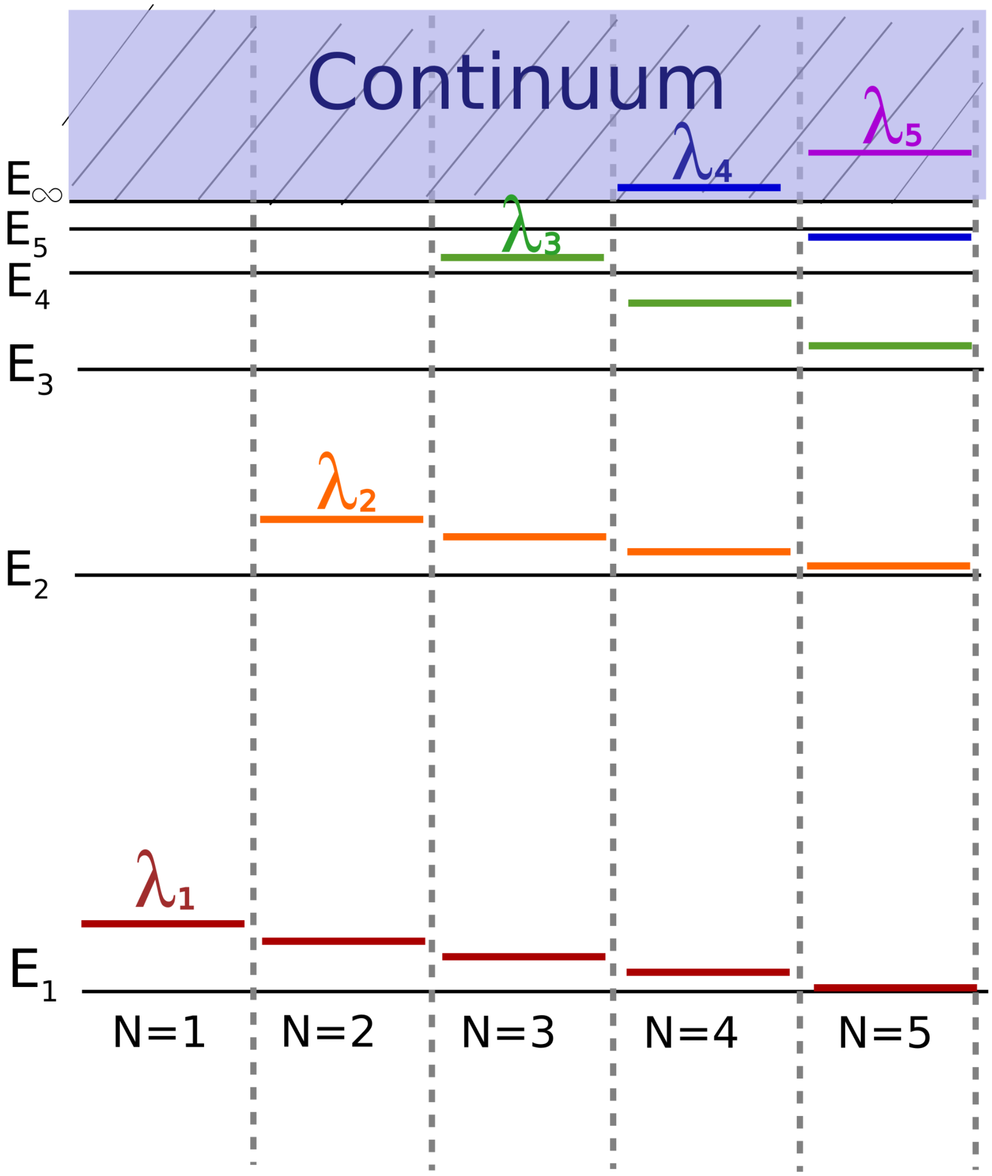

Figure 4.1: This diagram illustrates the Hylleras-Undheim-MacDonald theorem [1, 2]. The E_i are the exact eigenvalues of H, and the λ_i are the variational eigenvalues for a N-dimensional basis set. The previous N eigenvalues lie between the new N+1 eigenvalues as N increases

between the $N+1$ new eigenvalues, which is why it is referred to as the "interleaving" theorem. As N increases the eigenvalues progressively decrease until they reach the exact physical values, as can be seen in Figure 4.1. Additionally, some of the higher lying values actually lie in the continuum. The complete collection of variational solutions are termed pseudostates, as they form a discrete variational representation of the continuous physical spectrum. This is advantageous computationally, as we can do a discrete sum instead of an integration over the continuum, and relatively few pseudostates may be needed to represent the physical spectrum.

4.3 Pseudospectral Method Application to Perturbed Wave Functions

Since most problems in quantum mechanics cannot be solved exactly, it is often useful to split the Hamiltonian into two parts.

$$H = H^{(0)} + \lambda V \tag{4.11}$$

where V is treated as a small perturbation to the Hamiltonian and the Schrödinger equation can be solved exactly for $H^{(0)}$. In our case, the perturbation will be the Breit operators in order to get the relativistic corrections to the wave functions. These Breit operators will be discussed in Chapter 5, we present here the general solution letting V stand for any perturbation.

The time-independent Schrödinger equation, for a state Ψ_i, is

$$H\Psi_i = E\Psi_i \tag{4.12}$$

where i means initial. We now expand both Ψ_i and E_i as a power series in λ

$$\Psi_i = \Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)}... \tag{4.13}$$

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)}... \tag{4.14}$$

Keeping only terms linear in λ gives

$$H^{(0)}\Psi_i^{(1)} + V\Psi_i^{(0)} = E_i^{(0)}\Psi_i^{(1)} + E_i^{(1)}\Psi_i^{(0)} \tag{4.15}$$

$$\left(H^{(0)} - E_i^{(0)}\right)\Psi_i^{(1)} = \left(E_i^{(1)} - V\right)\Psi_i^{(0)} \tag{4.16}$$

which we can write as

$$\left(H^{(0)} - E_i^{(0)}\right)\left|\Psi_i^{(1)}\right\rangle = \left(E_i^{(1)} - V\right)\left|\Psi_i^{(0)}\right\rangle \tag{4.17}$$

If we act $\Psi_{i'}^{(0)}$ from the left on Eq.(4.17) and keep only terms linear in λ we can get the following expression for the first order correction to the energy.

$$E_{i'}^{(1)} = \frac{1}{\left\langle\Psi_{i'}^{(0)}|\Psi^{(0)}\right\rangle}\left[\left\langle\Psi_{i'}^{(0)}|V|\Psi^{(0)}\right\rangle + \left\langle\Psi_{i'}^{(0)}|H^{(0)} - E^{(0)}|\Psi^{(1)}\right\rangle\right] \tag{4.18}$$

Since by assumption $H_i^{(0)}|\Psi_i^{(0)}\rangle = E_i^{(0)}|\Psi_i^{(0)}\rangle$, and assuming that the functions are orthonormal (i.e$\left\langle\Psi_{i'}^{(0)}|\Psi_i^{(0)}\right\rangle = 1$ if and only if $i' = i$) we get

$$E_i^{(1)} = \left\langle\Psi_i^{(0)}|V|\Psi_i^{(0)}\right\rangle \tag{4.19}$$

We can rearrange Eq.(4.17) to

$$\left|\Psi_i^{(1)}\right\rangle = \frac{(E_i^{(1)} - V)|\Psi_i^{(0)}\rangle}{(H^{(0)} - E_i^{(0)})} \tag{4.20}$$

inserting a complete set of states gives

$$\left|\Psi_i^{(1)}\right\rangle = \sum_n \left|\Psi_n^0\right\rangle \frac{\left\langle \Psi_n^0 | (E_i^{(1)} - V) | \Psi_i^{(0)} \right\rangle}{E_n^{(0)} - E_i^{(0)}} \tag{4.21}$$

expanding the numerator

$$\left|\Psi_i^{(1)}\right\rangle = \sum_n \left|\Psi_n^0\right\rangle \frac{\left\langle \Psi_n^0 | E_i^{(1)} | \Psi_i^{(0)} \right\rangle}{E_n^{(0)} - E_i^{(0)}} + \sum_n \left|\Psi_n^0\right\rangle \frac{\left\langle \Psi_n^0 | (V) | \Psi_i^{(0)} \right\rangle}{E_i^{(0)} - E_n^{(0)}} \tag{4.22}$$

We will omit the term with $E_n^{(0)} = E_i^{(0)}$, if present, as that would cause the denominator to be 0. We can assume that $\left\langle \Psi_n^{(0)} | \Psi_i^{(0)} \right\rangle = 0$ for the remaining states. Thus we sum over all n except $n = i$

$$\sum_{n \neq i} |\Psi_n^0 > \frac{\left\langle \Psi_n^{(0)} | E_i^{(1)} | \Psi_i^{(0)} \right\rangle}{E_n^{(0)} - E_i^{(0)}} = \sum_{n \neq i} |\Psi_n^{(0)} > \frac{E_i^{(1)} \left\langle \Psi_n^{(0)} | \Psi_i^{(0)} \right\rangle}{E_n^{(0)} - E_i^{(0)}} = 0 \tag{4.23}$$

Thus we are left with

$$\left|\Psi_i^{(1)}\right\rangle = \sum_{n \neq i} \left|\Psi_n^{(0)}\right\rangle \frac{\left\langle \Psi_n^{(0)} | V | \Psi_i^{(0)} \right\rangle}{E_i^{(0)} - E_n^{(0)}} \tag{4.24}$$

In order to calculate the corrections to the wave function, we can replace the summation over the complete set of intermediate states (including the continuum) by a discrete summation over the set of N pseudostates (as discussed in Section 4.2).

Chapter 5

Corrections to the Wave Functions

We have discussed so far the relativistic corrections of $O(\alpha^2)$ to the nonrelativistic operator in the interaction matrix, which were obtained in Chapter 3. We will now discuss the relativistic corrections of $O(\alpha^2)$ to the Schrödinger wave functions. We need this corrected wave functions to evaluate the remaining terms

$$-\alpha^3 \left\langle \Psi_{1s}^{(1)} | \mathbf{p}_z | \Psi_{2p}^{(0)} \right\rangle = i\hbar\alpha^3 \left\langle \Psi_{1s}^{(1)} | \nabla_z | \Psi_{2p}^{(0)} \right\rangle \tag{5.1}$$

$$-\alpha^3 \left\langle \Psi_{2s}^{(0)} | \mathbf{p}_z | \Psi_{2p}^{(1)} \right\rangle = i\hbar\alpha^3 \left\langle \Psi_{2s}^{(0)} | \nabla_z | \Psi_{2p}^{(1)} \right\rangle \tag{5.2}$$

The previous chapter discussed the pseudospectral method, whereby with the use of variational methods one can make a pseudospectrum. This pseudospectrum can be used to calculate the corrections to the wave functions, as the summation over the continuum can be approximated by a discrete sum over the pseudostates. For the one-electron case we can calculate the corrections to the wave functions analytically. For the two-electron case one needs to use the pseudospectral method to obtain the wave function corrections.

In this chapter we will discuss first the Breit corrections, i.e relativistic corrections, and perturbation theory. We will then present the analytic first order wave functions (detailed discussion of the analytic wave functions are in the Appendix), these will be used as a reference for the approximate wave functions obtained by the pseudospectral method. Furthermore, in this chapter, we will compare the results obtained by the Pseudostate method using a linear basis set to the triangular basis set, which encompasses a larger energy spectrum.

5.1 The Breit Corrections

Since we have already shown the Foldy-Wouthuysen transformation (Chapter 3), we will use those results to get the Breit, i.e relativistic, corrections to the Hamiltonian and thus determine the Breit correction terms. These can also be derived from the Breit equation expanded in powers of $\frac{p}{mc}$ as shown by Bethe and Salpeter [34, p.181], or, starting from the Dirac equation, separating out the rest mass energy by defining $E' = E - mc^2$, and expanding the small component as done by Schiff [30].

The total energy is

$$E = \langle \Psi_j | H | \Psi_j \rangle \tag{5.3}$$

Thus only even terms that were in the Hamiltonian in Eq.(3.40) will contribute. This means

$$H = H^{(0)} - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{e\hbar^2}{8(mc)^2}(\nabla_r^2(\phi)) + \frac{e\hbar}{4(mc)^2}\frac{1}{r}\frac{\partial\phi}{\partial r}\boldsymbol{\sigma}\cdot\mathbf{L} \tag{5.4}$$

we can use atomic units and rewrite this as

$$H = H^{(0)} - \alpha^2\frac{\mathbf{p}^4}{8} + \alpha^2\frac{\pi\delta^3(\vec{r})}{2} + \alpha^2\frac{1}{2}\frac{1}{r}\frac{dV}{dr}\mathbf{L}\cdot\mathbf{S} \tag{5.5}$$

where we have used $\phi = -\frac{1}{r}$ and $\mathbf{S} = \frac{\boldsymbol{\sigma}}{2}$. $\mathbf{L}$ is the orbital angular momentum and $\mathbf{S}$ is the spin angular momentum.

There are thus three α^2 correction terms in the Hamiltonian. The first term, which we will from here on refer to as the p^4 *term*, refers to the correction due to the

”variation of mass with velocity” [34], meaning the change in the mass of the electron due to its relativisitic motion. This is independent of the spin of the electron. The second term, which we will now refer to as the $\delta^3(\vec{r})$ *term* is a term characteristic of the Dirac equation. This only affects the s-states as the wave functions with $l > 0$ vanish at the origin. This is also a spin independent term. The last term, is the *spin-orbit term* which arises from the interaction between the electron orbital magnetic moment and spin magnetic moment. This is the only spin dependent term. For the two-electron case there are some additional terms, which are given in [34, p.181]

5.2 The Wave Function Corrections Using the Analytic Method

From perturbation theory the first order perturbation equation is (see Section 4.3 for details)

$$H^{(0)}\Psi^{(1)} + V\Psi^{(0)} = E^{(0)}\Psi^{(1)} + E^{(1)}\Psi^{(0)} \tag{5.6}$$

where V is the perturbation,

$$(H^{(0)} - E^{(0)})\Psi^{(1)} + V\Psi^{(0)} - E^{(1)}\Psi^{(0)} = 0 \tag{5.7}$$

We can solve this differential equation using the Method of Frobenius [42]. We first let

$$\Psi^{(1)} = \left[\sum_s (q_s r^{s-2} + m_s r^{s-1}\ln(r))\right]\Psi^{(0)} \tag{5.8}$$

The logarithmic terms are included as they appear in the solutions for the 1s wave function correction as seen in Cohen and Dalgarno's paper [43]. Our results showed that these terms exist for both s and p-states as the coefficients for the logarithmic terms did not turn out to be 0 for the p-states. They seem to be a mathematic necessity, and they might arise in the s-states to describe the wave function behaviour near the nucleus (near 0). For p-states, the small component still behaves like an s-state near the nucleus. We know that

$$E^{(1)} = \left\langle \Psi^{(0)} | V | \Psi^{(0)} \right\rangle \tag{5.9}$$

and

$$H^{(0)} = \frac{p^2}{2} - \frac{1}{r} \tag{5.10}$$

$$E^{(0)} = -\frac{1}{2n^2} \tag{5.11}$$

where n is the principal quantum number and $\Psi^{(0)}$ is the regular Schrödinger wave function, and we have used atomic units ($m = e = \hbar = 1$). In our case, the perturbation is $V = \alpha^2 H_{rel}$, where H_{rel} was defined in Eq.(5.32)

Substituting all of these into Eq.(5.7), we can group all the terms with the same powers of r and thus determine the coefficients q_i and m_i. Details are given in Appendix and results will be also shown here.

5.2.1 Analytic Results for 1s

The spin-orbit term is 0 for the s-states so we need only consider the p^4 term and the $\delta^3(\vec{r})$ term in H_{rel} Eq.(5.32).

Solutions for $\Psi^{(1)}$ for the s-states for some perturbations have been previously determined by Cohen and Dalgarno [43]. Among these are the first order wave function correction for the perturbation $V = \nabla^4$ and for the perturbation $V = \delta^3(\vec{r})$ which are of interest to us since these functions are also in H_{rel}. These will provide a check for us to see if our results from the pseudospectrum method are correct, as well as enable an independent check of our analytic method.

The unnormalized wave function correction for $V = \nabla^4$, as determined in [43] is

$$\psi_{1s}^{(1)} = \left[4Z^3 r - 4\frac{Z}{r} + 8Z^2 \ln(r)\right] \Psi_{1s}^{(0)}$$

and for the perturbation $\pi\delta^3(\vec{r})$

$$\Psi_{1s}^{(1)} = \left[Z^2 r - \frac{1}{2r} + Z\ln(r)\right] \Psi_{1s}^{(0)}$$

where in both cases

$$\Psi_{1s}^{(0)} = \sqrt{\frac{Z^3}{\pi}} e^{-Zr}$$

These solutions can be used to find the first order corrections to the wave functions for the p^4 term and the $\delta^3(\vec{r})$ term, as the operators differ only by a constant. The wave functions were also normalized using the Gram Schmidt procedure. Since $(H^{(0)} - E^{(0)})\Psi^{(0)} = 0$ we can add an arbitrary amount of $\Psi^{(0)}$ to $\Psi^{(1)}$ and it still satisfies Eq.(5.32), i.e $\Psi^{(1)'} = \Psi^{(1)} + \epsilon\Psi^{(0)}$ is still a solution. The strategy is to choose ϵ so that $\left\langle \Psi^{(1')} | \Psi^{(0)} \right\rangle = 0$. This ensures that the full solution $\Psi^{(0)} + \lambda\Psi^{(1)}$ remains normalized at least up to terms linear in λ.

Thus using Cohen and Dalgarno's results [43], the first order wave function corrections for the perturbation $\frac{-p^4}{8}$ was determined to be

$$\Psi_{1s}^{(1)} = \left(- \ln(2) - \ln(r) + \frac{1}{2r} - \frac{r}{2} + \frac{(-4\gamma + 7)}{4} \right) \Psi_{1s}^{(0)} \tag{5.12}$$

where $\gamma = 0.577215664901532860606 5121$ is the Euler-Mascheroni constant. For the $\frac{\pi\delta^3(\vec{r})}{2}$ correction term, the normalized first order wave function correction was determined to be:

$$\Psi_{1s}^{(1)} = \left(\frac{\ln(2)}{2} + \frac{\ln(r)}{2} - \frac{1}{4r} + \frac{r}{2} + \frac{(2\gamma - 5)}{4} \right) \Psi_{1s}^{(0)} \tag{5.13}$$

Using these we can calculate the correction due to the $1s$ wave function correction, i.e Eq.(3.46)

$$-\alpha^3 \left\langle \Psi_{1s}^{(1)} | p_z | \Psi_{2p}^{(0)} \right\rangle \tag{5.14}$$

since $\Psi_{1s}^{(1)}$ is the sum of Eq.(5.12) and (5.13)

$$\left| \Psi_{1s}^{(1)} \right\rangle = \left| \Psi_{p^4}^{(1)} \right\rangle + \left| \Psi_{\delta}^{(1)} \right\rangle \tag{5.15}$$

we obtain

$$-\left\langle \Psi_{p^4}^{(1)} | p_z | \Psi_{2p}^{(0)} \right\rangle = \frac{\sqrt{2}(1 + 48\ln(3) - 96\ln(2)}{243} i = -0.074,544,415,992,783,892,407,877,82i \tag{5.16}$$

and

$$-\left\langle \Psi_{\delta}^{(1)} | p_z | \Psi_{2p}^{(0)} \right\rangle = \frac{\sqrt{2}(1 - 16\ln(3) + 32\ln(2)}{162} i = 0.048,911,825,793,701,370,473,911,68i \tag{5.17}$$

giving the result

$$-\left\langle \Psi_{1s}^{(1)} | p_z | \Psi_{2p}^{(0)} \right\rangle = \frac{\sqrt{2}(5 + 48\ln(3) - 96\ln(2))}{486} i = -0.025,632,590,199,082,521,933,966,15i \tag{5.18}$$

5.2.2 Analytic Results for 2p

Analytic solutions for the p-states have not been previously published and so are obtained here. Using the method outlined in the previous section, the first-order wave functions for the 2p state were determined and those results will be presented below

For the p-states there are two contributions, one from the p^4 term and one from the spin obit term in H_{rel} (see Eq.(5.32)).

For the perturbation $\frac{-p^4}{8}$ the first order wave function correction is

$$\Psi_{2p}^{(1)} = \left[\frac{-48\ln(r)r + 72 - 3r^2 + (97 - 48\gamma)r}{144r}\right]\Psi_{2p}^{(0)} \tag{5.19}$$

For a perturbation of $\frac{\mathbf{L}\cdot\mathbf{S}}{2r^3}$, the first order wave function corrections for the $2p_{1/2}$ and $2p_{3/2}$ are:

$$\Psi_{2p_{\frac{1}{2}}}^{(1)} = \left[\frac{-12\ln(r)r + 36 - 3r^2 + (31 - 12\gamma)r}{72r}\right]\Psi_{2p}^{(0)} \tag{5.20}$$

$$\Psi_{2p_{\frac{3}{2}}}^{(1)} = \left[\frac{12\ln(r)r - 36 + 3r^2 + (12\gamma - 31)r}{144r}\right]\Psi_{2p}^{(0)} \tag{5.21}$$

We note that

$$\Psi_{2p_{\frac{1}{2}}}^{(1)} = -\frac{1}{2}\Psi_{2p_{\frac{3}{2}}}^{(1)} \tag{5.22}$$

Using these we can calculate the correction due to the $2p$ wave function correction, i.e Eq. (3.47)

$$-\alpha^3\left\langle \Psi_{1s}^{(0)}|p_z|\Psi_{2p}^{(1)}\right\rangle \tag{5.23}$$

since $\Psi_{2p}^{(1)}$ is the sum of Eq.(5.19) and (5.20) or (5.21). For $2p_{\frac{1}{2}}$

$$\left|\Psi_{2p_{\frac{1}{2}}}^{(1)}\right\rangle = \left|\Psi_{p^4}^{(1)}\right\rangle + \left|\Psi_{SO_{\frac{1}{2}}}^{(1)}\right\rangle \tag{5.24}$$

and therefore

$$-\left\langle \Psi_{1s}^{(0)}|p_z|\Psi_{p^4}^{(1)}\right\rangle = \frac{\sqrt{2}(37 - 48\ln(3) - 48\ln(2))}{729}i = -0.109,533,314,191,598,355,423,887,2i \tag{5.25}$$

and

$$-\left\langle \Psi_{1s}^{(0)}|p_z|\Psi_{SO_{\frac{1}{2}}}^{(1)} \right\rangle = \frac{2\sqrt{2}(19+12\ln(3)-12\ln(2)}{729}i = 0.092,595,414,937,054,806,589,355,07i \tag{5.26}$$

giving the result

$$-\left\langle \Psi_{1s}^{(0)}|p_z|\Psi_{2p_{\frac{1}{2}}^{(1)}} \right\rangle = \frac{25}{48}+\frac{\ln(3)}{2}-\frac{\ln(2)}{2}i = -0.723,565,887,387,415,524,322,340,0i \tag{5.27}$$

For $2p_{\frac{3}{2}}$:

$$\left|\Psi_{2p_{\frac{3}{2}}}^{(1)}\right\rangle = \left|\Psi_{p^4}^{(1)}\right\rangle + \left|\Psi_{SO_{\frac{3}{2}}}^{(1)}\right\rangle \tag{5.28}$$

The p^4 correction is the same, the spin orbit term is

$$-\left\langle \Psi_{1s}^{(0)}|p_z|\Psi_{SO_{\frac{3}{2}}}^{(1)} \right\rangle = -\frac{\sqrt{2}(19+12\ln(3)-12\ln(2)}{729} = 0.09259541493705480658935507i \tag{5.29}$$

giving the result

$$-\alpha^3\left\langle \Psi_{1s}^{(0)}|p_z|\Psi_{2p_{\frac{3}{2}}}^{(1)} \right\rangle = \frac{25}{48}+\frac{\ln(3)}{2}-\frac{\ln(2)}{2} = -\alpha^3 0.72356588738741552432234 00i \tag{5.30}$$

5.3 The Wave Function Corrections using the Pseudostate Method

The purpose of this section is to test an alternative pseudostate method of finding approximate solutions to the perturbation equations. For two-electron problems, exact analytic solutions are not possible. For such cases, instead of solving the perturbation equation analytically we can instead express the solution in terms of pseudostates. We can treat H_{rel} as a perturbation, and use Eq.(5.33) from Chapter 4

$$\left|\Psi^{(1)}\right\rangle = \sum_{n=1}^{N} |\Psi_n^0\rangle \frac{\left\langle \Psi^0 | H_{rel} | \Psi_n^{(0)} \right\rangle}{E^{(0)} - E_n^{(0)}} \tag{5.31}$$

where the Ψ_n^0 are the pseudostates, N is the number of pseudostates and

$$H_{rel} = \frac{p^4}{8} + \frac{\pi\delta^3(\vec{r})}{2} + \frac{1}{2}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S} \tag{5.32}$$

Since the first-order correction due to the spin-orbit term vanishes for the 1s state, there are only two contributions to the wave function correction: the p^4 term and the $\delta^3(\vec{r})$ correction term. For the 1s state we need only evaluate

$$\left|\Psi_{1s}^{(1)}\right\rangle = \sum_{n=1}^{N} |\Psi_n^0\rangle \frac{\left\langle \Psi_{1s}^0 | \frac{-p^4}{8} | \Psi_n^{(0)} \right\rangle}{E_s^{(0)} - E_n^{(0)}} + \sum_{n=1}^{N} |\Psi_n^0\rangle \frac{\left\langle \Psi_{1s}^0 | \frac{\pi\delta^3(\vec{r})}{2} | \Psi_n^{(0)} \right\rangle}{2(E_s^{(0)} - E_n^{(0)})} \tag{5.33}$$

whereas for the 2p state, the $\delta^3(\vec{r})$ correction term vanishes, and there are again only two contributions to the wave function correction: the p^4 term and the spin orbit correction term. For the 2p state we need only evaluate

$$\left|\Psi_{2p}^{(1)}\right\rangle = \sum_{n=1}^{N} |\Psi_n^0\rangle \frac{\left\langle \Psi_{2p}^0 | \frac{-p^4}{8} | \Psi_n^{(0)} \right\rangle}{E_s^{(0)} - E_n^{(0)}} + \sum_{n=1}^{N} |\Psi_n^0\rangle \frac{\left\langle \Psi_{2p}^0 | \frac{1}{2}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S} | \Psi_n^{(0)} \right\rangle}{E_s^{(0)} - E_n^{(0)}} \tag{5.34}$$

The results from Eq.(5.33) and Eq.(5.34), depend largely on how well the pseudospectrum represents the actual physical spectrum. The following section examines two different pseudostate wave function representations and compares them.

5.4 Linear vs. Triangular Basis

We will now compare two different Sturmian basis sets that can be used to produce a pseudospectrum. In the simplest representations, which we will call the linear basis the pseudostates are of the form:

$$\Psi_n = e^{-\alpha_0 r} Y_{lm}(a_1 r^0 + a_2 r^1 + a_3 r^2 + a_4 r^3 \ldots. a_n r^q) \tag{5.35}$$

where q is the highest power of r, which can be set arbitrarily and $\alpha_0 = \frac{1}{n'}$ where n' is the principal quantum number of the particular states we are trying to approximate. A higher q means more peusodosates and a broader energy spectrum extending to higher energy. The number of pseudostates N is equal to the number of terms in each pseudostate. We can increase q until the answer converges to sufficient accuracy. For example, if we want to sum over s-states and only want 5 pseudostates, α_0 would be 1 and if we set q as 4, we would get a spectrum of 5 pseudostates with each pseudostate having 5 terms:

$$\begin{aligned}
\Psi_1 &= e^{-r} Y_{10}(a_1 r^0 + a_2 r^1 + a_3 r^2 + a_4 r^3 + a_5 r^4) \\
\Psi_2 &= e^{-r} Y_{10}(a_6 r^0 + a_7 r^1 + a_8 r^2 + a_9 r^3 + a_{10} r^4) \\
\Psi_3 &= e^{-r} Y_{10}(a_{11} r^0 + a_{12} r^{+} a_{13} r^2 + a_{14} r^3 + a_{15} r^4) \\
\Psi_4 &= e^{-r} Y_{10}(a_{16} r^0 + a_{17} r^1 + a_{18} r^2 + a_{19} r^3 + a_{20} r^4) \\
\Psi_5 &= e^{-r} Y_{10}(a_{21} r^0 + a_{22} r^1 + a_{23} r^2 + a_{24} r^3 + a_{25} r^4)
\end{aligned} \tag{5.36}$$

We shall now consider a different basis we shall label as the "triangular basis". The triangular basis was first used for the calculation of Bethe logarithms in helium-like systems [44], but has not been studied in much detail since. In the triangular basis, the pseudostate wave functions are of the form

$$\Psi_n =$$

$$Y_{lm}[e^{-\alpha_0 \lambda^q r}(r^{q-q})$$

$$+e^{-\alpha_0 \lambda^{q-1} r}(r^0 + r^{q-(q-1)})$$

$$+e^{-\alpha_0 \lambda^{q-2} r}(r^0 + r^1 + r^{q-(q-2)})$$

$$\vdots$$

$$+e^{-\alpha_0 \lambda^{q-q} r}(r^0 + r^1 + r^2 + r^3 .... r^q)]$$

Now we have two variables, q, the highest power of r, and λ, which is a variable scale parameter. The total number of terms in each pseudostate is $\frac{(q+1)(q+2)}{2}$, which is also the number of pseudostates and their related energies. The parameter λ controls "the spacing between the tiers of terms on different distance scales"[44], so as λ increases it covers a huge range of energies in the actual spectrum compared to the simple linear method, as can be seen in Figure 5.1. As an example, for the 1s state, if q is set to 4, we would have 15 pseudostates. The first pseudostate would be

$$\Psi_1 =$$

$$Y_{10}\Big[e^{-\lambda^4 r}\left(a_{15} r^0\right)$$

$$+e^{-\lambda^3 r}\left(a_{13} r^0 + a_{14} r^1\right)$$

$$+e^{-\lambda^2 r}\left(a_{10} r^0 + a_{11} r^1 + a_{12} r^2\right)$$

$$+e^{-\lambda^1 r}\left(a_6 r^0 + a_7 r^1 + a_8 r^2 + a_9 r^3\right)$$

$$+e^{-\lambda^0 r}\left(a_1 r^0 + a_2 r^1 + a_3 r^2 + a_4 r^3 + a_5 r^4\right)\Big]$$

An important limitation of the linear basis set is that the highest power N cannot

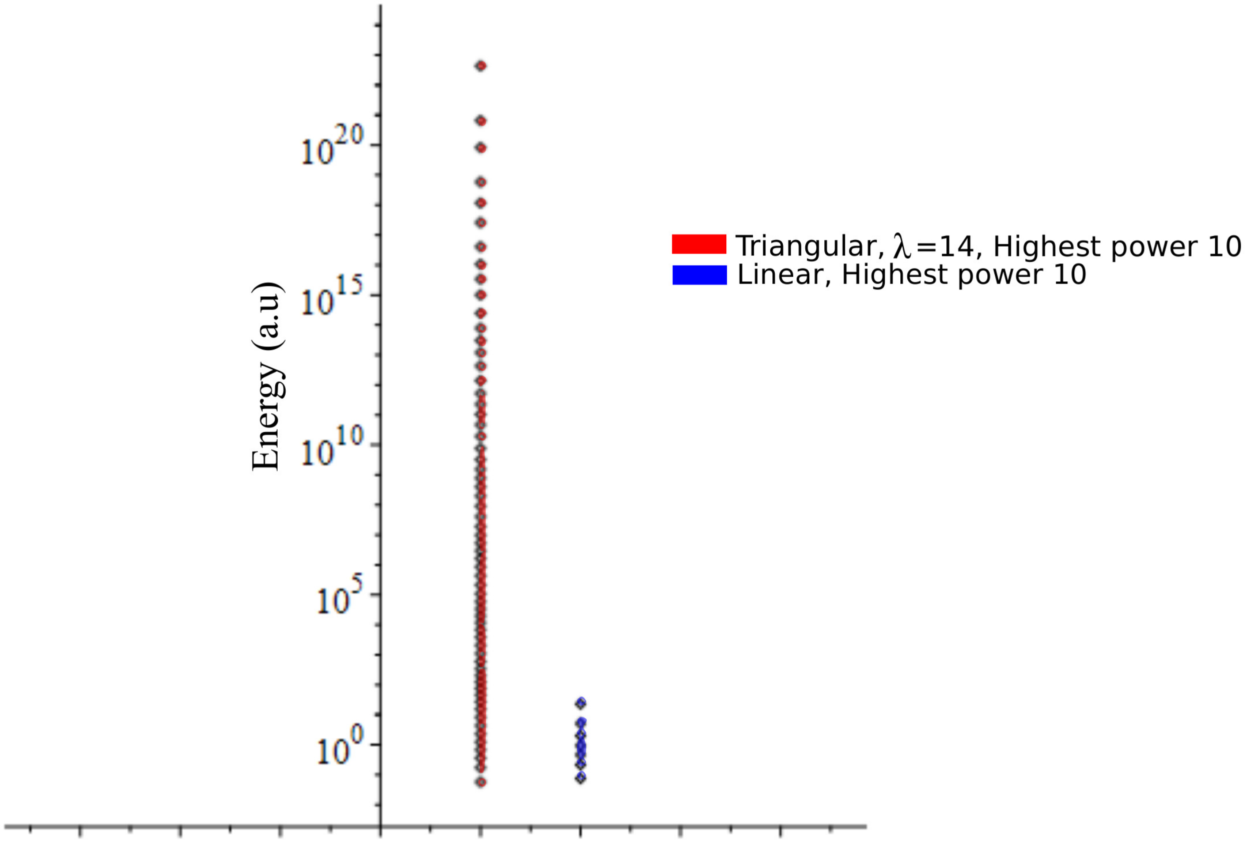

Figure 5.1: This diagram shows the energy spectrum for the 1s pseudostates for highest power 10, for both triangular and linear basis. The triangular one covers an enormously larger range of energies.

be increased indefinitely due to numerical round-off errors that produce negative eigenvalues for the overlap matrix. For example, in double precision, the highest value of N is approximately $N = 16$. This limits the accuracy that can be obtained.In order to compare these methods we will look at one of the correction terms that we need to calculate in Eq.(3.46):

$$\sum_{n=1}^{N} \left\langle \Psi_n^{(0)} | p_z | \Psi_{2p}^{(0)} \right\rangle \frac{\left\langle \Psi_{1s}^{0} | \frac{-p^4}{8} | \Psi_n^{(0)} \right\rangle}{E_s^{(0)} - E_n^{(0)}} \tag{5.37}$$

We will call this the p^4 *correction term for 1s.* The analytic value was determined in Eq.(5.16) in subsection 5.2.1 as $-0.074,544,415,992,783,892,407,877,82i$. Table 5.1 shows the values found using the linear basis, and Table 5.2 shows the values found using the triangular basis with $\lambda = 10$. The highest accuracy achieved in the linear basis values was 10^{-5} at the highest power of 14. The same accuracy of 10^{-5} can be achieved using the triangular basis at a highest power of 10. Thus, the triangular basis gives the same accuracy as the linear basis set but with a lower highest power of r, which is an advantage as we can now increase accuracy without running into problems such as round-off errors caused by increasing the highest power of r. Furthermore, at the highest power of 14 the triangular basis value is two orders of magnitude more accuarate. To compare convergence we can look at the difference between successive values. Looking at the values from both at a highest power of 11, the triangular basis value is smaller by two orders of magnitude thus it is converging quicker than the linear basis.

In order to compare their convergence we can also look at the values found by partial sums over pseudostates up to a certain energy. The values shown in Figure 5.3 give a clearer convergence pattern than the values in Figure 5.2, as they arrive at a clear steady value and a plateau.

It is thus clear that the triangular basis converges faster and gives more accurate

Table 5.1: Values for the p^4 correction term for 1s (i.e $\sum_{n=1}^{N} \left\langle \Psi_n^{(0)} | p_z | \Psi_{2p}^{(0)} \right\rangle \frac{\left\langle \Psi_{1s}^{0} | \frac{-p^4}{8} | \Psi_n^{(0)} \right\rangle}{E_s^{(0)} - E_n^{(0)}}$) using the linear basis. As the highest power is increased (and subsequently the number of pseudostates), the difference between successive values decrease and we also get closer to the analytic value

Max Power of R	**linear**	**Difference with previous value**	**Difference with Analytic Value**
6	-0.0793601567090413		-0.0048157407162575
7	-0.0723531313671880	0.0070070253418533	0.0021912846255958
8	-0.0754985392647251	0.0031454078975371	-0.0009541232719413
9	-0.0741423759205424	0.0013561633441827	0.0004020400722414
10	-0.0747094243847665	0.0005670484642241	-0.0001650083919827
11	**-0.0744778891018926**	**0.0002315352828739**	**0.0000665268908912**
12	-0.0745693128790127	0.0000914237771201	-0.0000248968862289
13	-0.0745317041795466	0.0000376086994661	0.0000127118132372
14	-0.0745391298868143	0.0000074257072677	0.0000052861059695

Table 5.2: Values for the p^4 correction term for 1s (i.e $\sum_{n=1}^{N} \left\langle \Psi_n^{(0)} | p_z | \Psi_{2p}^{(0)} \right\rangle \frac{\left\langle \Psi_{1s}^{0} | \frac{-p^4}{8} | \Psi_n^{(0)} \right\rangle}{E_s^{(0)} - E_n^{(0)}}$) using the triangular basis with a λ of 10. As the highest power is increased (and subsequently the amount of pseudostates), the difference between successive values decrease and we also gets closer to the analytic value

Max Power of R	**Triangular with λ 10**	**Difference with previous value**	**Difference with Analytic Value**
6	-0.0741626132868520		0.0003818027059318
7	-0.0743951738119599	0.0002325605251079	0.0001492421808239
8	-0.0745996584300792	0.0002044846181193	0.0000552424372954
9	-0.0745642821014297	0.0000353763286495	0.0000198661086459
10	-0.0745374174797260	0.0000268646217037	0.0000069985130578
11	-0.0745419927587497	**0.0000045752790237**	**0.0000024232340341**
12	-0.0745452432945680	0.0000032505358183	0.0000008273017842
13	-0.0745446951898728	0.0000005481046952	0.0000002791970890
14	-0.0745443226806348	0.0000003725092380	0.0000000933121490

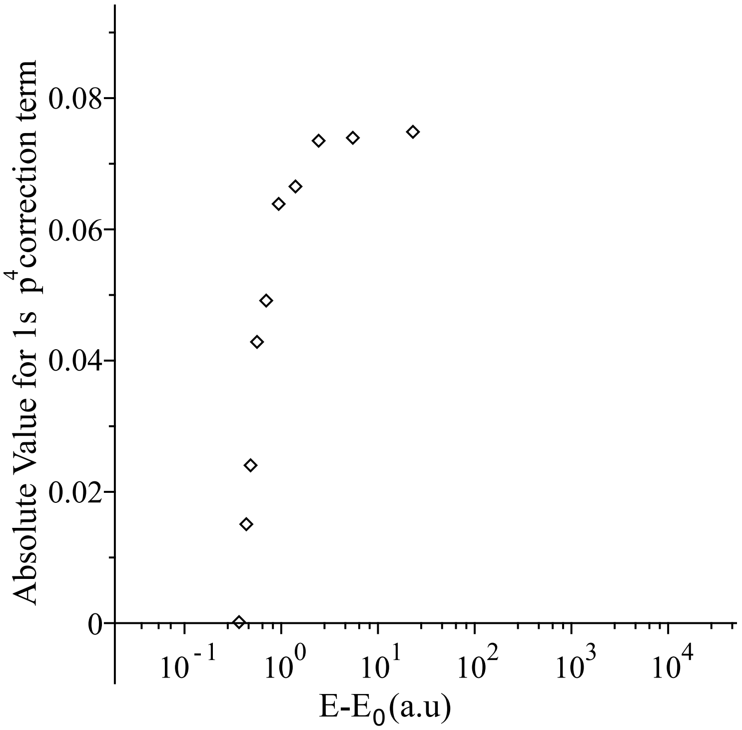

Figure 5.2: The contributions to the p^4 correction term for 1s (i.e $\sum_{n=1}^{N}\left\langle \Psi_n^{(0)}|p_z|\Psi_{2p}^{(0)}\right\rangle \frac{\left\langle \Psi_{1s}^{0}|\frac{-p^4}{8}|\Psi_n^{(0)}\right\rangle}{E_s^{(0)}-E_n^{(0)}}$) by the partial sums over pseudostates up to a certain energy, using a linear basis with a highest power of 10. The absolute value was taken for clarity in the graph

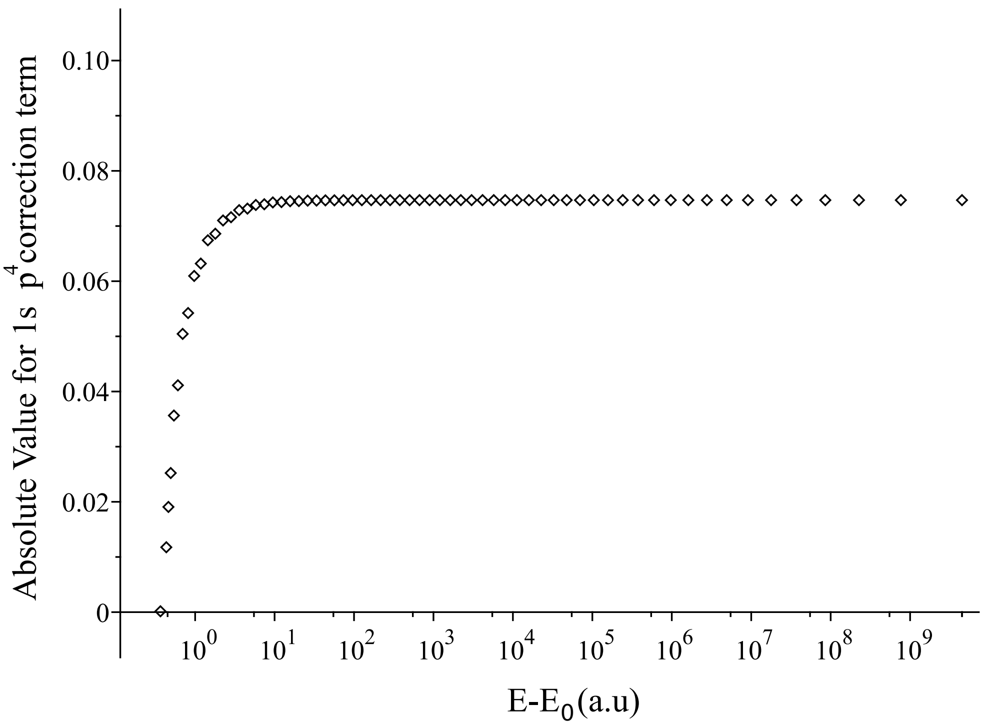

Figure 5.3: The contributions to the p^4 correction term for 1s (i.e $\sum_{n=1}^{N}\left\langle \Psi_n^{(0)}|p_z|\Psi_{2p}^{(0)}\right\rangle \frac{\left\langle \Psi_{1s}^{0}|\frac{-p^4}{8}|\Psi_n^{(0)}\right\rangle}{E_s^{(0)}-E_n^{(0)}}$) by the partial sums over pseudostates up to a certain energy, using a triangular basis with λ of only 3 and a highest power of 10. The absolute value was taken for clarity in the graph

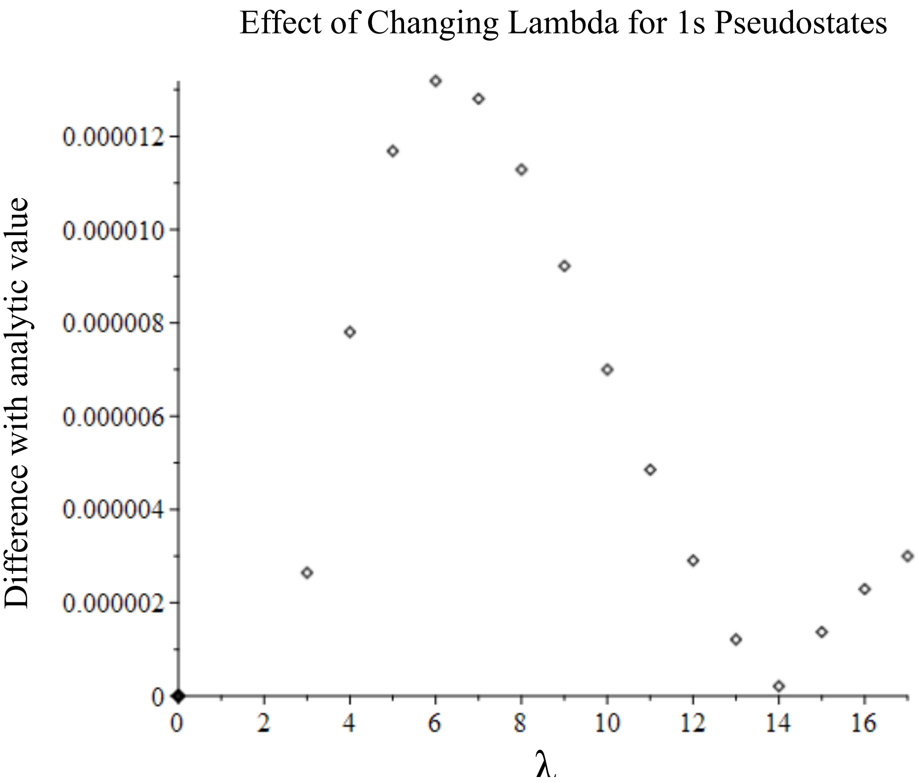

Figure 5.4: Plot of the deviation of the p^4 correction term for 1s ((i.e $\sum_{n=1}^{N} \left\langle \Psi_n^{(0)}|p_z|\Psi_{2p}^{(0)} \right\rangle \frac{\left\langle \Psi_{1s}^{0}|\frac{-p^4}{8}|\Psi_n^{(0)} \right\rangle}{E_s^{(0)}-E_n^{(0)}}$) from the expected analytic value, with changing lambda, while the highest power of r is fixed at 10. A minimum can be seen at a λ of 14.

values as compared to the linear basis. As the highest power of r is increased the values improve for both; however, computation time also increases. We can however modify the λ parameter; with an optimal value of λ we don't need to increase the highest power as much. The optimal value of λ is chosen which minimizes the difference between successive values, thus giving the least error. In our case since the analytic value is known, the optimal value of λ is that which gives the closest value to the analytic value. For the 1s pseudostate spectrum, the optimal value of λ is 14 as can be seen in Figure 5.4.

Due to the λ the pseudostates in the triangular basis set can span a larger portion of the spectrum and thus converge faster. As we increase the number of pseudostates, the dependance with λ becomes less. Ideally we want to keep the number of pseudostates to a minimum, and find the ideal λ which gives us the optimum value. We thus get a better value compared with the linear basis with minimal increase in computation time.

5.5 Pseudostate Wave Functions Vs. Analytic

We have seen that the triangular basis is a significantly better basis set than the linear basis set. We will now compare the first order wave function correction obtained using the pseudospectral method (with a triangular basis), with the analytic first order wave function corrections. Figure 5.5 shows a plot of the $\Psi_{1s}^{(1)}$ obtained from the pseudostate method compared with the analytic one. A triangular basis was used with $\lambda = 14$, (which as shown in Figure 5.4 this was the optimal value for $1s$) and the highest power of r was 6 which is very low. This shows that even with a small highest power of r, and subsequently less pseudostates, we still acheive a good representation of the wave function. Figure 5.6 shows the difference between the absolute values of the $\Psi_{1s}^{(1)}$ obtained from the pseudostate method with the $\Psi_{1s}^{(1)}$ obtained from the analytic method for $r = 0.1..20$. The plot shows values from $r = 0.1$ as there is a much larger deviation near $r = 0$. They differ by a very small amount ($O(10^{-3})$) and the values become even closer to each other as r increases. The agreement can be improved by increasing the highest power of r, and subsequently the number of pseudostates. Similar results were obtained for the $2p$ case.

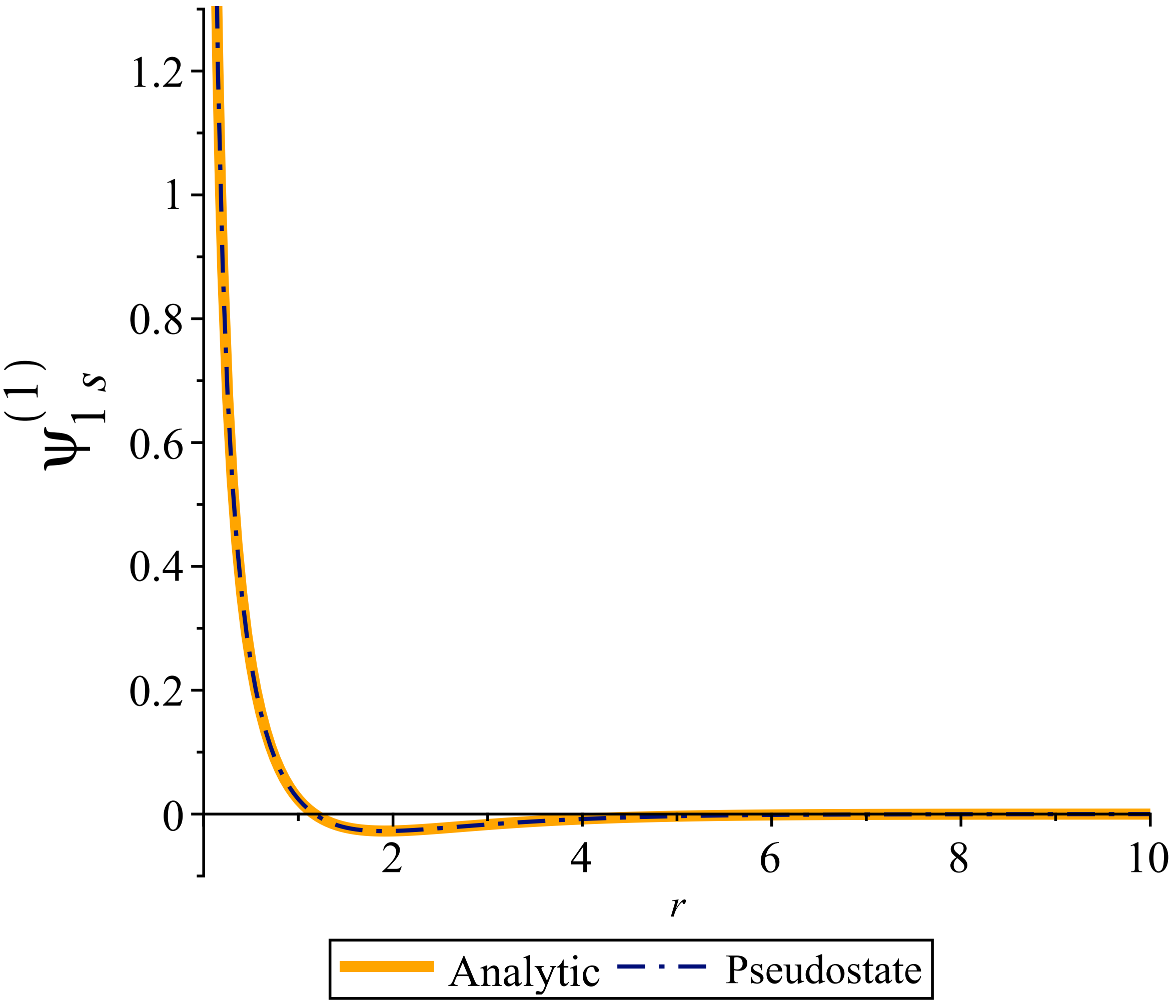

Figure 5.5: Plot of the analytic $\Psi_{1s}^{(1)}$ and the $\Psi_{1s}^{(1)}$ (for $r = 0.1..20$) obtained from pseudostates using a triangular basis set with a $\lambda = 14$ and a highest power of 6. The two wave functions overlap almost exactly.

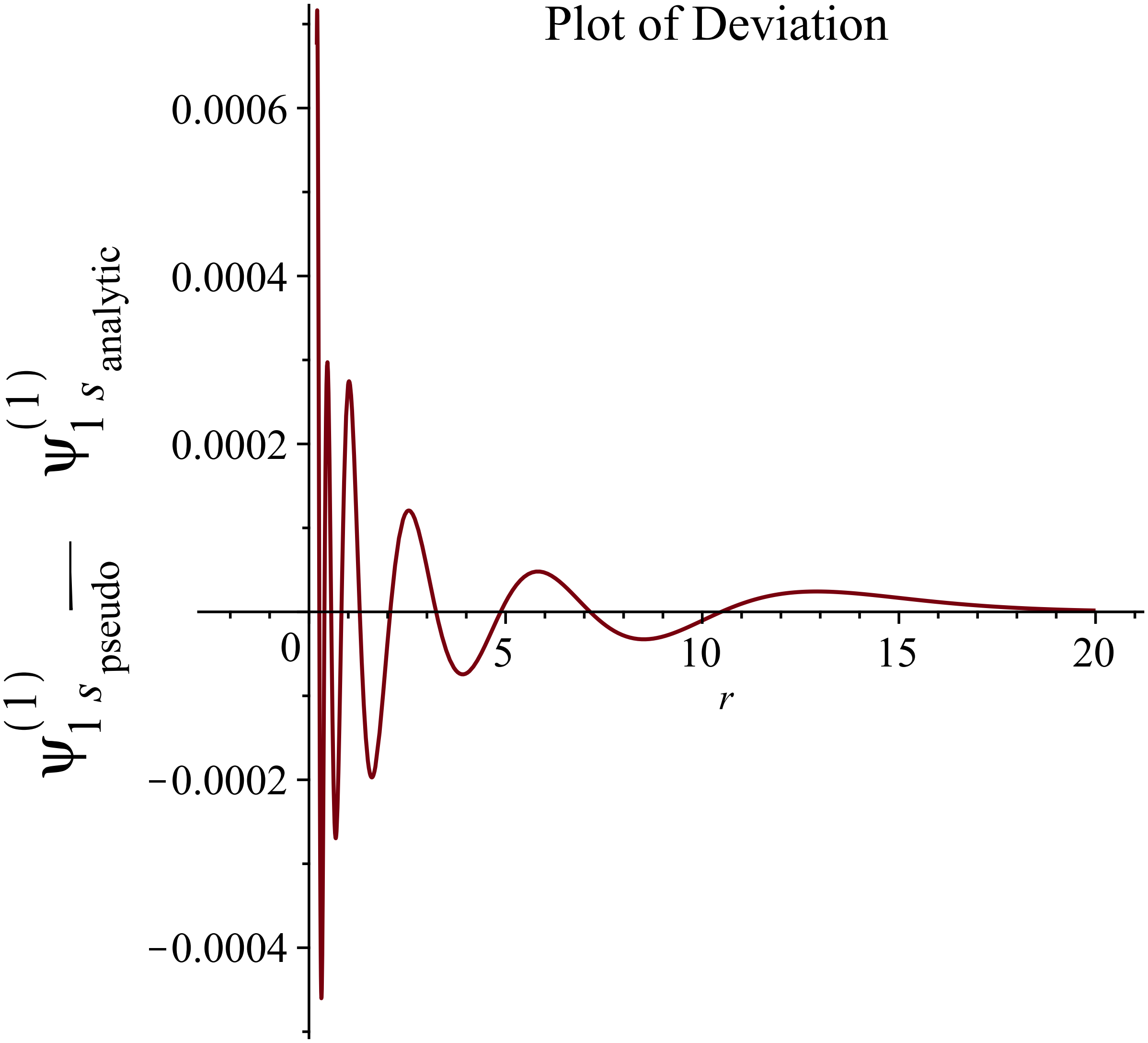

Figure 5.6: Plot of the difference (for $r = 0.1..20$) between the absolute values of the $\Psi_{1s}^{(1)}$ obtained from the pseudostate method (triangular basis, $\lambda = 14$, highest power of 6) with the $\Psi_{1s}^{(1)}$ obtained from the analytic method. The deviation is small and decreases as r increases.

Chapter 6

Results

The goal was to show that by using equivalent nonrelativistic operators and relativistically corrected Schrödinger wave functions we can obtain the same results as using relativistic operators and Dirac wave functions, correct up to some fixed order in powers of the fine structure constant α. Thus we would like to show that

$$\left\langle \Psi_j^D | \vec{\alpha} \cdot \mathbf{A} | \Psi_i^D \right\rangle = \left\langle \Psi_j^{(0)} + \alpha^2 \Psi_j^{(1)} | T^S | \Psi_i^{(0)} + \alpha^2 \Psi_i^{(1)} \right\rangle \tag{6.1}$$

where the left side is evaluated up to $O(\alpha^2)$. We have discussed already the corrections to the operator that arise from Foldy-Wouthuysen transformation. We also discussed the pseudostate method as a technique to determine the corrections to the wave functions, and compared the linear and triangular basis. Furthermore, we presented the analytic wave functions and used them as a reference for the corrected wave functions.

We now will proceed to evaluate all the terms in Eq. (6.1). We will consider the transition from a $2p$ state to a $1s$ state. Due to the angular momenta coupling, there are two possible $2p$ states: $2p_{1/2}$ and $2p_{3/2}$. Further we are using the long wavelength approximation (see Section 2.1), so we let $\mathbf{A} = \hat{\mathbf{z}}$

For the relativistic term, i.e left side of Eq.(6.1), we use the following to evaluate it [20]

$$(-1)^{j'-1/2}\frac{\eta}{\sqrt{6}}\sqrt{(2j'+1)(2j+1)}\times\begin{pmatrix} j' & 1 & j \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} M_{j'j} \tag{6.2}$$

where

$$M_{j'j} = i\left(\frac{\left[(\kappa_{j'}-\kappa_j)I^{+}_{L+1}+2I^{-}_{L+1}\right]}{\sqrt{2}} - \sqrt{2}\left[(\kappa_{j'}-\kappa_j)I^{+}_{L-1}+2I^{-}_{L-1}\right]\right) \tag{6.3}$$

with

$$I^{\pm} = \int_0^{\infty}(P_{j'}Q_j \pm Q_{j'}P_j)j_L\left(\frac{wr}{c}\right)dr \tag{6.4}$$

where $j=\frac{1}{2}$ and $j'=\frac{1}{2}$ or $\frac{3}{2}$ depending on which transition we are calculating, κ is the Dirac quantum number ($\kappa = \mp(j+\frac{1}{2})$ for $j = l \pm \frac{1}{2}$), and η is the normalization constant. P and Q are the large and small radial radial components of the Dirac bispinor, as given in [34, p.69] expanded in terms of α and only kept up to order α^2. j_L is a spherical Bessel function and as we are using the long wavelength approximation we will only use the first term so it's just 1.

For the nonrelativistic formalism, i.e the right side of Eq.(6.1), we need to evaluate the following terms:

$$-\alpha\left\langle\Psi_j^{(0)}|\frac{e}{m}\mathbf{A}\cdot\mathbf{p}|\Psi_i^{(0)}\right\rangle \tag{6.5}$$

$$-\alpha^3\left\langle\Psi_j^{(1)}|\frac{e}{m}\mathbf{A}\cdot\mathbf{p}|\Psi_i^{(0)}\right\rangle \tag{6.6}$$

$$-\alpha^3\left\langle\Psi_j^{(0)}|\frac{e}{m}\mathbf{A}\cdot\mathbf{p}|\Psi_i^{(1)}\right\rangle \tag{6.7}$$

$$\alpha^3\left\langle\Psi_j^{(0)}|H_{FW}|\Psi_i^{(0)}\right\rangle \tag{6.8}$$

The last three terms, which are the relativistic corrections of $O(\alpha^2)$ are each composed of two terms. Thus the relativistic corrections require the calculation of the following six terms:

$$-\alpha^3 \left\langle \Psi^{(1)}_{1s_{p^4}} | \mathbf{p}_z | \Psi^{(0)}_{2p_j} \right\rangle \tag{6.9}$$

$$-\alpha^3 \left\langle \Psi^{(1)}_{1s_{\delta(r)}} | \mathbf{p}_z | \Psi^{(0)}_{2p_j} \right\rangle \tag{6.10}$$

$$-\alpha^3 \left\langle \Psi^{(0)}_{1s} | \mathbf{p}_z | \Psi^{(1)}_{2p_{p^4}} \right\rangle \tag{6.11}$$

$$-\alpha^3 \left\langle \Psi^{(0)}_{1s} | \mathbf{p}_z | \Psi^{(1)}_{2p_{L\cdot S}} \right\rangle \tag{6.12}$$

$$\frac{\alpha^3}{4} \left\langle \Psi^{(0)}_{1s} | (\mathbf{p}^2\mathbf{p}_z + \mathbf{p}_z\mathbf{p}^2) | \Psi^{(0)}_{2p} \right\rangle \tag{6.13}$$

$$-\frac{\alpha^3}{2} \left\langle \Psi^{(0)}_{1s} | (\boldsymbol{\sigma} \cdot (\mathbf{E} \times \hat{z})) | \Psi^{(0)}_{2p} \right\rangle \tag{6.14}$$

We are interested in calculating the corrections of order $O(\alpha^2)$ compared to the nonrelativistic term (Eq.(6.5)), so for both the relativistic and nonrelativistic methods we will factor out the α term thus our results will be in the form of

$$C\alpha(1 + \alpha^2 \times \text{corrections})$$

where C is the leading nonrelativistic value for the matrix element. The first four terms arise due to the wave function corrections, they can be seen in Table 6.1. For the pseudostate method we used a triangular basis set with a λ of 14 and a highest power 18. The last two terms were already determined in Chapter 3, factoring out the first term gives:

$$\frac{\frac{i\alpha^3}{4} \left\langle \Psi^{(0)}_{1s} | \nabla^2\nabla_z + \nabla_z\nabla^2) | \Psi^{(0)}_{2p} \right\rangle}{\alpha \left\langle \Psi^{(0)}_{1s} | \frac{e}{m}\mathbf{A} \cdot \mathbf{p} | \Psi^{(0)}_{2p} \right\rangle} = -\alpha^2 \frac{3}{8} \tag{6.15}$$

and the spin term gives different results for the j's:

$$\frac{-\frac{\alpha^3}{2}\left\langle \Psi^{(0)}_{1s}|(\boldsymbol{\sigma}\cdot(\nabla\phi\times\hat{\mathbf{z}}))|\Psi^{(0)}_{2p_{\frac{1}{2}}}\right\rangle}{\alpha\left\langle \Psi^{(0)}_{1s}|\frac{e}{m}\mathbf{A}\cdot\mathbf{p}|\Psi 2p^{(0)}\right\rangle} = -\alpha^2\frac{3}{8} \tag{6.16}$$

$$\frac{-\frac{\alpha^3}{2}\left\langle \Psi^{(0)}_{1s}|(\boldsymbol{\sigma}\cdot(\nabla\phi\times\hat{\mathbf{z}}))|\Psi^{(0)}_{2p_{\frac{3}{2}}}\right\rangle}{\alpha\left\langle \Psi^{(0)}_{1s}|\frac{e}{m}\mathbf{A}\cdot\mathbf{p}|\Psi^{(0)}_{2p}\right\rangle} = \alpha^2\frac{3}{16} \tag{6.17}$$

6.1 $2p$ to $1s$ transition

We will consider first simply the spin-independent result. Using the Dirac transition amplitudes and averaging over the spin quantum numbers to remove the spin dependence we get

$$\left\langle \Psi^D_j|\vec{\alpha}\cdot\mathbf{A}|\Psi^D_i\right\rangle \propto 1+\alpha^2\left(-\frac{19}{288}+\frac{4\ln(3)}{6}-\frac{4\ln(2)}{3}\right) \tag{6.18}$$

For the nonrelativistic evaluation we need only the contributions from the following four terms, as these are spin independent

$$\alpha^3\left\langle \Psi^{(1)}_{1s_{p^4}}|\mathbf{p}_z|\Psi^{(0)}_{2p_j}\right\rangle \tag{6.19}$$

$$\alpha^3\left\langle \Psi^{(1)}_{1s_{\delta(r)}}|\mathbf{p}_z|\Psi^{(0)}_{2p_1}\right\rangle \tag{6.20}$$

$$\alpha^3\left\langle \Psi^{(0)}_{1s}|\mathbf{p}_z|\Psi^{(1)}_{2p_{p^4}}\right\rangle \tag{6.21}$$

$$\frac{\alpha^3}{4}\left\langle \Psi^{(0)}_{1s}|(\mathbf{p}^2\mathbf{p}_z+\mathbf{p}_z\mathbf{p}^2)|\Psi^{(0)}_{2p}\right\rangle \tag{6.22}$$

Term*	Analytic	Pseudospectral
$\left\langle \Psi_{1s}^{(1)} \middle\vert \mathbf{p}_z \middle\vert \Psi_{2p_j}^{(0)} \right\rangle_{p^4}$	$\frac{1}{48} + \ln(3) - 2\ln(2) = 0.18869055298173422765744 08 \cdot (-\sqrt{2})$	$\mathbf{0.18869055}3076249336937 9541 \cdot (-\sqrt{2})$
$\left\langle \Psi_{1s}^{(1)} \middle\vert \mathbf{p}_z \middle\vert \Psi_{2p_j}^{(0)} \right\rangle_{\delta(r)}$	$\frac{1}{32} - \frac{\ln(3)}{2} + \ln(2) = 0.1238080590403065940120889 \cdot (\sqrt{2})$	$\mathbf{0.123808059}0875641170202376 \cdot (\sqrt{2})$
$\left\langle \Psi_{1s}^{(0)} \middle\vert \mathbf{p}_z \middle\vert \Psi_{2p}^{(1)} \right\rangle_{p^4}$	$\frac{37}{144} + \frac{\ln(3)}{3} - \frac{\ln(2)}{2} = 0.2772562015474833371667144 \cdot (\sqrt{2})$	$\mathbf{0.2772562015}553156022067018 \cdot (\sqrt{2})$
for j=1/2 $\left\langle \Psi_{1s}^{(0)} \middle\vert \mathbf{p}_z \middle\vert \Psi_{2p_j}^{(1)} \right\rangle_{L\cdot S}$	$\frac{19}{72} + \frac{ln(3)}{6} - \frac{\ln(2)}{6} = 0.2343821440594199791793050 \cdot (\sqrt{2})$	$\mathbf{0.23438214405941997}78042009 \cdot (\sqrt{2})$
for j=3/2 $\left\langle \Psi_{1s}^{(0)} \middle\vert \mathbf{p}_z \middle\vert \Psi_{2p_j}^{(1)} \right\rangle_{L\cdot S}$	$-\frac{19}{144} - \frac{ln(3)}{12} + \frac{\ln(2)}{12} = 0.1171910720297099895896524 \cdot (-\sqrt{2})$	$\mathbf{0.11719107202970998}8723867 \cdot (-\sqrt{2})$

Table 6.1: The table shows the relativistic correction terms arising from the corrections to the wave functions obtained from both the analytic and pseudospectral method. For the pseudospectral method we have used a triangular basis with $\lambda = 14$ and a highest power of 18. The last two rows are the spin dependent terms, the first one for a transition from $2p_{\frac{1}{2}}$ and the other for $2p_{\frac{3}{2}}$. In all cases the value shown is the value of the term divided by the nonrelativistic term, i.e Eq.(6.5)

*This is the value of the matrix shown divided by the leading nonrelativistic term, i.e the value shown for $\left\langle \Psi_{1s}^{(1)} \middle| \mathbf{p}_z \middle| \Psi_{2p_j}^{(0)} \right\rangle_{p^4}$ is actually$\frac{\left\langle \Psi_{1s}^{(1)} \middle| \mathbf{p}_z \middle| \Psi_{2p_j}^{(0)} \right\rangle_{p^4}}{\left\langle \Psi_{1s}^{(0)} \middle| \frac{e}{m}\mathbf{A}\cdot\mathbf{p} \middle| \Psi 2p^{(0)} \right\rangle}$

Using analytic wave functions we obtain

$$\begin{aligned}\left\langle \Psi_j^{(0)} + \alpha^2\Psi_j^{(1)} | T^S | \Psi_i^{(0)} + \alpha^2\Psi_i^{(1)} \right\rangle &\propto 1 + \alpha^2\left(-\frac{19}{288} + \frac{4\ln(3)}{6} - \frac{4\ln(2)}{3}\right) \\ &= 1 + \alpha^2(-0.0746582224120578919491607)\end{aligned} \tag{6.23}$$

which matches exactly with the relativistic case. Using pseudostates results in

$$\left\langle \Psi_j^{(0)} + \alpha^2\Psi_j^{(1)} | T^S | \Psi_i^{(0)} + \alpha^2\Psi_i^{(1)} \right\rangle \propto 1 + \alpha^2(-\mathbf{0.0746582224}6761371580508678) \tag{6.24}$$

with matches up to 10 decimal places.

6.2 $2p_{\frac{1}{2}}$ to $1s$ transition

The relativistic result, i.e left side of Eq.(6.1) for the $2p_{\frac{1}{2}}$, is

$$\left\langle 1s | \vec{\alpha} \cdot \mathbf{A} | 2p_{\frac{1}{2}} \right\rangle = \frac{32\eta\alpha i}{81\sqrt{3}}\left(1 + \alpha^2\left(-\frac{17}{96} + \ln(3) - \frac{3\ln(2)}{2}\right)\right) \tag{6.25}$$

this requires the evaluation of all six terms for the nonrelativistic method. Using the analytic wave functions and summing the contributions from all the terms gives

$$\begin{aligned}&\frac{16\sqrt{2}\alpha i}{81\sqrt{3}}\left((1 + \alpha^2\left(-\frac{17}{96} + \ln(3) - \frac{3\ln(2)}{2}\right)\right) \\ &= \frac{16\sqrt{2}\alpha i}{81\sqrt{3}}\left((1 + \alpha^2\left(-0.1181918155051416060639363\right)\right)\end{aligned} \tag{6.26}$$

where we see that the α^2 corrections match exactly. For the pseudostate method we get the following result

$$\frac{16\sqrt{2}\alpha i}{81\sqrt{3}}\left((1 + \alpha^2\left(-\mathbf{0.118191855}608973605322189\right)\right) \tag{6.27}$$

where it matches up to 9 digits after the decimal.

6.3 $2p_{\frac{3}{2}}$ to $1s$ transition

The relativistic result, i.e left side of Eq.(6.1) for the $2p_{\frac{3}{2}}$, is

$$\left\langle 1s|\vec{\alpha}\cdot\mathbf{A}|2p_{\frac{3}{2}}\right\rangle = \frac{32\eta\sqrt{2}\alpha i}{81\sqrt{3}}\left(1+\alpha^2\left(-\frac{1}{96}+\frac{3\ln(3)}{4}-\frac{5\ln(2)}{4}\right)\right) \tag{6.28}$$

this requires the evaluation of all six terms for the nonrelativistic method. Summing the contributions from all the terms and using the analytic wave functions gives

$$\begin{gathered}\frac{32\alpha i}{81\sqrt{3}}\left((1+\alpha^2\left(-\frac{1}{96}+\frac{3\ln(3)}{4}-\frac{5\ln(2)}{4}\right)\right)\\ \frac{32\alpha i}{81\sqrt{3}}\big((1+\alpha^2\,(-0.05289142586551603489177 30)\big)\end{gathered} \tag{6.29}$$

once again, this matches exactly with the relativistic case. The result using the pseudostate method is:

$$\frac{32\alpha i}{81\sqrt{3}}\big((1+\alpha^2\,(-\mathbf{0.052891425}92127207624535330)\big) \tag{6.30}$$

which matches up to 9 digits after the decimal.

6.4 $3p$ to $2s$ transitions

We have thus far shown results for the $2p$ to $1s$ transitions. We will repeat the procedure for the $3p$ to $2s$ as a further test of the validity of the operators and the wave functions. In this case the radial parts are different, while the angular parts are the same. In order to compute the transition probability, we need to first determine the analytic wave functions. For the $2s$ wave functions we can refer to

Cohen and Dalgarno's [43] results, and we obtained the $3p$ wave functions ourselves, The normalized analytic first order wave function corrections for both are presented in the Appendix.

The relativistic result, i.e left side of Eq.(6.1) for the $3p_{\frac{1}{2}}$ case is

$$\left\langle 2s|\vec{\alpha}\cdot\mathbf{A}|3p_{\frac{1}{2}}\right\rangle = \frac{-128\eta\sqrt{6}\alpha i}{3125}\left(1+\alpha^2\left(\frac{13}{96}-\frac{\ln(3)}{2}-\frac{3\ln(2)}{2}+\ln(5)\right)\right) \tag{6.31}$$

Using the nonrelativistic operators and the analytic corrected wave functions,we get

$$\frac{128\sqrt{3}\alpha i}{3125}\left(1+\alpha^2\left(\frac{13}{96}-\frac{\ln(3)}{2}-\frac{3\ln(2)}{2}+\ln(5)\right)\right) \tag{6.32}$$

where the α^2 terms match exactly. For the $3p_{\frac{3}{2}}$, the relativistic value is

$$\left\langle 2s|\vec{\alpha}\cdot\mathbf{A}|3p_{\frac{3}{2}}\right\rangle = \frac{-256\sqrt{3}\alpha i}{3125}\left(1+\alpha^2\left(-\frac{9}{32}-\frac{\ln(3)}{2}-\ln(2)+\frac{3\ln(5)}{4}\right)\right) \tag{6.33}$$

Using the nonrelativistic operators and the analytic corrected wave functions, we get:

$$\frac{128\sqrt{6}\alpha i}{3125}\left(1+\alpha^2\left(-\frac{9}{32}-\frac{\ln(3)}{2}-\ln(2)+\frac{3\ln(5)}{4}\right)\right) \tag{6.34}$$

where once again the α^2 terms match exactly.

6.5 Discussion

We have seen for all cases, including the spin dependent case, that the α^2 correction terms using the equivalent nonrelativsitic operators and the analytic first order wave function corrections match exactly with the relativistic result. The logarithmic terms come only from the corrections to the wave functions, whereas the numerical terms can come either from the Foldy-Wouthuysen corrections or the wave function corrections. Since the logarithmic terms and the numerical terms match with the relativistic case, we can conclude that our analytic wave functions were correctly obtained and also the operators obtained from the Foldy-Wouthuysen transformation are correct.

The pseudostate result is only accurate within 5 digits after the decimal. Looking at Table 6.1, which compares the individual values between analytic and pseudostate wave functions, we see that the $1s$ wave function corrections are the limiting factor. For the p states, the $L \cdot S$ values are the most accurate, followed by the p^4 corrections. We even used a $\lambda = 14$ which as shown in Fig. 5.4 is the optimal value for the $1s$ pseudostates, however the results from the $1s$ corrections are significantly less accurate. It could be that the near-zero behaviour of the 1s state could be a contributing factor, as for p-states the wave function vanishes at zero. We saw in Figure 5.6 that the deviation was increasing as we neared zero, while in Figure 5.5 we saw that the wave function is large near zero. This means a large contribution comes from the near zero portion of the wave function, which has the largest deviation from the analytic. This could explain why our $s - states$ are limiting our accuracy. Further, if we consider the analytic wave function correction for $1s$ for the $-\frac{p^4}{8}$ perturbation:

$$\Psi_{1s}^{(1)} = \left(-\ln(2) - \ln(r) + \frac{1}{2r} - \frac{r}{2} + \frac{(-4\gamma + 7)}{4} \right) \Psi_{1s}^{(0)} \tag{6.35}$$

we see that it contains logarithmic functions and also $\frac{1}{r}$ terms, whereas the wave function obtained from our pseudostate method only contains positive powers of r. Implementing logarithmic terms or terms of negative powers of r in our pseudostates could improve the results obtained from the pseudostate method. We also repeated the procedure with $2s$ and $3p$ states and saw the same result, namely that the s states gave less accurate values than the p states. Let's look at the first order wave function correction for $2p$ for a perturbation of $\frac{-p^4}{8}$

$$\Psi_{2p}^{(1)} = \frac{-48\ln(r)r + 72 - 3r^2 + (97 - 48\gamma)r}{144r} \Psi_{2p}^{(0)} \tag{6.36}$$

At first glance it seems this also has a $\frac{1}{r}$ term, however it is being multiplied by

$$\Psi_{2p}^{(0)} = \sqrt{\frac{2}{\pi}} \frac{r\cos\theta}{8} e^{-r/2} \tag{6.37}$$

Therefore, $\Psi_{2p}^{(1)}$ only has positive powers of r and since our pseudostates are composed of only positive powers of r, the $2p$ wave functions obtained from the pseudostate method gave results closer to those obtained by the analytic wave functions.

Chapter 7

Conclusion

The Dirac equation provides a fully relativistic covariant equation which can be used to calculate relativistic transition rates but only for one-electron systems. For the two-electron case, one can either use approximate relativistic wave functions or obtain equivalent nonrelativistic operators that can be used with Schrödinger wave functions; an approach that is preferred for low Z atoms. We have employed the second method and used equivalent nonrelativistic operators to calculate relativistic transition rates.

Using the Foldy-Wouthuysen transformation we derived the equivalent nonrelativistic operators for the transition amplitude, which matched with the one-electron terms in Lin's paper [24]. We used a pseudostate method to obtain the relativisitically corrected wave functions, and tested two different Sturmian basis sets showing that the triangular basis set provides a significant advantage. We also obtained the analytic form of the relativistic corrected wave functions for the p-states, which have not been published before. Using the analytic forms of the wave functions for s-states[43] and p-states, we were able to asses the accuracy of the pseudostate method.

Our results show that by using equivalent nonrelativistic operators obtained from the Foldy-Wouthuysen transformation and relativistically corrected Schrödinger wave function, one can get the relativistic corrections up to α^2. The two matched exactly when using analytic wave functions, thus providing a theoretical framework for the two-electron case. For the pseudostates, the accuracy was limited by the s-states which might be improved if one includes a $\frac{1}{r}$ or a logarithmic term in the pseudostates. The triangular basis set was shown to be a much better choice than a linear basis set, providing a much broader spectrum, converging quicker than the linear basis set and increasing the accuracy by two orders of magnitude.

Daniel Venn [45] successfully implemented the pseudospectral method for helium for electric dipole transitions and verified that the hydrogenic results are recovered in the limit of large Z by using the analytic wave functions obtained in this thesis.

Future work would be to implement a $\frac{1}{r}$ term or logarithmic term in the pseudostates and see if this improves the results from the pseudospectral method. One should also repeat this method for the full vector potential $\mathbf{A} = \hat{\epsilon} e^{-i\mathbf{k}\cdot\mathbf{r}}$ and not just the leading term, and prove that it still agrees with Dirac Theory up to order α^2. One can then apply this method to the two-electron case.

Appendix A

Analytic First Order Wave Function Corrections

We will now present the method used to solve for the analytic form of the first order corrected wave functions. Using this method we obtained expressions for the correction to the wave functions for $2p$ and $3p$ states, which have not been published yet.

From perturbation theory the first order perturbation equation is (see Section 4.3)

$$H^{(0)}\Psi^{(1)} + V\Psi^{(0)} = E^{(0)}\Psi^{(1)} + E^{(1)}\Psi^{(0)} \tag{A.1}$$

where V is the perturbation. We can rearrange all terms to one side

$$(H^{(0)} - E^{(0)})\Psi^{(1)} + V\Psi^{(0)} - E^{(1)}\Psi^{(0)} = 0 \tag{A.2}$$

where we know the following:

$$H^{(0)} = \frac{p^2}{2} + e\phi \tag{A.3}$$

$$E^{(0)} = -\frac{1}{2n^2} \tag{A.4}$$

$$E^{(1)} = \left\langle \Psi^{(0)} | V | \Psi^{(0)} \right\rangle \tag{A.5}$$

where n is the principal quantum number and $\Psi^{(0)}$ is the regular Schrödinger wave function, and we have used atomic units ($m = e = \hbar = 1$)

We can solve this differential equation using the Method of Frobenius [42]. Cohen and Dalgarno [43] published the corrections to the $1s$ and $2s$ wave functions for different perturbations. His functions had negative and positive powers of r, and also logarithmic terms. In order to determine the wave functions for the p-state we define our wave function to be some combination of r terms and logarithmic terms

$$\Psi^{(1)} = (\sum_s (q_s r^{s-2} + m_s r^{s-1} \ln(r)))\Psi^{(0)} \tag{A.6}$$

We now substitute this into Eq. (A.1) and group all the terms with the same powers of r and also group the logarithmic terms that have the same power of r. The coefficient of each r, which is composed of the terms a_i and b_i, must be 0, as Eq.(A.1) is zero. This enables us to determine the coefficients a_i and b_i.

For example, suppose we want to determine the first order wave function correction for the $2p$ state if our perturbation is $\mathbf{p^4}$. Then we have:

$$\Psi^{(1)} = (\sum_s (q_s r^{s-2} + m_s r^{s-1} \ln(r)))\Psi^{(0)}_{2p} \tag{A.7}$$

If we substitute this into Eq. (A.1), and collect terms with the same powers of r then

$$\begin{aligned}
&\sum_{s=1} (-m_{s+1}(-3-s)(s) + m_s(s-1))r^{s-1}\ln(r) \\
&+ \sum_{s=4} ((q_{s+1}(s-1)(-s-2) + q_s(s-2))r^{s-2}) + (2q_1 + 8)r^{-2} \\
&+ (-q_1 - 3m_1 + 4)r^{-1} + (-2m_2 - 4q_3 + m_1 - 2)r^1 + (2q_4 + q_3 - \frac{1}{6})r^0 = 0
\end{aligned} \tag{A.8}$$

this gives us the relations

$$\begin{aligned} -m_{s+1}(-3-s)(s)+m_s(s-1)&=0 \quad s=1..n \\ q_{s+1}(s-1)(-s-2)+q_s(s-2)&=0 \quad s=4..n \\ 2q_1+8&=0 \\ -q_1-3m_1+4&=0 \\ -2m_2-4q_3+m_1-2&=0 \\ 2q_4+q_3-\frac{1}{6}&=0 \end{aligned} \tag{A.9}$$

which means

$$\begin{aligned} m_{s+1}&=\frac{m_s(s-1)}{s(3+s)} \quad s=1..n \\ q_{s+1}&=\frac{q_s(s-2)}{(s-1)(s+2)} \quad s=4..n \\ q_1&=-4 \\ m_1&=\frac{8}{3} \\ q_3&=\frac{1}{6} \\ q_4&=0 \end{aligned} \tag{A.10}$$

The first recursion relation is null because of the $(s-1)$ term. Only m_1 can exist. The second recursion relation is also null as $q_4=0$ so all the next terms will be zero as well. This leaves us with

$$\left(\frac{r}{6}-\frac{4}{r}+\frac{8\ln(r)}{3}\right)\Psi_{2p} \tag{A.11}$$

One can do this by hand and determine the recursion relations as shown above. It can also be done in Maple, which has a built in function called *collect(f,r)* which collects terms of the same power of r in the expression f. However it will group terms such as $r\ln(r)$ and r together. Thus, it is advisable to increase first the powers of r until one notices that the additional terms have coefficients of 0 (i.e if no term greater then r^m contributes). Then, increase the powers of the r in the logarithmic terms successively until a solution is achieved. All the coefficients in the $\Psi^{(1)}$ can thus be determined, except the r^0 term. This can be set arbitrarily, it doesn't affect the wave function or the expectation values, as it goes away if you normalize the wave function. The resulting $\Psi^{(1)}$ are not normalized, and can be normalized using the Gram Schmidt procedure,

$$\left|\Psi^{(1)'}\right\rangle = \left|\Psi^{(1)}\right\rangle - \left\langle\Psi^{(0)}|\Psi^{(1)}\right\rangle\left|\Psi^{(0)}\right\rangle \tag{A.12}$$

where $\left|\Psi^{(1)'}\right\rangle$ is the normalized wave function.

The results for the s-state corrections matched with those presented by Cohen and Dalgarno [43], providing a check for our method. The p-state wave functions were then obtained which have not been published before. we will now present the normalized first order corrections for the s and p states.

A.1 S-State First Order Analytic Wave Functions

Cohen and Dalgarno [43] have presented the unnormalized first order wave function corrections for some perturbations. Using their results, we obtained the normalized analytic wave functions

The first order wave function corrections for the perturbation $\frac{-p^4}{8}$ for the 1s and 2s are

$$\Psi^{(1)}_{1s} = \left[-\ln(2) - \ln(r) + \frac{1}{2r} - \frac{r}{2} + \frac{(-4\gamma+7)}{4}\right]\Psi^{(0)}_{1s} \tag{A.13}$$

$$\Psi^{(1)}_{2s} = \left[\frac{(2-r)\ln(r) - \frac{1}{r} - \frac{3}{16}r^2 + (\frac{47}{16} - 16\gamma)r + 2\gamma - \frac{15}{8}}{(r-2)}\right]\Psi^{(0)}_{2s} \tag{A.14}$$

and for the $\frac{\pi\delta^3(\vec{r})}{2}$ perturbation, the normalized first order wave function correction are

$$\Psi_{1s}^{(1)} = \left[\frac{\ln(2)}{2} + \frac{\ln(r)}{2} - \frac{1}{4r} + \frac{r}{2} + \frac{(2\gamma - 5)}{4}\right]\Psi_{1s}^{(0)} \tag{A.15}$$

$$\Psi_{2s}^{(1)} = \left[\frac{(4r-8)\ln(r) + \frac{4}{r} + r^2 + (4\gamma - 13)r + (-8\gamma + 6)}{8(r-2)}\right]\Psi_{2s}^{(0)} \tag{A.16}$$

where

$$\Psi_{1s}^{(0)} = -\sqrt{\frac{1}{\pi}}e^{-r} \tag{A.17}$$

$$\Psi_{2s}^{(0)} = -\sqrt{\frac{2}{\pi}}\frac{(r-2)}{8}e^{-\frac{r}{2}} \tag{A.18}$$

and $\gamma = 0.5772156649015328606065121$ is the Euler-Mascheroni constant.

A.2 P-State First Order Analytic Wave Functions

Using the method outlined in the beginning of this Appendix, the first-order wave functions for 2p and 3p states were determined and those results will be presented below.

We first show the results for 2p wave functions. For a perturbation of $\frac{-p^4}{8}$ the first order wave function correction is

$$\Psi_{2p}^{(1)} = \left[\frac{-48\ln(r)r + 72 - 3r^2 + (97 - 48\gamma)r}{144r}\right]\Psi_{2p}^{(0)} \tag{A.19}$$

For a perturbation of $\frac{\mathbf{L}\cdot\mathbf{S}}{2r^3}$, the first order wave function corrections for the $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ are:

$$\Psi_{2p_{\frac{1}{2}}}^{(1)} = \left[\frac{-12\ln(r)r + 36 - 3r^2 + (31 - 12\gamma)r}{72r}\right]\Psi_{2p}^{(0)} \tag{A.20}$$

$$\Psi_{2p_{\frac{3}{2}}}^{(1)} = \left[\frac{12\ln(r)r - 36 + 3r^2 + (12\gamma - 31)r}{144r}\right]\Psi_{2p}^{(0)} \tag{A.21}$$

Note that

$$\Psi^{(1)}_{2p_{\frac{1}{2}}} = -\frac{1}{2}\Psi^{(1)}_{2p_{\frac{3}{2}}} \tag{A.22}$$

where

$$\Psi^{(0)}_{2p} = \sqrt{\frac{2}{\pi}}\frac{r\cos\theta}{8}e^{-r/2} \tag{A.23}$$

We now present the results for 3p wave functions. For a perturbation of $\frac{-p^4}{8}$ the first order wave function correction is

$$\Psi^{(1)}_{3p} = \left[\frac{(108-18r)(\frac{\ln(2r)}{\ln(3)}) - \frac{162}{r} - r^2 + (54-18\gamma)r + 108\gamma - 189}{54(r-6)}\right]\Psi^{(0)}_{3p} \tag{A.24}$$

For the $3p_{\frac{1}{2}}$ state, the first order wave function correction due to the spin orbit term is

$$\Psi^{(1)}_{3p_{\frac{1}{2}}} = \left[\frac{(216-36r)(\frac{\ln(2r)}{\ln(3)}) - \frac{648}{r} - 4r^2 + (-36\gamma + 129)r216\gamma - 288}{216(r-6)}\right]\Psi^{(0)}_{3p} \tag{A.25}$$

For the $3p_{\frac{3}{2}}$ state, it is

$$\Psi^{(1)}_{3p_{\frac{3}{2}}} = \left[\frac{(216-26r)(-\frac{\ln(2r)}{\ln(3)}) + \frac{648}{r} + 4r^2 + (36\gamma - 129)r - 216\gamma + 288}{432(r-6)}\right]\Psi^{(0)}_{3p} \tag{A.26}$$

where

$$\Psi^{(0)}_{3p} = -\sqrt{\frac{2}{\pi}}\frac{(r-6)r\cos(\theta)}{81}e^{-\frac{r}{3}} \tag{A.27}$$

and $\gamma = 0.577215664901532860606512\,1$ is the Euler-Mascheroni constant.

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