

# Investigation of the Higher Order Zeeman Effect

By

**Evan M. R. Petrimoulx**

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by

Evan M. R. Petrimoulx

APPROVED BY:

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Initial. Last Name  
Department of Mechanical, Automotive and Materials Engineering

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Initial. Last Name  
School of Computer Science

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Initial. Last Name  
Department of Physics

April 11, 2025

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## DEDICATION

I would like to dedicate this thesis to my parents, for encouraging me to work hard and follow my dreams, and to Helena, for always believing in me and being my biggest supporter.

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# CHAPTER 1

## *Introduction*

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- 1.1 Background and Motivation
- 1.2 Overview of Research Projects
- 1.3 Methodology Overview
- 1.4 Research Significance
- 1.5 Dissertation Structure

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# CHAPTER 2

## *Theoretical Methods*

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### 2.1 Overview

This chapter provides an overview of all theoretical methods used throughout this dissertation. It gives the theoretical building blocks upon which the dissertation is constructed, ranging from the set of units used in the problem, to perturbation equation solutions and methods for verifying calculations. As stated in the introduction, this thesis is based upon calculating matrix elements between two sets of wavefunctions connected by an operator. These matrix elements arise from perturbation theory and are necessary for computing energy shifts due to external fields such as those present in the higher-order Zeeman effect. The foundation of theory is presented here, but the more specific calculations related to solving for the Zeeman effect are presented in the relevant chapter below.

The chapter begins first by discussing atomic units in Sec. 2.2, then introduces the Schrödinger equation for the one-electron problem as well as its solution for hydrogenic wavefunctions in Sec. 2.3. Next, Perturbation Theory is introduced in Sec. 2.5, and how it is to approximate the new eigenvalues and eigenstates of the Zeeman-perturbed Hamiltonian is discussed. Sec. 2.4 reviews various integration techniques that are implemented both analytically and programmatically in order to simplify the calculation process, followed by an introduction to solving recursion relations in Sec. 2.6. This is the core step in determining the perturbed wavefunctions used throughout the rest of the study. Finally, this chapter concludes with the discussion of the Dalgarno Interchange Theorem and how it serves as a critical check on the

correctness of the obtained perturbed wavefunctions.

## 2.2 Atomic Units

First proposed by Hartree in November of 1928, atomic units have since become the standard across all of atomic physics. Atomic units were designed with the purpose of *”eliminating various universal constants from equations and also to avoid high powers of 10 in numerical work”* [23]. Hartree proposed that physical quantities such as the mass are measured in terms of the mass of the electron  $m_e$ . The charge measured in terms of the electron charge,  $e$ , the vacuum permittivity in terms of  $4\pi\epsilon_0$ , and the angular momentum in terms of  $\hbar$ . Their standard definitions in both S.I. units and atomic units are stated in Table. 2.2.1 [2, 3, 4, 5, 6, 7]. Written mathematically;

$$\hbar = m_e = e = 4\pi\epsilon_0 = 1 . \quad (1)$$

Scaling these units out of the problem greatly simplifies the calculation. Once a result is found, multiplying the unscaled units back into the answer retrieves the desired result in standard SI units. While the use of atomic units can make any work done by hand much simpler to manage, it also benefits numerical work that is done computationally. Machine error is an unavoidable reality of programmed solutions

Symbol	Name	Value in S.I	Value in a.u.
$\hbar$	Reduced Planck’s constant	$1.054\,571\,817\dots \times 10^{-34} \text{ J s}$	1
$m_e$	Electron mass	$9.109\,383\,713\,9(28) \times 10^{-31} \text{ kg}$	1
$e$	Electron charge	$1.602\,176\,634 \times 10^{-19} \text{ C}$	1
$\epsilon_0$	Electric permittivity	$8.854\,187\,818\,8(14) \times 10^{-12} \text{ F/m}$	$\frac{1}{4\pi}$
$c$	Speed of light	$299\,792\,458 \text{ m/s}$	137.035 999 177(21)
$\alpha$	Fine structure constant	$7.297\,352\,564\,3(11) \times 10^{-3}$	$\frac{1}{137.035\,999\,177(21)}$

Fig. 2.2.1: Table of fundamental constants expressed in S.I. units and atomic units.

and working in units which avoids extreme values both large and small helps to mitigate the uncertainty present in high precision calculations. In addition, exact analytical results need not be limited by the values of the fundamental constants. This thesis utilizes atomic units both analytically and numerically to simplify the calculation process throughout.

A consequence of utilizing atomic units is the need to redefine key fundamental physical quantities in terms of these scaled values. An example of key importance in the investigation of the higher-order Zeeman effect is the atomic unit of magnetic field strength, otherwise referred to as the atomic unit of magnetic flux density [1].

$$B_{\text{a.u.}} = \frac{\hbar}{ea_0^2} . \quad (2)$$

This value is composed of the Bohr radius  $a_0$ , electron charge  $e$ , and  $\hbar$ , the unit of action. The Bohr radius is defined as the most probable distance between an electron in the ground state of hydrogen and its nucleus. It can be described by the following equation [22]

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2m_e} = \frac{\hbar}{m_e c \alpha} . \quad (3)$$

The Bohr radius itself is defined using a similar combination of fundamental constants which after applying the rules for atomic units, should equal 1. It can now be seen that all units in the atomic unit of field strength also become 1 as intended. At the end of the problem, the desired result in S.I units is retrieved by simply multiplying the determined result by the atomic unit of magnetic field strength when its constants are not scaled to 1. This is equivalent to multiplying the result in atomic units by [1].

$$B_{\text{a.u.}} = 2.35051757077(73) \times 10^5 \text{ T} \quad (4)$$

The numbers in parenthesis here denote the uncertainty of the quantity. Another key benefit in atomic units is that it allows us to define almost all fundamental quantities in terms of two constants; the speed of light,  $c$  and the fine structure constant,  $\alpha$ . This allows one to express key physical laws in a way that highlights fundamental dimensionless relationships rather than specific unit-dependant values.

The fine structure constant was introduced in 1916 by Arnold Sommerfeld when he was investigating the gap in the spectral lines of the hydrogen atom [30]. He compared his work with the Michelson Morley experiment from 1887 where the spectral lines were shown and it was deduced that the universe is not permeated by the aether [25]. It is defined as the following dimensionless quantity

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.035\,999\,177(21)} \quad (5)$$

which in atomic units is just the following relationship with the speed of light

$$\alpha = \frac{1}{c} . \quad (6)$$

The fine structure constant is often used as an essential expansion parameter, treating relativistic effects as a perturbation in  $\alpha$ .<sup>1</sup> Applying the atomic unit scaling to the fine structure constant shown in equation (6) confirms that the second equivalence in equation (3) remains equal to 1.

Applying this technique to problems in atomic physics gives a powerful way of simplifying calculations while providing an easy conversion factor to SI units for comparison of theory and experiment. This dissertation considers all equations and quantities in atomic units unless further specified otherwise.

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<sup>1</sup>More on this is discussed in Sec. 3.5.2

## 2.3 One-electron Schrödinger equation

Discovered by Schrödinger in 1926, the Schrödinger equation is a nonrelativistic solution to any quantum-mechanical system [29]. Consider the two-body problem with a nucleus and a single orbiting electron<sup>2</sup>. The electron interacts with the nucleus via the Coulomb interaction described by the potential

$$V(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0\vec{r}}. \quad (7)$$

The energy of the system is written using the Hamiltonian, where the potential is the Coulomb potential. This can be written as

$$H = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0\vec{r}}. \quad (8)$$

All observable quantities correspond to hermitian operators that act on the wavefunction  $\psi$ . The wavefunction  $\psi$  is a normalized vector in Hilbert space,  $\mathcal{H}$  containing all information pertaining to the system. The Hamiltonian is thus a hermitian operator that satisfies the eigenvalue problem

$$\hat{H}|\psi\rangle = E_n|\psi\rangle \quad (9)$$

This is the Schrödinger equation. It can be applied to the two-body problem by substituting for the momentum its quantum operator analog. This results in the expression

$$\hat{H}\psi = \frac{-\hbar^2}{2m_e}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0\vec{r}}\psi = E_n\psi. \quad (10)$$

---

<sup>2</sup>It is assumed here that the nucleus is a point particle with infinite mass.



This is a second-order partial differential equation. Assuming spherical symmetry allows one to split the solution to any system into two separable parts; The radial part and the angular part.

$$\psi_{nlm} = R_{nl}(r)Y_m^\ell(\cos \theta) \quad (11)$$

For a two body hydrogenic system the solutions for each are written in terms of Laguerre polynomials and spherical harmonics. The radial equation has the following solutions [8]

$$R_{nl}(r) = \frac{2Z}{n^2} \sqrt{\frac{Z(n-\ell-1)!}{(n+\ell)!}} \left(\frac{2Zr}{n}\right)^\ell e^{\frac{-Zr}{n}} L_{n-\ell-1}^{(2\ell+1)}(2Zr/n) \quad (12)$$

Where  $Z$  is the nuclear charge atomic number,  $\ell$  is the angular momentum quantum number,  $n$  is the principle quantum number, and  $L_{n-\ell-1}^{(2\ell+1)}(2Zr/n)$  is the generalized Laguerre polynomial (which is defined in Appendix C.4). The radial part of the solution can also be written in terms of the confluent hypergeometric function [? ]

$$R_{nl}(r) = \frac{1}{(2\ell+1)} \sqrt{\frac{(n+\ell)!}{(n-\ell-1)!2n}} \left(\frac{2Z}{n}\right)^{\frac{3}{2}} e^{\frac{-Zr}{n}} \times \left(\frac{2Zr}{n}\right) F\left(-(n-\ell-1), 2\ell+2, \frac{2Zr}{n}\right) \quad (13)$$

Additionally, the spherical harmonics are

$$Y_\ell^m(\theta, \phi) = (-1)^m \sqrt{\frac{(2\ell+1)}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} P_\ell^m(\cos \theta) e^{im\phi} \quad (14)$$

where  $\ell$  is the angular momentum quantum number,  $m$  is the magnetic quantum number, and  $P_\ell^m(\cos \theta)$  is the associated Legendre polynomial (which is discussed

further in Appendix C.3). A key feature of the spherical harmonics which is utilized in Sec. 2.4 is that the spherical harmonics form a normalized complete set of orthogonal basis functions. The ability to separate the solution into two independent parts plays a crucial role in simplifying the task at hand and is exploited when evaluating integrals involving these wavefunctions in Chapter 3.

## 2.4 Integration Techniques

In this section a standard approach to solving the integrals pertaining to the various matrix elements required throughout is discussed. A matrix element of an operator  $V$ , such as  $\langle \psi^n | V | \psi^m \rangle$ , where  $V$  is a perturbed Hamiltonian, can be used to approximate the behaviour of quantum systems under small disturbances. Calculating their matrix elements gives insight to the system's behaviour, revealing properties such as transition rates or behaviour in an external field ???. The calculation of these matrix elements requires integration over the states as well as the operator acting on a state, which can involve radial and angular pieces. As discussed in the previous section, the ability to separate the solution into a radial part as well as an angular part significantly simplifies the solution process relative to a direct calculation. Instead of having to integrate a single function over all three dimensions in spherical coordinates, the solution is split into two steps which are calculated independently. Assuming that  $V(\vec{r})$  can also be partitioned into  $V(\vec{r}) = V_r V_\Omega$ ,

$$\langle \psi^n | V | \psi^m \rangle = \int_0^\infty r^2 \psi^n(r) V_r \psi^m(r) dr \int_\Omega \sin \theta \psi^n(\theta, \phi) V_\Omega \psi^m(\theta, \phi) d\Omega \quad (15)$$

where  $\Omega$  represents the solid angles for  $\theta$  and  $\phi$ . The total problem can then be solved with the simple combination of calculated integrals.

$$\langle \psi^n | V | \psi^m \rangle = I_{\text{radial}} \cdot I_{\text{angular}} . \quad (16)$$

This section serves as a general introduction to the process of calculating matrix elements, but Sec. 2.4.1 and Sec. 2.4.2 discuss further the specifics and techniques used to calculate each piece of the solution.

### 2.4.1 The angular part

As mentioned previously, the angular part of the solution to any matrix element is

$$I_{\text{angular}} = \int_{\Omega} \sin \theta \psi^n(\theta, \phi) V_{\Omega} \psi^m(\theta, \phi) d\Omega . \quad (17)$$

Since hydrogenic wavefunctions are used to calculate matrix elements for the higher order Zeeman effect, integrals of this form with one or more spherical harmonics within the integrand appear. The calculation of the angular integrals is simplified by exploiting the nature of the spherical harmonic function. Since it forms a complete set of orthogonal basis functions, for any integral involving  $\theta$  and  $\phi$ , the integrand is written in terms of spherical harmonic functions. Using the orthogonality of the basis functions the integral of any two spherical harmonics is

$$\int_0^{\pi} \int_0^{2\pi} Y_{\ell}^m(\theta, \phi) Y_{\ell'}^{m'}(\theta, \phi) d\theta d\phi = \delta_{\ell\ell'} \delta_{mm'} . \quad (18)$$

For all angular integrals where the spherical harmonics contain different angular momentum or magnetic quantum numbers, the result is zero. If given a scenario where three spherical harmonics are multiplied together (i.e, there are three spherical harmonic functions to integrate), the result can be expressed in terms of Wigner  $3j$ -symbols according to [?] ]

$$\int_0^\pi \int_0^{2\pi} \sin \theta \, d\theta d\phi \, Y_{\ell_1}^{m_1}(\theta, \phi) Y_{\ell_2}^{m_2}(\theta, \phi) Y_{\ell_3}^{m_3}(\theta, \phi) = \quad (19)$$

$$\sqrt{\frac{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_3 + 1)}{4\pi}} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

where the set of 6 parameters inside the brackets at the end of the expression is called a 3j symbol, which has the following definition [17]:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 - j_2 - m_3} (2j_2 + 1)^{\frac{1}{2}} \langle j_1, m_1, j_2, m_2 | j_1, j_2, j_3 - m_3 \rangle \quad (20)$$

where  $\langle j_1, m_1, j_2, m_2 | j_1, j_2, j_3 - m_3 \rangle$  is known as a vector coupling coefficient and is defined as [17]

$$\begin{aligned} \langle j_1, m_1, j_2, m_2 | j_1, j_2, j, m \rangle &= \delta(m_1 + m_2 + m) \times \\ &\sqrt{\frac{(2j + 1)(j_1 + j_2 - j)!(j_1 - j_2 + j)!(-j_1 + j_2 + j)!}{(j_1 + j_2 + j + 1)!}} \times \\ &\sqrt{(j_1 + m_1)!(j_1 - m_1)!(j_2 + m_2)!(j_2 - m_2)!(j + m)!(j - m)!} \times \\ &\sum_z \frac{(-1)^z}{z!(j_1 + j_2 - j - z)!(j_1 - m_1 - z)!(j_2 + m_2 - z)!(j - j_2 + m_1 + z)!(j - j_1 - m_2 + z)!} \end{aligned} \quad (21)$$

This provides a closed form solution to any angular integrals involving three angular momenta. Since the spherical harmonics form a complete set of orthonormal functions, any expression in terms of 3 or more angular momenta is written by substituting linear combinations of spherical harmonics for the angular parts of the integral. The 3-j symbols are applied to such a system allowing one to avoid the direct integration and replace it with the closed form solution in equations (20) and (21).

The ability to substitute the angular part of the integral with a closed form solution

in terms of Wigner-3j symbols allows for easy computation providing exact analytic solutions to part of the problem being discussed.

### 2.4.2 The radial part

The radial part of the hydrogenic wavefunction is  $R_{n\ell}(r)$ , stated in equation (12). The perturbed wavefunctions will thus also resemble a similar form since they serve as small corrections to the original solution<sup>3</sup>. Removing the terms not dependant on  $r$  outside of the integrand (which are dependant on the perturbed wavefunction being investigated as well as the angular momentum and principle quantum numbers), a series of integrals that resemble the following form emerge<sup>4</sup>

$$I_{\text{radial}} = \int_0^\infty r^j e^{-\alpha r} dr \quad (22)$$

where  $j \in \mathbb{R}^+$ , and  $\alpha \in \mathbb{R}^+$ . This integral is a special one, being in the form of the gamma function integral<sup>5</sup>,  $\Gamma(z)$ . The Gamma function integral has the following solution

$$\int_0^\infty r^j e^{-\alpha r} dr = \frac{\Gamma(j+1)}{\alpha^{j+1}} \quad (23)$$

where as long as  $j+1 \in \mathbb{Z}^{0,+}$ , the gamma function simplifies to a factorial, and the following relation emerges;

$$\int_0^\infty r^j e^{-\alpha r} dr = \frac{j!}{\alpha^{j+1}}. \quad (24)$$

Fitting the integrals to the gamma function not only makes the task of computing

---

<sup>3</sup>See Sec. 2.5 for more details.

<sup>4</sup>This is shown explicitly in Sec. C.4.

<sup>5</sup>This function is technically Gamma function-esque, but can be manipulated into the form of the Gamma function. This is shown in greater detail in Sec. C.2.

the integrals significantly easier, but also makes the integration computationally stable. The solution provides a simple formula to implement when calculating radial integrals, and allows one to skip the implementation of well known numerical integration methods such as Euler’s method or any Runge-Kutta methods [26]. While these methods are powerful, they do have significant drawbacks compared to the derived analytical solutions due to error propagation and machine-precision and computation time.

The ability to compute these radial hydrogenic wavefunction integrals exactly is not only a satisfying result mathematically, but opens the door for more difficult problems in atomic physics where machine error is the determining step in the accuracy of a high-precision calculation<sup>6</sup>.

## 2.5 Perturbation Theory

To quantify how a magnetic field affects atomic energy levels, the shifts induced by the Zeeman effect must be determined. Since this interaction modifies the Hamiltonian slightly compared to the field-free case, perturbation theory is utilized to provide a systematic way to approximate the new eigenvalues and eigenstates.

To start we write the perturbed Hamiltonian as a sum of two terms;

$$\hat{H} = H^0 + \lambda H' \tag{25}$$

where  $H^0$  is the unperturbed Hamiltonian and  $H'$  is the perturbation.  $\lambda$  is a perturbation expansion parameter used to group together terms involving some power of  $\lambda$ . expanding the wavefunction and the energy of the system as a power series in  $\lambda$  gives

---

<sup>6</sup>Such problems include the calculation of Hylleraas wavefunctions for three body atomic systems such as  $H^-$ , He, or  $Li^+$ , where the radial integrals follow a similar but more complex closed form solution.

[22]

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots \quad (26)$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (27)$$

where each superscript is a higher order correction to the original wavefunction. Each higher order term is less impactful to the solution (by a factor of  $\lambda$ ) but still contributes a small amount. The first order perturbation equation is

$$(H^0 - E^0) |\psi^1\rangle = - (V - E^1) |\psi^0\rangle . \quad (28)$$

To find the first order correction to the energy,  $E^1$ , simply multiply through by  $\langle\psi^0|$ . This gives

$$\langle\psi^0|H^0 - E^0|\psi^1\rangle = -\langle\psi^0|V|\psi^0\rangle + E^1\langle\psi^0|\psi^0\rangle . \quad (29)$$

The first term is zero because  $(H^0 - E^0) |\psi^0\rangle = 0$ .  $\langle\psi^0|\psi^0\rangle = 1$  because of the normalization condition for the original unperturbed wavefunction. The normalization condition states that for each order of the perturbation

$$\langle\psi_n|\psi_n\rangle = 1 . \quad (30)$$

But since  $|\psi^0\rangle$  is already normalized, the following condition must be imposed;

$$\langle\psi^0|\psi^1\rangle = 0 . \quad (31)$$

Which ensures that the two states are orthogonal. The end result is

$$E^1 = \langle \psi^0 | V | \psi^0 \rangle . \quad (32)$$

In general, any higher order energy can be found with the following expression, which stems from the same process performed here for the first order energy.

$$E^n = \langle \psi_{n-1} | V | \psi_0 \rangle . \quad (33)$$

Similarly to the standard quantum mechanical Hamiltonian, the perturbation equation is a second order partial differential equation. However, the perturbing term in the equation as well as the higher order corrections to the energy serve as inhomogeneous terms. To solve this it is assumed that the higher order wavefunction is of the form of a power series in  $r$ , and the method of Frobenius is used to check if a solution of this form exists. This is discussed in the following section.

To calculate a higher order correction to the wavefunction, a similar process is repeated. This time starting with the second order equation

$$(H^0 - E^0) |\psi^2\rangle = - (V - E^1) |\psi^1\rangle + E^2 |\psi^0\rangle . \quad (34)$$

As it can be seen above, the second order solution requires the solution from the first order equation. The requirement of solving the previous correction in order to get the current one makes the processing of calculating higher order corrections quite laborious, and developing a method to solve for higher order corrections computationally removes the burden of solving lengthy equations by hand. The adaptation of solving the higher order perturbation equations computationally is discussed in Sec. D.



## 2.6 Recursion relations

When solving the perturbation equation, one ends up with an inhomogeneous second order partial differential equation. To solve for the radial piece of the corrected wavefunction, one can use the method of Frobenius. The method of Frobenius was developed by Ferdinand Georg Frobenius in 1869 and is a method of solving equations of the following form [31]:

$$\frac{d^2u}{dx^2} + \frac{d^2u}{dy^2} + k^2u = 0 . \quad (35)$$

The method of Frobenius involves assuming the solution is of the form of a power series, and then solving for terminating recursion relations to check if a finite solution exists. The method of solving these recurrence relations is what will be highlighted in this section.

A recurrence relation is an equation where the  $n^{\text{th}}$  term of a sequence is dependant on some combination of its previous terms in the sequence. A simple example of a recurrence relation is the Fibonacci numbers [19].

$$F_n = F_{n-1} + F_{n-2} . \quad (36)$$

But these equations can only be solved if there is an inidicial equation. An indicial equation is an equation which gives the condition that somewhere, the sequence stops, or is no longer defined by its previous term. In this case, it is the equation for the lowest starting power of  $r$  in the power series solution. A good example of this is the factorial function. The  $n^{\text{th}}$  factorial number is determined by

$$n! = n(n-1)! \quad (37)$$

where  $0!$  is not dependant on  $-1!$ , but is equivalent to 1. The recurrence relation stops here. If the recurrence relation did not have an indicial equation, and kept referring to the previous iteration forever, there would be no solution to  $n!$ . Recurrence relations can be written going downwards, as shown by the Fibonacci numbers and the factorial examples, or they can be written going upwards. This is best shown by the following recurrence relation

$$\sum_{j=0}^{\infty} \left[ Z(j-1)a_{j-1} - \frac{j(j+1)}{2}a_j \right] r^{j-2} = - \left( \frac{1}{r} + Z \right) . \quad (38)$$

The recurrence relation can be identified by writing out values for different  $j$

$$\begin{array}{ll} j = 0 & -Za_{-1} = 0 \\ j = 1 & a_1 = -1 \\ j = 2 & Za_1 - 3a_2 = -Z \\ & -Z + 3a_2 = -Z \\ & a_2 = 0 \\ j = 3 & 2Za_2 + 6a_3 = 0 \\ & a_3 = 0 \\ \vdots & \vdots \end{array} \quad (40)$$

It can be seen here that for every term after  $a_1$ , the series gives zero. The recurrence relation was used for each iteration including the indicial equation for  $j = 0$  and it has been shown that the sequence terminates, providing a non-divergent answer. If this was the solution to the PDE given by the Frobenius method, it would mean that the solution is in the form of a power series and the PDE is solved using the closed form solution.

## 2.7 The Dalgarno Interchange Theorem

Now that the perturbation equation, the matrix elements associated with it, and the ground work for the Hydrogenic wavefunctions has been laid out, a way to confirm the calculations is desirable. This presents itself as the Dalgarno Interchange Theorem. The theorem states that given any two perturbations  $V$  and  $W$ , thier first order equations can be written as

$$(H^0 - E^0) \psi^1 + V\psi^0 = E^1\psi^0 \quad (41)$$

$$(H^0 - E^0) \varphi^1 + W\psi^0 = F^1\psi^0 . \quad (42)$$

Multiplying equation (41) by  $\varphi^1$  and equation (42) by  $\psi^1$  and then integrating and subtracting (41) from (42) gives

$$\langle \psi^0 | V | \psi^1 \rangle - \langle \psi^0 | W | \varphi^1 \rangle = 0 . \quad (43)$$

Therefore

$$\langle \psi^0 | V | \psi_1 \rangle = \langle \psi^0 | W | \varphi^1 \rangle . \quad (44)$$

So given any two perturbations, the respective perturbation equations can be solved to retrieve  $\varphi^1$  and  $\psi^1$ . Using these solutions the two matrix elements can be computed with the perturbed wavefunction and its opposing perturbation from the opposing equation, and the result should be the same! This method serves as a check that the solutions are correct. Once the perturbing terms for the relativistic magnetic dipole operator and the relativistic correction have been calculated, the Dalgarno Interchange theorem can be used to verify that the calculations were correct.

The synthesis of all these methods is reached by perturbing the nuclear charge of the hydrogen atom to model a  ${}^3\text{He}^+$  atom, and then solving the perturbation equation to find the higher order Zeeman effects. This will require the calculation of matrix elements for  $\frac{1}{r}$  for relativistic corrections, and for the cubic Zeeman effect, the  $r^2$  matrix element for magnetic effects. these matrix elements can be computed by utilizing the discussed integration techniques above, as well as verify the calculated results for each using the Dalgarno interchange theorem.

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# CHAPTER 3

## *The Higher Order Zeeman Effect*

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### 3.1 Overview

In this chapter the Zeeman Effect is introduced, and the motivation, direct applications, and the higher order Zeeman Effect is discussed. The main focus of this chapter is to show the effect of the quadratic Zeeman Effect, and show how using the relativistic magnetic dipole operator in conjunction with the relativistic corrections to  ${}^3\text{He}^+$  yields a cubic Zeeman Effect. The effects of both the quadratic and cubic corrections are discussed in great detail, and the impact of the effect on high precision measurements is displayed for various magnetic field strengths.

Sec. 3.2 starts with the history of the Zeeman effect, its origins and discovery. Afterwards the motivation for the project in Sec. 3.3 is discussed. Here, some current experiments in the field such as the  $g-2$  experiment conducted at the Max Planck Institute as well as applications to high-precision magnetometry are highlighted. Some additional applications in the field of atomic physics such as ... are introduced as well. In Sec. 3.4, the ordinary Zeeman effect and quadratic Zeeman effect are derived using the canonical momentum. Their respective theories are introduced and applications to atomic systems such as  ${}^3\text{He}^+$  are discussed. Moving towards higher order systems, the cubic Zeeman effect is introduced. Starting with the effects that contribute to the cubic Zeeman effect such as the relativistic magnetic dipole operator in Sec. 3.5.1 and the quadratic Zeeman effect, the relativistic correction to  ${}^3\text{He}^+$  is derived and shown in Sec. 3.5.2. these effects are combined to yield a  $B^3$  contribution

to the energy splitting within the presence of an external magnetic field. Afterwards, Sec. 3.6 discusses the results of the calculation and its applications.

## 3.2 History

The Zeeman effect was first introduced by Pieter Zeeman, who discovered in 1896 that in the presence of a static magnetic field, spectral lines could be split into many components. After the discovery of quantum mechanics, the behaviour was found to be described as a perturbation of the Hamiltonian using the magnetic moment of the atom and the magnetic field.

Since its discovery, the Zeeman effect has played a large role in the field of atomic physics and magnetometry, which is the study of the intensity of magnetic field across space and time. There have been several calculations to include the relativistic corrections [32, 33], field inhomogeneities, and quadratic effects in hydrogenic systems [20]. However, little is known about its behavior in helium atoms such as  $^3\text{He}^+$  and  $^3\text{He}$ , which is of key interest in magnetometry and the muon magnetic moment anomaly ( $\mu_g - 2$ ), for which there is a  $5.0\sigma$  discrepancy [9] with the standard model prediction.

## 3.3 Motivation

### 3.3.1 The $g - 2$ experiment

The Dirac equation is a very successful and well studied equation in quantum mechanics. Its success comes from its ability to predict 2 important phenomena; the existence of antimatter and the magnetic dipole moment of the electron. The Dirac equation predicts that the magnetic dipole of the electron should be twice that of the classical prediction. This result is expressed in terms of the g-factor which the Dirac equation predicts is equal to 2. While the Dirac prediction is much closer to experimental findings, there is still a difference between the experimentally measured value

of  $g$  and the equations prediction. This is called the  $g - 2$  anomaly. The anomaly is represented by

$$a = \frac{g - 2}{2} . \quad (1)$$

The discrepancy of  $g$  is caused by higher-order contributions from quantum field theory and to this day is yet to be properly explained.

$$a_{\mu}^{\text{SM}} = a_{\mu}^{\text{QED}} + a_{\mu}^{\text{EW}} + a_{\mu}^{\text{hadron}} \quad (2)$$

The first two terms can be derived from first principles, but the hadronic term cannot be calculated precisely on its own and is estimated from experimental results. The effort to measure the muon magnetic moment precisely is an active area of research. The work presented in this thesis aids in the investigation of the  $g - 2$  anomaly by providing corrections to the Zeeman splitting in  $^3\text{He}^+$ , the element used in the magnetometry experiment to measure the anomaly. Accounting for higher order corrections to the Zeeman effect may help consolidate the discrepancy between theory and experiment and help researchers further understand the muon magnetic moment and its impact on muonic systems.

### 3.3.2 High-precision magnetometry

### 3.3.3 Connection to Atomic Physics

## 3.4 The Zeeman effect

When an atom is placed in an external magnetic field, its energy levels are shifted. The shifting of energy levels is known as the Zeeman effect. The effect is derived from the Schrodinger equation and the canonical momentum. The canonical momentum is a conserved quantity that describes a moving charged particle. It can be written

as

$$\vec{p} = m\vec{v} + e\vec{A}. \quad (3)$$

Where  $m\vec{v}$  is the classical definition of the momentum, and  $e\vec{A}$  is the extension from electrodynamics that accounts for the impact of an external magnetic field on a charged particle. This term is required in order to ensure that the conservation of momentum holds true, since charged particles subject to an external magnetic field travel in a circular path dependant on the direction of the field.

The canonical momentum then is also written in replacement to the typical momentum operator in quantum mechanics, giving the canonical momentum operator

$$\hat{p}_{\text{canonical}} = i\hbar\vec{\nabla} + e\hat{A}. \quad (4)$$

Where  $\hat{A}$  is the vector potential operator. For an external magnetic field of strength  $B$  pointing in the  $\hat{k}$  direction the operator becomes

$$\hat{A} = \frac{B}{2} (y\hat{i} - x\hat{j}). \quad (5)$$

Substituting this in for the vector potential operator in the canonical momentum and placing it into the Hamiltonian equation one gets

$$\hat{H} = \frac{\left(i\hbar\vec{\nabla} + \frac{Be}{2}(y\hat{i} - x\hat{j})\right)^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}. \quad (6)$$



Which when expanded gives

$$\hat{H} = \frac{-\hbar^2 \nabla^2}{2m} - \frac{i\hbar e B}{4mc} \vec{\nabla} \cdot [\hat{y}\hat{i} - \hat{x}\hat{j}] - \frac{i\hbar e B}{4mc} [\hat{y}\hat{i} - \hat{x}\hat{j}] \cdot \vec{\nabla} + \frac{e^2 B^2}{8mc} (x^2 + y^2) - \frac{Ze^2}{4\pi\epsilon_0 r} . \quad (7)$$

This equation is crucial for incorporating electromagnetic effects into the Hamiltonian. The first term in the expanded Hamiltonian is the standard operator. The first term and last term of the equation can be combined to write the ordinary Hamiltonian

$$\hat{H} = \hat{H}_{\text{Standard}} - \frac{i\hbar e B}{4mc} \vec{\nabla} \cdot [\hat{y}\hat{i} - \hat{x}\hat{j}] - \frac{i\hbar e B}{4mc} [\hat{y}\hat{i} - \hat{x}\hat{j}] \cdot \vec{\nabla} + \frac{e^2 B^2}{8mc} (x^2 + y^2) . \quad (8)$$

When  $\vec{\nabla} \cdot \hat{A} = 0$ , it is permitted to replace  $\nabla \cdot \hat{A}$  with  $\hat{A} \cdot \vec{\nabla}$  [28]. Performing the dot product in the next term gives

$$\hat{H} = \hat{H}_{\text{Standard}} - \frac{i\hbar e B}{2mc} \left[ y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right] + \frac{e^2 B^2}{8mc} (x^2 + y^2) . \quad (9)$$

This term is analogous to the orbital angular momentum operator in the  $\hat{k}$  direction

$$L_z = xp_y - yp_x = i\hbar \left[ y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right] . \quad (10)$$

Substituting this into the expression for the total Hamiltonian

$$\hat{H} = \hat{H}_{\text{Standard}} + \frac{eB}{2mc} L_z + \frac{e^2 B^2}{8mc} (x^2 + y^2) . \quad (11)$$

The middle term is the angular magnetic moment of the system, and the final term containing a  $B^2$  is known as the quadratic Zeeman effect  $\hat{H}_Z^{(2)}$ . The orbital angular

magnetic moment is [12]

$$\vec{\mu}_\ell = \frac{e}{2mc} \vec{L} . \quad (12)$$

Thus the Hamiltonian for a system subject to an external magnetic field is

$$\hat{H} = \hat{H}_{\text{Standard}} + \hat{H}_{\vec{\mu}_\ell} + \hat{H}_Z^{(2)} . \quad (13)$$

Since the magnetic field in question is considered to be in the positive  $\hat{k}$  direction, the linear Zeeman effect term is written in terms of the orbital magnetic moment

$$\hat{H}_Z^{(1)} = \vec{\mu}_\ell \cdot \vec{B} . \quad (14)$$

Accounting for the intrinsic spin of the electron, an additional term can be added to the Hamiltonian called the spin interaction [28]

$$\hat{H}_{\text{Spin}} = -g_s \frac{eB}{2mc} \vec{S} . \quad (15)$$

Where  $\vec{S}$  is the spin angular momentum operator. This expression is defined as the spin magnetic moment  $\vec{\mu}_s$ , and contains the Larmor frequency  $\omega = \frac{eB}{2m}$  [21].

$$\vec{\mu}_s = g_s \frac{e}{2mc} \vec{S} . \quad (16)$$

Here,  $g_s$  is the electron g-factor. The spin magnetic moment and the angular magnetic moment both scale linearly in  $B$ . The two effects are combined into what is known as the linear Zeeman effect.

$$\hat{H}_Z = -(\vec{\mu}_\ell + \vec{\mu}_s) \cdot \vec{B} . \quad (17)$$

The linear Zeeman effect has the following eigen energy solutions

$$E_{n,m_s,m_\ell} = -\frac{E_0}{n^2} + \mu_B B(m_\ell + 2m_s) . \quad (18)$$

So it is seen that depending on the magnetic quantum number, the energy levels split apart. Their corresponding new energies depend on this magnetic quantum number as well as the principle quantum number  $n$ , and scale linearly with magnetic field strength  $B$ . This is shown effectively in figure. 3.4.1a.

The  $B^2$  term is the quadratic Zeeman effect and is written on its own as

$$\hat{H}_Z = \frac{B^2 e^2}{8m_e} (x^2 + y^2) . \quad (19)$$

Using  $x^2 + y^2 = r^2 - z^2 = \frac{2}{3}r^2 [P_0(\cos \theta) - P_2(\cos \theta)]$  where  $P_2(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1)$  and  $P_0(\cos \theta) = 1$  are Legendre polynomials,

$$\hat{H}_Z = \frac{B^2 e^2}{12m_e} r^2 (P_0(\cos \theta) - P_2(\cos \theta)) . \quad (20)$$

The total Hamiltonian including the quadratic Zeeman perturbation is then

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{B^2 e^2}{12m_e} r^2 (P_0(\cos \theta) - P_2(\cos \theta)) . \quad (21)$$

Where the quadratic Zeeman term is treated as a perturbation. Using the ground state wavefunction of hydrogen for  $Z = 2$  for the  ${}^3\text{He}^+$  atom, the perturbation equa-

### 3. THE HIGHER ORDER ZEEMAN EFFECT

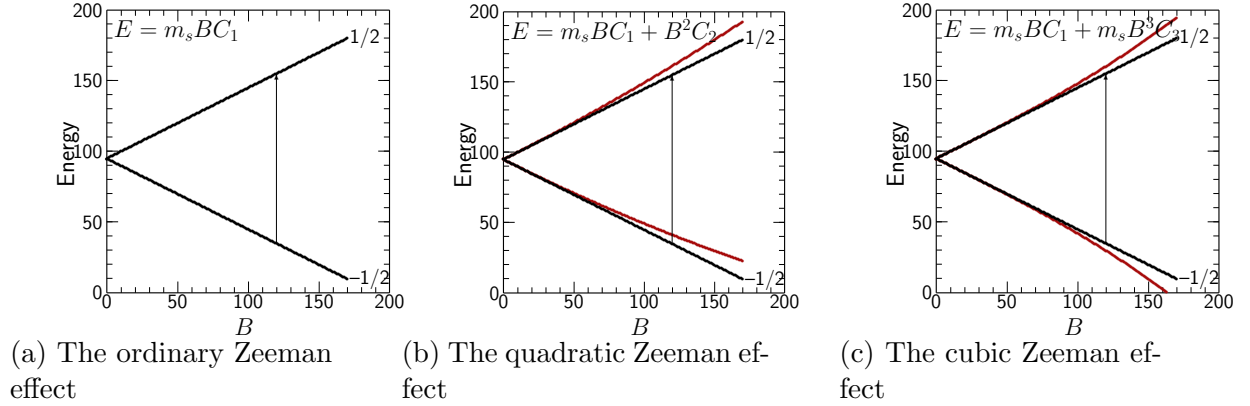


Fig. 3.4.1: The Zeeman effect energy splitting for each order

tion then reads

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} - E^{(0)}\right)|\psi^{(1)}\rangle = \left(\frac{B^2 e^2}{12m_e}r^2 - E^{(1)}\right)\frac{Z^{\frac{3}{2}}e^{-Zr}}{\sqrt{\pi}}. \quad (22)$$

Where the  $P_2(\cos\theta)$  term is zero since the problem involves spherically symmetric  $S$  states<sup>1</sup>. This perturbation equation can be solved using the method of Frobenius, where the form of  $|\psi^{(1)}\rangle$  is assumed to be of a power series.

$$|\psi^{(1)}\rangle = \sum_{j=0}^{\infty} Z^{\frac{3}{2}} a_j r^j e^{-Zr} \quad (23)$$

Inserting  $|\psi^{(1)}\rangle$  into the perturbation equation the expression reads

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} - E^{(0)}\right)\sum_{j=0}^{\infty} a_j r^j e^{-Zr} = \left(\frac{B^2 e^2}{12m_e}r^2 - E^{(1)}\right)\frac{e^{-Zr}}{\sqrt{\pi}}. \quad (24)$$

Performing the differentiation followed by a shift of summation indices the expression

---

<sup>1</sup>This can be proven by performing the necessary integrals with the  $P_2(\cos\theta)$  term included. The result is that the  $P_2(\cos\theta)$  integral is 0

simplifies to

$$\sum_{j=0}^{\infty} \left[ Z(j-1)a_{j-1} - \frac{j(j+1)}{2}a_j \right] r^{j-2} = - \left( \frac{B^2 e^2}{12m_e} r^2 - E^{(1)} \right) \frac{1}{\sqrt{\pi}}. \quad (25)$$

Using equation (32),  $E^{(1)}$  is found to be

$$E^{(1)} = \frac{1}{4Z^2} \gamma^2. \quad (26)$$

Where  $\gamma^2 \equiv \frac{B^2 e^2}{m}$ . The final expression before solving the recursion relation in the method of Frobenius yields

$$\sum_{j=0}^{\infty} \left[ Z(j-1)a_{j-1} - \frac{j(j+1)}{2}a_j \right] r^{j-2} = -\frac{1}{12} \gamma^2 \left( r^2 + \frac{3}{Z^2} \right) \frac{1}{\sqrt{\pi}}. \quad (27)$$

Grouping the powers of  $r$  from the LHS and the RHS of the equation produces a set of recursive relations that need to be solved. After substituting the correct integers for  $j$  for each equation it is seen that there are only two instances when the series terms are non-zero. These terms are for  $j = 2$  and  $j = 3$ . All other terms in the series are zero and thus non-contributing. The solution for  $|\psi^{(1)}\rangle$  is thus

$$|\psi^{(1)}\rangle = \sum_{j=0}^{\infty} a_j r^j e^{-Zr} = a_0 e^{-Zr} + a_2 r^2 e^{-Zr} + a_3 r^3 e^{-Zr} \quad (28)$$

Plugging in the found values for  $a_2$  and  $a_3$  yield

$$|\psi^{(1)}\rangle = \sum_{j=0}^{\infty} a_j r^j e^{-Zr} = a_0 e^{-Zr} - \frac{1}{12} \gamma^2 \frac{1}{Z^2 \sqrt{\pi}} r^2 e^{-Zr} - \frac{1}{36Z \sqrt{\pi}} \gamma^2 r^3 e^{-Zr}. \quad (29)$$

Currently,  $a_0$  is still undetermined. It is found by imposing the orthogonality condition between  $|\psi^{(0)}\rangle$  and  $|\psi^{(1)}\rangle$

$$\langle \psi^{(0)} | \psi^{(1)} \rangle = 0 . \quad (30)$$

This orthogonality relation is a choice, and it not required by any law or rule. It is necessary in order to compute  $a_0$  and is only allowed to be chosen due to the nature of the perturbation equation. It exploits the use of the Hermitian property of the Hamiltonian that allows the operator to act to the left instead of the right. Multiplying through the original perturbation equation given in (21) ensures that  $(\hat{H} - E^{(0)})$  is zero, implying that any quantity can be added to  $|\psi^{(1)}\rangle$  and the equation still holds true. Thus, we can add some amount to  $|\psi^{(1)}\rangle$  to ensure it is orthogonal without breaking the equality. This is a subtle trick, but one that is necessary to compute the full perturbed wavefunction<sup>2</sup>. The  $a_0$  coefficient can thus be determined by calculating the integral

$$\langle \psi^{(0)} | \psi^{(1)} \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin \theta \left( a_0 - \frac{1}{12} \gamma^2 \frac{1}{\sqrt{\pi}} \left[ \frac{1}{Z^2} r^2 + \frac{1}{3Z} r^3 \right] \right) \frac{Z^{\frac{3}{2}} e^{-2Zr}}{\sqrt{\pi}} = 0 . \quad (31)$$

And so  $a_0$  is found to be

$$a_0 = \frac{11}{2Z^4 \sqrt{\pi}} \frac{1}{12} \gamma^2 . \quad (32)$$

Thus, the full first order correction to the ground state hydrogenic wavefunction subject to an external magnetic field is

$$|\psi^{(1)}\rangle = \frac{1}{12} \gamma^2 \frac{1}{\sqrt{\pi}} \left[ \frac{11}{2Z^4} - \frac{1}{Z^2} r^2 - \frac{1}{3Z} r^3 \right] e^{-Zr} . \quad (33)$$

---

<sup>2</sup>Further explanation of the Hermitian operator rule as well as imposing the orthogonality condition is shown in Appendix .B

### 3.5 The Cubic Zeeman Effect

The following section discusses the main focus of this thesis, the Cubic Zeeman effect. While the linear Zeeman effect as well as the quadratic Zeeman effect have been studied for hydrogenic systems, little is known about any higher order contributions. This section investigates the combination of the magnetic dipole moment operator and the quadratic Zeeman effect to determine the relativistic effects of  ${}^3\text{He}^+$  that when applied, reveal a contribution to the energy shift that is dependant on the cube of the magnetic field strength.

The section starts out by first introducing the relativistic magnetic dipole moment operator ( $Q_{M1}$ ) and discusses its properties and significance to the Zeeman effect. Sec. 3.5.2 discusses the combination of the relativistic magnetic dipole moment operator with the quadratic Zeeman effect discussed in Sec .3.4 to calculate the relativistic corrections to  ${}^3\text{He}^+$ . Accounting for both interactions gives a correction to the energy splitting of  ${}^3\text{He}^+$  dependant on  $B^3$ .

#### 3.5.1 The relativistic magnetic dipole moment operator

The relativistic magnetic dipole moment operator represents the interaction of a magnetic dipole moment with an external magnetic field. It is described via the following relation

$$Q_{M1} = \mu_B \left( 1 - \frac{2p^2}{3m^2c^2} + \frac{Ze^2}{12\pi\epsilon_0 mc^2 r} \right) \vec{\sigma} \cdot \vec{B} \quad (34)$$

Where  $\mu_B$  is the Bohr magneton

$$\mu_B = \frac{e\hbar}{2mc} \quad (35)$$

The second term in the brackets of the relativistic magnetic dipole moment opera-

tor accounts for the relativistic correction to the kinetic energy of the electron, and the third term is the potential energy due to the Coulomb interaction between the electron and the nucleus. The first term corresponds to the ordinary Zeeman Effect, which does not contribute to the sum over states due to orthogonality.

The ordinary Zeeman effect contributes to  $Q_{M1}$  in  ${}^3\text{He}^+$  because it has non-zero spin due to the missing electron. For systems such as  ${}^3\text{He}$ , the ordinary Zeeman effect will not contribute. The expression can be simplified in order to make the perturbation being applied to the hydrogenic wavefunction clearer. Starting with the original expression

$$Q_{M1} = \mu_B \left( 1 - \frac{2p^2}{3m^2c^2} + \frac{Ze^2}{12\pi\epsilon_0 mc^2 r} \right) \vec{\sigma} \cdot \vec{B}, \quad (36)$$

the first term can be pulled out of the expression, and the  $p^2$  term can be written to fit the form of the Hamiltonian

$$Q_{M1} = \mu_B \vec{\sigma} \cdot \vec{B} + \frac{\mu_B}{3mc^2} \left( \frac{-4p^2}{2m} + \frac{Ze^2}{4\pi\epsilon_0 r} \right) \vec{\sigma} \cdot \vec{B}. \quad (37)$$

Substituting in the Hamiltonian  $\hat{H} = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} \longrightarrow \frac{p^2}{2m} = \hat{H} + \frac{Ze^2}{4\pi\epsilon_0 r}$  the  $Q_{M1}$  operator becomes

$$Q_{M1} = \mu_B \vec{\sigma} \cdot \vec{B} + \frac{\mu_B}{3mc^2} \left( -4\hat{H} - \frac{4Ze^2}{4\pi\epsilon_0 r} + \frac{Ze^2}{4\pi\epsilon_0 r} \right) \vec{\sigma} \cdot \vec{B}. \quad (38)$$

Simplifying the expression into 3 terms

$$Q_{M1} = \mu_B \vec{\sigma} \cdot \vec{B} + \frac{4}{3} \frac{\mu_B}{mc^2} \vec{\sigma} \cdot \vec{B} \hat{H} + \frac{5}{3} \frac{\mu_B Ze^2}{4\pi\epsilon_0 mc^2} \vec{\sigma} \cdot \vec{B} \frac{1}{r}. \quad (39)$$

Substituting in the fine structure constant  $\alpha$



$$Q_{M1} = \mu_B \vec{\sigma} \cdot \vec{B} + \frac{4}{3} \frac{\mu_B}{mc^2} \vec{\sigma} \cdot \vec{B} \hat{H} + \frac{5}{3} \frac{\mu_B Z \alpha \hbar}{mcr} \vec{\sigma} \cdot \vec{B}. \quad (40)$$

The Bohr radius  $a_0$  is also substituted into the expression, thus giving the final result

$$Q_{M1} = \mu_B \vec{\sigma} \cdot \vec{B} + \frac{4}{3} \frac{\mu_B}{mc^2} \vec{\sigma} \cdot \vec{B} \hat{H} + \frac{5}{3} \mu_B Z \alpha^2 a_0 \vec{\sigma} \cdot \vec{B} \frac{1}{r}. \quad (41)$$

The relativistic magnetic dipole moment operator is then written as a perturbation of  $r^{-1}$  to the Hamiltonian. Now that the operator has been introduced, the total Zeeman effect for the system can be derived. The total Zeeman effect utilizes not only the electronic Zeeman effect discussed above, but also accounts for the nuclear Zeeman effect. The Hamiltonian for the system now includes the standard definition, the linear electronic Zeeman effect, the quadratic electronic Zeeman effect and the ordinary nuclear Zeeman effect. This is described mathematically as

$$\hat{H}_Z = \frac{e\hbar}{2M} g_I \left[ \vec{B} \cdot \vec{\sigma}_N + \frac{M}{m} \left( \frac{g_s}{g_I} Q_{M1} + \frac{B^2 e}{3g_I \hbar} r^2 (P_0(\cos \theta) - P_2(\cos \theta)) \right) \right] \quad (42)$$

Inserting the  $Q_{M1}$  operator into the equation yields

$$\hat{H}_Z = \frac{e\hbar}{2M} g_I \left[ \vec{B} \cdot \vec{\sigma}_N + \frac{M}{m} \left( \frac{g_s}{g_I} \left( \mu_B \vec{\sigma} \cdot \vec{B} + \frac{4}{3} \frac{\mu_B}{mc^2} \vec{\sigma} \cdot \vec{B} \hat{H} + \frac{5}{3} \mu_B Z \alpha^2 a_0 \vec{\sigma} \cdot \vec{B} \frac{1}{r} \right) + \frac{B^2 e}{3g_I \hbar} r^2 \right) \right] \quad (43)$$

The new Hamiltonian combines previously mentioned effects, and has terms linearly scaling in  $B$ , as well as quadratically scaling in  $B$ . Several new factors have arisen due to the inclusion of the nuclear magnetic moment such as  $g_I$ , the nuclear g-factor,  $g_s$ , the electron spin g-factor, and  $M$ , the mass of the nucleus.  $\vec{\sigma}_N$  is the nuclear spin operator, which is analogous to the electron spin matrices  $\vec{\sigma}$ . It's subscript is maintained to help distinguish between the nuclear and electronic effects present in the Hamiltonian. Traditionally, the nuclear contribution is ignored as its effect on the system is significantly smaller than the effect present from the electronic terms.

The reason the nuclear effect is so much smaller than the electronic effect is because its impact is suppressed by the mass of the nucleus. Since the mass of the electron is so much smaller than the nuclear mass, its impact is a factor of  $\frac{M}{m}$  stronger than the nuclear effects.

The inclusion of the  $Q_{M1}$  operator in the Zeeman effect adds a linear scaling of  $B$  to the overall energy of the system. This operator can be combined with the quadratic Zeeman operator discussed previously to yield a relativistic correction to  $^3\text{He}^+$ . This relativistic correction scales with  $B^3$  and will be the primary focus of this thesis moving forwards. The inclusion of this higher order Zeeman effect adds a small correction to the Zeeman splitting which has since been unaccounted for in high precision magnetometry. The perturbative effects of the relativistic magnetic dipole moment operator is examined below and explores how it modifies the structure of the Hamiltonian.

Within the  $Q_{M1}$  operator, it has been shown that the  $p^2$  term can be written in terms of the original Hamiltonian, there is not a need to perform a perturbation about  $p^2$  in order to receive the desired correction to the energy. Thus the perturbation equation for the  $Q_{M1}$  operator is

$$(H^{(0)} - E^{(0)}) |\Psi^{(1)}\rangle = - \left( \frac{5}{3} \mu_B Z \alpha^2 a_0 \frac{1}{r} \vec{\sigma} \cdot \vec{B} - E^{(1)} \right) \frac{e^{-Zr}}{\sqrt{\pi}}. \quad (44)$$

Similarly to Sec. 3.4, the first order corrected wavefunction is assumed to be of the form of a power series, so that the method of Frobenius can be applied. This gives a similar result to the quadratic Zeeman derivation, but the inhomogeneous terms on the right hand side of the equation now correlate to different powers of  $r^3$ .

---

<sup>3</sup>Note here that  $a_0$  is the Bohr radius, not the zeroeth term in the sum. Similarly to the derivation for the quadratic Zeeman effect, there is no  $a_0$  term from the summation, and it is determined later. The conflict in notation is avoided for now.

$$\sum_{j=0}^{\infty} \left[ Z(j-1)a_{j-1} - \frac{j(j+1)}{2}a_j \right] r^{j-2} = - \left( \frac{5}{3}\mu_B Z\alpha^2 a_0 \frac{1}{r} \vec{\sigma} \cdot \vec{B} - E^{(1)} \right) \frac{1}{\sqrt{\pi}} \quad (45)$$

Where  $E^{(1)}$  is defined by equation (32)

$$E^{(1)} = \frac{5}{3}Z^2\alpha^2 a_0 \mu_B \vec{\sigma} \cdot \vec{B} \quad (46)$$

This gives the final result before the recursion relation step

$$\sum_{j=0}^{\infty} \left[ Z(j-1)a_{j-1} - \frac{j(j+1)}{2}a_j \right] r^{j-2} = -\frac{5}{3}Z\alpha^2 a_0 \mu_B \left( \frac{1}{r} - Z \right) \frac{1}{\sqrt{\pi}} \vec{\sigma} \cdot \vec{B} \quad (47)$$

The recursion relation is solved once again similarly to that of the quadratic Zeeman perturbation, but this time only a single term in the series appears as nonzero. The first order correction to the hydrogenic wavefunction for a  $\frac{1}{r}$  perturbation is

$$|\Psi^{(1)}\rangle = a_0 e^{-Zr} + a_1 r e^{-Zr} \quad (48)$$

The  $a_0$  term is determined by the orthogonality imposed on the system once again and the integration yields<sup>4</sup>

$$a_0 = -\frac{5}{3}\alpha^2 \bar{a}_0 \mu_B \vec{\sigma} \cdot \vec{B} \frac{1}{\sqrt{\pi}} \frac{3}{2}. \quad (49)$$

Thus the final expression for the correction to the hydrogenic wavefunction for a perturbation of the relativistic magnetic dipole operator is

---

<sup>4</sup>Note that due to the conflicting notation, the Bohr radius is denoted as  $\bar{a}_0$ .

$$|\Psi^{(1)}\rangle = \frac{5}{3}Z\alpha^2a_0\mu_B\vec{\sigma} \cdot \vec{B} \frac{1}{\sqrt{\pi}}e^{-Zr} \left(-\frac{3}{2Z} + r\right) \quad (50)$$

Now that the  $Q_{M1}$  operator

### 3.5.2 The relativistic correction to ${}^3\text{He}^+$

Combining the relativistic magnetic dipole moment with the quadratic Zeeman operator, we can write down the relativistic corrections for  ${}^3\text{He}^+$ . The relativistic correction is

$$C_{\text{rel}}^{(2)} = \sum_{n=1}^{\infty} \frac{\langle \psi^0 | Q_{M1} | \psi^n \rangle \langle \psi^n | V_Z^{(2)} | \psi^0 \rangle}{E_0 - E_n}. \quad (51)$$

Replacing the infinite sum of the hydrogenic spectrum with the sum over the pseudospectrum for either the quadratic Zeeman operator or the relativistic magnetic dipole operator gives a simplified definition for the relativistic correction. To ensure correctness, both approaches are calculated, and the Dalgarno interchange theorem 2.7 is used to verify that both solutions are the same. Starting with the quadratic Zeeman operator, define

$$|\psi^{(1)}\rangle = \sum_{n=1}^{\infty} \frac{|\psi^n\rangle \langle \psi^n | V_Z^{(2)} | \psi^0 \rangle}{E_0 - E_n}, \quad (52)$$

so that the relativistic correction now reads

$$C_{\text{rel}}^{(2)} = \langle \psi^0 | Q_{M1} | \psi^{(1)} \rangle. \quad (53)$$

$|\psi^{(1)}\rangle$  is also written in equation (33), and the solution to  $C_{\text{rel}}^{(2)}$  is now just an integral

$$C_{\text{rel}}^{(2)} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin \theta \psi^0 Q_{M1} \psi^{(1)} dr d\theta d\phi. \quad (54)$$

expanding  $\psi^1$  and  $\psi^0$  and simplifying

$$C_{\text{rel}}^{(2)} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r \sin \theta \frac{5}{36} \gamma^2 \frac{e^{-2Zr}}{\pi} \left[ \frac{11}{2Z^4} - \frac{1}{Z^2} r^2 - \frac{1}{3Z} r^3 \right] \mu_B \alpha^2 a_0 \vec{\sigma} \cdot \vec{B} Z^{\frac{5}{2}} dr d\theta d\phi \quad (55)$$

Which after integration gives

$$C_{\text{rel}}^{(2)} = \frac{5}{12} \gamma^2 \mu_B \alpha^2 a_0 Z^{-\frac{7}{2}} \vec{\sigma} \cdot \vec{B}. \quad (56)$$

It can be seen that the relativistic correction to  ${}^3\text{He}^+$  includes a  $B^3$  scaling. This electronic effect further splits the energy levels of  ${}^3\text{He}^+$  when subjected to an external magnetic field. The  $\vec{\sigma} \cdot \vec{B}$  term ensures that the splitting is dependent on the magnetic quantum number  $m$ , so the shift to the energy is a noticeable effect that further increases the splitting between the states. This result is verified using the Dalgarno interchange theorem by defining

$$|\varphi^{(1)}\rangle = \sum_{n=1}^{\infty} \frac{\langle \psi^0 | Q_{M1} | \psi^n \rangle \langle \psi^n |}{E_0 - E_n}, \quad (57)$$

which means that the relativistic correction can also be defined as

$$C_{\text{rel}}^{(2)} = \langle \varphi | V_Z^{(2)} | \psi^0 \rangle. \quad (58)$$

According to the Dalgarno interchange theorem, this expression for  $C_{\text{rel}}^{(2)}$  should be the same as the result found in equation (56). In integral form this reads

PUT SOMETHING HERE

$$C_{\text{rel}}^{(2)} = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin \theta \frac{5}{3} Z \alpha^2 a_0 \mu_B \vec{\sigma} \cdot \vec{B} \frac{e^{-Zr}}{\sqrt{\pi}} \left[ -\frac{3}{2Z} + r \right] \frac{1}{12} \gamma^2 r^2 \frac{Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{\pi}} dr d\theta d\phi. \quad (59)$$

Which becomes

$$C_{\text{rel}}^{(2)} = \frac{5}{12} \gamma^2 \mu_B \alpha^2 a_0 Z^{-\frac{7}{2}} \vec{\sigma} \cdot \vec{B}. \quad (60)$$

Thus it has been proven via the Dalgarno interchange theorem that all previous calculations have been correct, and the relativistic corrections for  ${}^3\text{He}^+$  have been successfully derived. Reversing the substitution of all of the physical constants one gets

$$C_{\text{rel}}^{(2)} = \frac{5}{12} \frac{B^3 e^5 \hbar Z^{-\frac{7}{2}}}{m^3 c^3 4\pi \epsilon_0} m_s. \quad (61)$$

Which has units of energy per tesla.  $m_s$  denotes the magnetic quantum number, which can take values of  $\pm\frac{1}{2}$ . From this, the further splitting of energy states based on magnetic field strength is evident. The relationship behaves like the splitting shown in figure 3.4.1c. This factor is not suppressed by the mass of the nucleus like the other effects discussed in the previous section, and thus becomes impactful to the systems behaviour for all magnitudes of magnetic field, regardless of its seemingly small correction. This is demonstrated in Table ??.

## 3.6 Results

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## CHAPTER 4

### *Conclusion and Future Work*

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#### 4.1 Overview

#### 4.2 Consolidation of Results

#### 4.3 Synthesis of Conclusions

#### 4.4 Future Work

#### 4.5 Theoretical and Practical Impact

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# APPENDIX A

## *Derivation of the Recursion Relations*

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The aim of this section is to guide the reader through a more in depth derivation of the recursion relations for the quadratic zeeman effect as well as the relativistic magnetic dipole operator perturbations to the Hamiltonian. Starting with the first order perturbation equation

$$(H^0 - E^0) |\psi^1\rangle = - (V - E^1) |\psi^0\rangle , \quad (1)$$

$E^1$  can be found by multiplying through by  $\langle\psi^0|$

$$\langle\psi^0|H^0 - E^0|\psi^1\rangle = -\langle\psi^0|V - E^1|\psi^0\rangle . \quad (2)$$

The first term is 0 due to the orthogonality of states which is imposed and discussed in Sec. 3. The expression now reads

$$\begin{aligned} -\langle\psi^0|V - E^1|\psi^0\rangle &= 0 \\ \langle\psi^0|V|\psi^0\rangle &= \langle\psi^0|E^1|\psi^0\rangle \\ \langle\psi^0|V|\psi^0\rangle &= E^1\langle\psi^0|\psi^0\rangle \end{aligned}$$

So



$$E^1 = \langle \psi^0 | V | \psi^0 \rangle . \quad (3)$$

For the  $r^2$  perturbation, one gets

$$E^1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin \theta \frac{2Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{4\pi}} \frac{B^2 e^2}{12m} r^2 \frac{2Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{4\pi}} dr d\theta d\phi$$

$$E^1 = 4\pi \int_0^\infty \frac{Z^3 e^{-2Zr}}{\pi} \frac{B^2 e^2}{12m} r^4 dr$$

$$E^1 = \frac{Z^3 B^2 e^2}{3m} \frac{4!}{(2Z)^5}$$

$$E^1 = \frac{B^2 e^2}{4Z^2 m}$$

Here, we let  $\frac{B^2 e^2}{m} \equiv \gamma^2$  [24], and we end up with the final result for  $E^1$  to be

$$E^1 = \frac{1}{4Z^2} \gamma^2 . \quad (4)$$

The perturbing potential  $V$  also is written in terms of  $\gamma^2$

$$V = \frac{B^2 e^2}{12m} r^2 = \frac{1}{12} \gamma^2 r^2 \quad (5)$$

Assuming that  $|\psi^1\rangle$  is of the form of a power series

$$|\psi^1\rangle = \sum_{j=0}^{\infty} Z^{\frac{3}{2}} a_j r^j e^{-Zr} \quad (6)$$

and substituting both  $E^1$  and  $|\psi^1\rangle$  into the perturbation equation

$$(H^0 - E^0) \sum_{j=0}^{\infty} Z^{\frac{3}{2}} a_j r^j e^{-Zr} = \left( \frac{1}{12} \gamma^2 r^2 - \frac{1}{4Z^2} \gamma^2 \right) \frac{Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{\pi}}. \quad (7)$$

Substituting the Hamiltonian in atomic units

$$\left( \frac{1}{2} \nabla^2 + \frac{Z}{r} - E_0 \right) \sum_{j=0}^{\infty} a_j r^j e^{-Zr} = \left( \frac{1}{12} \gamma^2 r^2 - \frac{1}{4Z^2} \gamma^2 \right) \frac{Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{\pi}}$$

$$\begin{aligned} \frac{1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \sum_{j=0}^{\infty} a_j r^j e^{-Zr} + Z \sum_{j=0}^{\infty} a_j r^{j-1} e^{-Zr} - E^0 \sum_{j=0}^{\infty} a_j r^j e^{-Zr} \\ = \left( \frac{1}{12} \gamma^2 r^2 - \frac{1}{4Z^2} \gamma^2 \right) \frac{Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{\pi}}. \end{aligned}$$

$$\begin{aligned} \left( \frac{Z^2}{2} - E^0 \right) \sum_{j=0}^{\infty} a_j r^j - Zr \sum_{j=0}^{\infty} a_j r^{j-2} (j+1) + \sum_{j=0}^{\infty} \frac{j(j+1)}{2} a_j r^{j-2} \\ + Z \sum_{j=0}^{\infty} a_j r^{j-1} - E^0 \sum_{j=0}^{\infty} a_j r^j = \frac{1}{12} \gamma^2 \left( r^2 - \frac{3}{Z^2} \right) \frac{1}{\sqrt{\pi}}. \end{aligned}$$

Since  $E^0 = \frac{Z^2}{2}$ , the first term is zero and the equation becomes

$$-Zr \sum_{j=0}^{\infty} a_j r^{j-2} (j+1) + \sum_{j=0}^{\infty} \frac{j(j+1)}{2} a_j r^{j-2} + Z \sum_{j=0}^{\infty} a_j r^{j-1} = \frac{1}{12\sqrt{\pi}} \gamma^2 \left( r^2 - \frac{3}{Z^2} \right).$$

Performing a shift of summation index to group all of the summations together

$$\sum_{j=0}^{\infty} \left[ Z(j-1) a_{j-1} - \frac{j(j+1)}{2} a_j \right] r^{j-2} = -\frac{1}{12} \gamma^2 \left( r^2 - \frac{3}{Z^2} \right) \frac{1}{\sqrt{\pi}}. \quad (8)$$

Which is equation (25) in Sec. 3.4. Writing out the first few recursion relations by

grouping the powers of  $r$  together

$$\begin{array}{lll}
j = 0 & -Za_{-1} = 0 & a_{-1} = 0 \\
j = 1 & -a_1 = 0 & a_1 = 0 \\
j = 2 & Za_1 - 3a_2 = \frac{1}{12}\gamma^2 \frac{3}{Z^2} \frac{1}{\sqrt{\pi}} & a_2 = -\frac{1}{12}\gamma^2 \frac{1}{Z^2 \sqrt{\pi}} \\
j = 3 & 2Za_2 - 6a_3 = 0 & a_3 = -\frac{1}{32Z\sqrt{\pi}}\gamma^2 \\
j = 4 & 3Za_3 - 10a_4 = -\frac{1}{12}\gamma^2 \frac{1}{\sqrt{\pi}} & a_4 = 0 \\
j = 5 & 4Za_4 - 15a_5 = 0 & a_5 = 0 \\
\vdots & \vdots & \vdots
\end{array}$$

It is clearly seen above that all other cases of  $a_j$  must be zero after  $j = 3$ . The recursion relation has been solved and a closed form solution for  $|\psi^1\rangle$  can be written in terms of a power series in  $r$  using  $a_0$ ,  $a_2$ , and  $a_3$ .  $a_0$  is an undetermined coefficient here that does not appear in the recursion relation. it is determined by imposing the normalization condition which is shown in Sec. 3.4.

The identical process is carried out for the relativistic magnetic dipole moment operator perturbation, with the only difference being that the perturbing potential has changed. No operators act on the perturbing potential throughout the perturbation expansion, so the result will remain the same as in the example above. Applying the same process the first order correction to the wavefunction for the relativistic magnetic dipole moment operator is

$$\sum_{j=0}^{\infty} \left[ Z(j-1)a_{j-1} - \frac{j(j+1)}{2}a_j \right] r^{j-2} = - \left( \frac{5}{3}\mu_B Z\alpha^2 a_0 \vec{\sigma} \cdot \vec{B} \frac{1}{r} - E^1 \right) \frac{1}{\sqrt{\pi}}. \quad (9)$$

$E^1$  is determined in the standard way<sup>1</sup>

$$E^1 = \langle \psi^0 | \frac{5}{3} \mu_B Z \alpha^2 a_0 \vec{\sigma} \cdot \vec{B} \frac{1}{r} | \psi^0 \rangle$$

$$E^1 = \int_0^\infty \int_0^{2\pi} \int_0^\pi r^2 \sin \theta \frac{2Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{4\pi}} \frac{5}{3} \mu_B Z \alpha^2 a_0 \vec{\sigma} \cdot \vec{B} \frac{1}{r} \frac{2Z^{\frac{3}{2}} e^{-Zr}}{\sqrt{4\pi}} dr d\theta d\phi$$

$$E^1 = 4\pi \int_0^\infty r \sin \theta \frac{Z^3 e^{-2Zr}}{\pi} \frac{5}{3} \mu_B Z \alpha^2 a_0 \vec{\sigma} \cdot \vec{B} dr d\theta d\phi$$

$$E^1 = \frac{5}{3} 4\pi Z^4 \alpha^2 a_0 \mu_B \vec{\sigma} \cdot \vec{B} \int_0^\infty r e^{-2Zr} dr$$

$$E^1 = \frac{5}{3} 4\pi Z^4 \alpha^2 a_0 \mu_B \vec{\sigma} \cdot \vec{B} \frac{1!}{(2Z)^2}$$

$$E^1 = \frac{5}{3} Z^2 \alpha^2 a_0 \mu_B \vec{\sigma} \cdot \vec{B}$$

So the final expression for the recursion relations for the relativistic magnetic dipole moment operator is

$$\sum_{j=0}^{\infty} \left[ Z(j-1)a_{j-1} - \frac{j(j+1)}{2} a_j \right] r^{j-2} = -\frac{5}{3} \alpha^2 Z a_0 \mu_B \left( \frac{1}{r} - Z \right) \frac{1}{\sqrt{\pi}} \vec{\sigma} \cdot \vec{B}. \quad (10)$$

The series converges after  $j = 1$ , as shown below.

---

<sup>1</sup>Note that  $a_0$  here is for the Bohr radius.  $a_0$  is also the zeroeth term in the summation, but the form of the summation here dictates that there is no  $a_0$  term present.

# A. DERIVATION OF THE RECURSION RELATIONS

$$\begin{array}{lll}
j = 0 & -Za_{-1} = 0 & a_{-1} = 0 \\
j = 1 & -a_1 = -\frac{5}{3}\alpha^2 Z a_0 \mu_B \frac{1}{\sqrt{\pi}} \vec{\sigma} \cdot \vec{B} & a_1 = \frac{5}{3}\alpha^2 Z a_0 \mu_B \frac{1}{\sqrt{\pi}} \vec{\sigma} \cdot \vec{B} \\
j = 2 & Za_1 - 3a_2 = \frac{5}{3}\alpha^2 Z^2 a_0 \mu_B \frac{1}{\sqrt{\pi}} \vec{\sigma} \cdot \vec{B} & a_2 = 0 \\
j = 3 & 2Za_2 - 6a_3 = 0 & a_3 = 0 \\
j = 4 & 3Za_3 - 10a_4 = 0 & a_4 = 0 \\
j = 5 & 4Za_4 - 15a_5 = 0 & a_5 = 0 \\
\vdots & \vdots & \vdots
\end{array}$$

Thus the recursion relations for the relativistic magnetic dipole moment operator and the quadratic Zeeman operator have been solved, and thier respective first order corrections to the hydrogenic wavefunction have been calculated.

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## APPENDIX B

### *Left-acting Operators*

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This section contains the proof for the ability of hermitian operators to act to the left as well as to the right. The specific case discussed here uses the Hamiltonian, but this can be similarly shown for any hermitian operator. Given the matrix element

$$\langle\psi|\hat{H}|\phi\rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{H} \phi(x) dx \quad (1)$$

$$\langle\psi|\hat{H}|\phi\rangle = \int_{-\infty}^{\infty} \psi^*(x) -i\hbar \frac{d\phi(x)}{dx} dx , \quad (2)$$

applying integration by parts gives

$$\langle\psi|\hat{H}|\phi\rangle = [\psi^*(x)\phi(x)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} -i\hbar \frac{d\psi^*(x)}{dx} \phi(x) dx \quad (3)$$

$$\langle\psi|\hat{H}|\phi\rangle = \int_{-\infty}^{\infty} i\hbar \frac{d\psi^*(x)}{dx} \phi(x) dx . \quad (4)$$

Which is the same as writing

$$\langle\psi|\hat{H}|\phi\rangle = \int_{-\infty}^{\infty} \phi(x) \hat{H} \psi^*(x) dx \quad (5)$$

So it is shown that the Hamiltonian is capable of acting to the right or to the left, and it is up to the user which way they want to apply the operation.

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# APPENDIX C

## *Special Functions*

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### C.1 Overview

This section of the appendix discusses the special functions used throughout this thesis, providing their definitions and properties in greater detail than discussed in the main body of this paper. The introduction to these functions is brief, and are placed here for convenience of the reader. Sec .C.2 introduces the gamma function and its properties, and its use in providing a closed solution to many of the integrals present in the matrix elements discussed in Sec .2.4 is highlighted. Sections C.4 and C.5 introduce the Laguerre polynomials and the spherical harmonic function respectively, which are key to the solution of hydrogenic wavefunctions used in this thesis. Additionally, the confluent hypergeometric function is discussed in Sec .C.6, where an alternative formulation of the radial wavefunctions for hydrogen is given. Finally, the chapter concludes with the description of Legendre polynomials, which can be used in a similar manner to the spherical harmonics due to their property of forming a complete set of orthogonal functions.

### C.2 The gamma function

The gamma function  $\Gamma(z)$  is an extension of the factorial function into the complex plane.

$$\Gamma(z) \in \mathbb{C} \tag{1}$$

For the case where the input parameter  $z \in \mathbb{Z}^+$ , the function is equal to [11]

$$\Gamma(n) = (n-1)! . \quad (2)$$

This is a relation of key importance in Sec. 2.4.2, where the radial integral is replaced with a factorial function for positive integers of  $j$  in the sum.

The gamma function also has an integral definition, which is known as the Euler integral

$$\Gamma(z) = \int_0^\infty e^{-t} t^{z-1} dt, \quad \Re(z) > 0 . \quad (3)$$

This integral is defined as long as the real part of  $z$  is greater than zero. This integral closely resembles the radial integrals present in Sec. 2.4.2, which are of the form

$$I_{\text{radial}} = \int_0^\infty r^j e^{-\alpha r} dr \quad (4)$$

To fit the gamma function, perform a change of variables  $t = \alpha r$ ,  $dt = \alpha dr$ .

$$I_{\text{radial}} = \int_0^\infty \left( \frac{t}{\alpha} \right)^j e^{-t} \frac{1}{\alpha} dt \quad (5)$$

$$I_{\text{radial}} = \frac{1}{\alpha^{j+1}} \int_0^\infty t^j e^{-t} dt \quad (6)$$

So the solution to the radial integral is shown to be

$$I_{\text{radial}} = \frac{\Gamma(j+1)}{\alpha^{j+1}} \quad (7)$$



if  $j \in \mathbb{Z}^+$ , the relationship between the gamma function and the factorial function can be used. The values of  $j$  are the summation indices for each power of  $r$ <sup>1</sup>. Since the summation indices are constrained to a set of integers from 0 to infinity, it can be said that

$$\forall j, j \in \mathbb{Z}^{0+} \quad (8)$$

Additionally, the 0<sup>th</sup> power of  $r$  (corresponding to  $j = 0$ ) does not appear in the recursion relations of the expanded sum in 3.5.1, and is zero in 3.4. This further restricts the set of  $j$  indices in both problems to

$$\forall j, j \in \mathbb{N} \quad (9)$$

Since the set of natural numbers only contains positive integers, the euler integral only evaluates values for positive integer  $j$ . The gamma function by its original definition is then replaced by the factorial function, giving the solution to the radial integrals used in sections 2.4.2, 3.4 and 3.5.1.

### C.3 Legendre Polynomials

The Legendre equation is

$$(1 - x^2)P''(x) - 2xP'(x) + \lambda P(x) = 0 . \quad (10)$$

This differential equation can be solved with a series solution about  $x = 0$  and has a radius of convergence of 1. If  $\lambda$  has the value  $l(l+1)$ , where  $l \in \mathbb{Z}$ , the series truncates after  $x^l$ . The series solution to this ODE is

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<sup>1</sup>See sections 3.4 and 3.5.1 for the summation expressions for each.

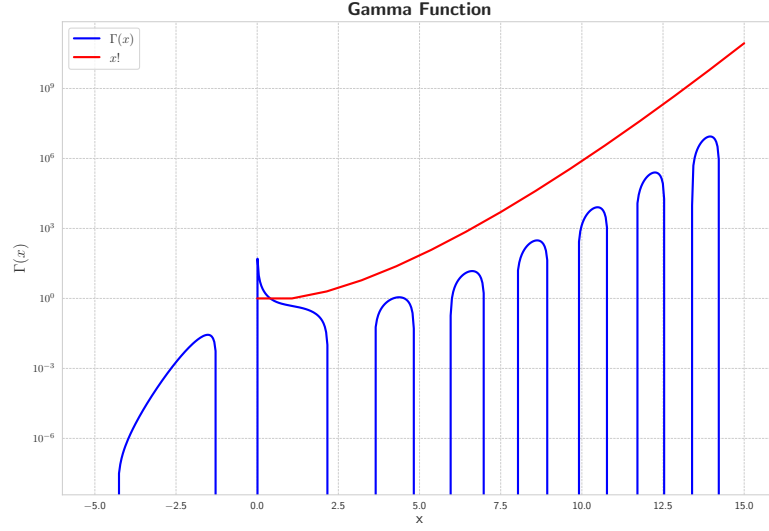


Fig. C.2.1: Graph of the gamma function compared to the factorial function.

$$g(x, t) = \sum_{l=0}^{\infty} P_l(x) t^l \quad (11)$$

Where  $g(x, t)$  is the generating function which produces the possible solutions to the Legendre Equation. Each solution to the Legendre equation generated by  $g(x, t)$  is called a Legendre polynomial. These polynomials can be produced with the following equation

$$P_l(x) = \sum_{n=0}^{\lfloor \frac{l}{2} \rfloor} (-1)^k \frac{(2l - 2k)!}{2^n k! (n - k)! (n - 2k)!} x^{n-2k} \quad (12)$$

where  $\lfloor x \rfloor$  is the floor function, which rounds down to the nearest integer value. This formulation is of key importance for programmed implementation, since a discrete formula is simple to compute. A more helpful definition of the Legendre polynomial comes from the Rodriguez formula [11]

Legendre Polynomials
$P_0(x) = 1$
$P_1(x) = x$
$P_2(x) = \frac{1}{2}(3x^2 - 1)$
$P_3(x) = \frac{1}{2}(5x^3 - 3x)$
$P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$

Fig. C.3.1: Table of the first few Legendre Polynomials

$$P_n(x) = \frac{1}{2^n n!} \left( \frac{d}{dx} \right)^n (x^2 - 1)^n \quad (13)$$

This formulation is much more useful for analytical work. The first few Legendre Polynomials are given below

Another key feature of the Legendre polynomials is that they form a complete set of orthogonal basis functions, meaning that for each value of  $l$ , the associated Legendre polynomial is orthogonal to all other Legendre polynomials with different  $l$ .

$$\int_{-1}^1 P_l(x) P_{l'}(x) dx = \frac{2}{2l+1} \delta_{l,l'} \quad (14)$$

The Legendre polynomials appear in the angular part of the solution to hydrogenic wavefunctions as discussed in Sec. 2.4.1. They are also incorporated into the spherical harmonic function discussed in Sec. C.5.

## C.4 Laguerre Polynomials

The Laguerre ODE is

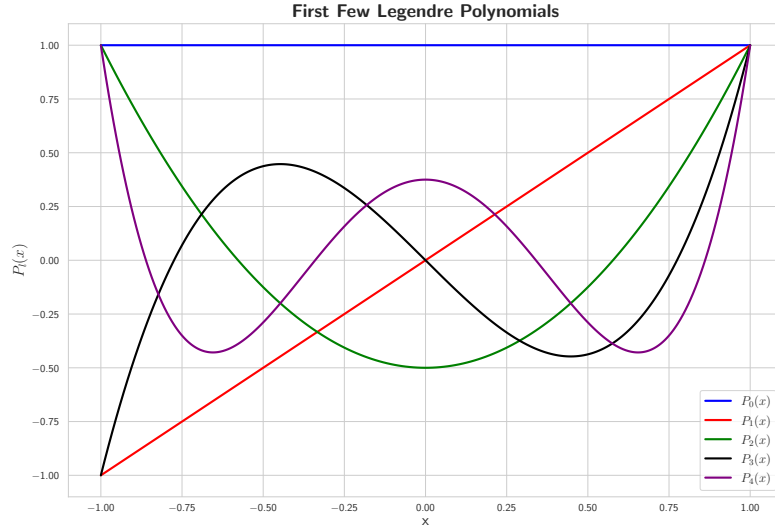


Fig. C.3.2: Graph of the first few Legendre polynomials

$$xy''(x) + (1-x)y'(x) + ny(x) = 0 \quad (15)$$

which has unique solutions which are known as Laguerre polynomials. These polynomials can be generated given the following formula

$$L_n(x) = \frac{e^x}{n!} \left( \frac{d}{dx} \right)^n (x^n e^{-x}) . \quad (16)$$

Where the generating function  $g(x, t)$  is given by [11]

$$g(x, t) = \frac{e^x}{2\pi i} \oint_C \frac{e^{-z}}{z - x - tz} dz = \frac{e^{\frac{-xt}{(1-t)}}}{1-t} = \sum_{n=0}^{\infty} L_n(x) t^n \quad (17)$$

Similarly to the Legendre polynomials and spherical harmonic functions, the Laguerre polynomials also form a complete set of orthogonal basis functions.

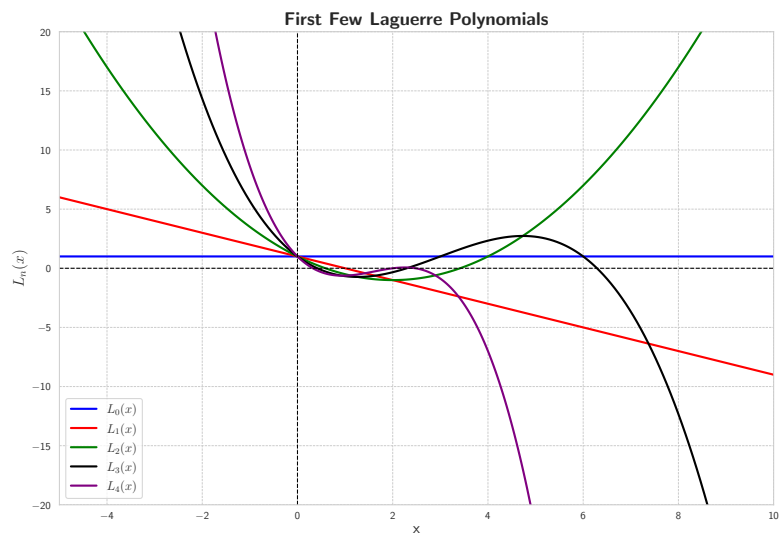


Fig. C.4.1: Graph of the first few Laguerre polynomials

Laguerre polynomials

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$$L_0(x) = 1$$

$$L_1(x) = -x + 1$$

$$L_2(x) = \frac{x^2 - 4x + 2}{2!}$$

$$L_3(x) = \frac{x^3 + 9x^2 - 18x + 6}{3!}$$

$$L_4(x) = \frac{x^4 - 16x^3 + 72x^2 - 96x + 24}{4!}$$


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$$\int_0^\infty L_n(x) L_m(x) e^{-x} dx = \delta_{mn} \quad (18)$$

The Laguerre polynomials are used to describe the radial part of the solution to hydrogenic wavefunctions, as discussed in Sec. 2.4.2.

## C.5 Spherical Harmonics

Spherical harmonics appear most commonly when solving Laplace's equations in spherical coordinates. It is composed of the Legendre polynomials with an additional phase about the azimuthal angle  $\phi$  [27]. Laplace's equation is

$$\nabla^2 f(r, \theta, \phi) = 0 \quad (19)$$

The solution to this equation is separable, so the angular part of the solution can be written as a product of two functions

$$\Theta(\theta)\Phi(\phi) = P_l^m(\cos(\theta))e^{im\phi} . \quad (20)$$

The product of these two angular functions is called the spherical harmonic function, it is denoted by

$$Y_l^m(\theta, \phi) = P_l^m(\cos(\theta))e^{im\phi} . \quad (21)$$

Where  $P_m^l(\cos \theta)$  is the associated Legendre polynomial, which is related to the standard Legendre polynomial by

$$P_l^m(x) = (-1)^m (1-x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} (P_l(x)) \quad (22)$$

The spherical harmonic functions for a complete set of orthogonal basis functions

$$\int_0^{2\pi} \int_0^\pi Y_l^m(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) d\theta d\phi = \delta_{ll'} \delta_{mm'} \quad (23)$$

Spherical harmonic functions

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$Y_0^0(\theta, \phi) = \sqrt{\frac{1}{4\pi}}$		
$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$	$Y_1^{\pm 1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$	
$Y_2^0(\theta, \phi) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$	$Y_2^{\pm 1}(\theta, \phi) = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi}$	$Y_2^{\pm 2}(\theta, \phi) = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi}$

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Fig. C.5.1: Table of the first few spherical harmonic functions

The spherical harmonic functions play a key role in the solution to the angular part of the hydrogenic wavefunctions in the derivation of the quadratic Zeeman effect and the relativistic magnetic dipole moment operator.

## C.6 Confluent Hypergeometric Function

The confluent hypergeometric function is a special form of the standard hypergeometric function. The confluent hypergeometric functions are produced from the solution to the differential equation

$$xy'' + (c - x)y' - ay = 0 \quad (24)$$

where there are two possible solutions

$$y_1(x) = 1 + \frac{a}{c} \frac{x}{1!} + \frac{a(a+1)}{c(c+1)} \frac{x^2}{2!} + \cdots \equiv M(a, c; x) \quad (25)$$

$$y_2(x) = x^{1-c} M(a - c + 1, 2 - c; x) . \quad (26)$$

The function  $M(a, c; x)$  is called the confluent hypergeometric function [27]. It can also be described by the following integral

$$M(a, c; x) = \frac{\Gamma(c)}{\Gamma(a)\Gamma(c-a)} \int_0^1 e^{tx} t^{a-1} (1-t)^{c-a-1} dt, \quad (27)$$

which converges so long that  $c > a > 0$ . The confluent hypergeometric function is a more generalized version of many of the special functions discussed in this chapter, and depending on the choice of  $a$  and  $c$ , are capable of producing the other special functions. For example, the Laguerre polynomials can be expressed in terms of the confluent hypergeometric function as

$$M(a, b; x) = \frac{\Gamma(1-a)\Gamma(b)}{\Gamma(b-a)} L_a^{b-1}(x) . \quad (28)$$

$L_a^{b-1}(x)$  is known as the associated Laguerre polynomial, and is related to the standard Laguerre polynomial discussed in Sec. C.4 by

$$L_n^k(x) = (-1)^k \frac{d^k}{dx^k} L_{n+k}(x) . \quad (29)$$

In the relation given in equation (28),  $k = b - 1$ , and  $n = a$ . The confluent hypergeometric function is used to represent the radial solutions to the hydrogenic wavefunctions discussed in sections 3.4 and 3.5.1.



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## APPENDIX D

### *Methods of solving for higher-order perturbations programmatically*

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This section serves as a reference to the codes implemented to solve higher order perturbations for the quadratic Zeeman effect and the relativistic magnetic dipole moment operator. The codes can be found on the authors GitHub page at [epetrimoulx/Higher-Order-Zeeman-Effect](https://github.com/epetrimoulx/Higher-Order-Zeeman-Effect). The code is designed such that the order of the perturbation being considered is decided by the user. The first and second order perturbation equations look like

$$(H^0 - E^0) |\psi^1\rangle = (V - E^1) |\psi^0\rangle \quad (1)$$

$$(H^0 - E^0) |\psi^2\rangle = V|\psi^1\rangle + E^1|\psi^1\rangle + E^2|\psi^0\rangle \quad (2)$$

The second order perturbation equation is dependant on the answer for  $|\psi^{(1)}\rangle$  from the first order perturbation equation. However, if the second order solution is expressed in terms of the first order solution

$$(H^0 - E^0) |\psi^2\rangle = (V - E^1) (H^0 - E^0)^{-1} E^{(1)} |\psi^{(0)}\rangle + E^2 |\psi^0\rangle . \quad (3)$$

This can be treated as just solving the first order equation again but with a modified

inhomogeneous term on the RHS of the equation.

$$(H^0 - E^0) |\psi^n\rangle = F(V, \psi^{n-1}) + E^n |\psi^0\rangle . \quad (4)$$

This “folding” of the perturbation equation at higher order onto itself using the previous solutions from the lower order equations allows for the iterative calculation of higher order perturbations. The main issue with this strategy is that the equations become too long for any human to do by hand, but computationally, this can be calculated to  $n^{\text{th}}$  order easily so long that the user carefully accounts for higher order contributing states such as the  $d$ -states which arise in second order perturbations of  $r^2$ .

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- [2] Codata value: electron mass.
- [3] Codata value: elementary charge.
- [4] Codata value: fine-structure constant.
- [5] Codata value: reduced planck constant.
- [6] Codata value: speed of light in vacuum.
- [7] Codata value: vacuum electric permittivity.
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# VITA AUCTORIS

NAME: Evan Petrimoulx

Windsor Ontario,  
Canada:

2003:

Highschool Diploma:

University of Windsor, Undergraduate Honours  
Physics, Windsor, Ontario, 2025