Investigation of the Higher Order Zeeman Effect

By

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A Thesis
Submitted to the Faculty of Graduate Studies
through the Department of Physics
in Partial Fulfillment of the Requirements for
the Degree of Bachelors of Science (With Thesis)
at the University of Windsor

Windsor, Ontario, Canada

2025

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I would like to dedicate this thesis to . . .

AKNOWLEDGEMENTS

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CHAPTER 2

Theoretical Methods

2.1 Overview

This chapter will provide an overview of all theoretical methods used throughout this dissertation. It will provide 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 will be presented here, but the more specific calculations related to solving for the Zeeman effect will be presented in the relevant chapter below.

The chapter will begin by first discussing atomic units in Sec. 2.2, then move on and introduce the Schrödinger equation for the one-electron problem as well as its solution for hydrogenic wavefunctions in Sec. 2.3. Next, Perturbation Theory will be introduced in Sec. 2.5, and describe how it can be used to approximate the new eigenvalues and eigenstates of the Zeeman-perturbed Hamiltonian. Sec. 2.4 will discuss various integration techniques that will be 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 will conclude with the discussion of the Dalgarno Interchange Theorem and

how it can serve 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*" [20]. 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;

$$\hbar = m_e = e = 4\pi\epsilon_0 = 1 \ . \tag{1}$$

Scaling these units out of the problem greatly simplifies the calculation. Once a result is found, one can multiply the unscaled units back into the answer to retrieve 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 can also benefit numerical work that is done computationally. Machine error is an unavoidable reality of programmed

Symbol	Name	Value in S.I	Value in a.u.
$\hbar$	Reduced Planck's constant	$1.054\ 571\ 817... \times 10^{-34}$ J s	1
m_e	Electron mass	$9.109\ 383\ 713\ 9(28) \times 10^{-31}$ kg	1
e	Electron charge	$1.602\ 176\ 634 \times 10^{-19}$ C	1
ϵ_0	Electric permittivity	$8.854\ 187\ 818\ 8(14) \times 10^{-12}$ F/m	$\frac{1}{4\pi}$
c	Speed of light	$299\ 792\ 458$ m/s	$137.035\ 999\ 177(21)$
α	Fine structure constant	$7.297\ 352\ 564\ 3(11) \times 10^{-3}$	$7.297\ 352\ 564\ 3(11) \times 10^{-3}$

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

solutions and working in units which avoids extreme values both large and small can help mitigate the uncertainty present in high precision calculations. This thesis will utilize 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].

$$B_{\text{a.u.}} = \frac{\hbar}{ea_0^2} \ . \tag{2}$$

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 [19]

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

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 can be retrieved by simply multipling 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].

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

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, α. 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 [24]. 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 [21]. It is defined as the following dimensionless quantity

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = 7.2973525643(11) \times 10^{-3} \tag{5}$$

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

$$\alpha = \frac{1}{c} \ . \tag{6}$$

The fine structure constant is often used as an essential expansion parameter, treating relativistic effects as a perturbation in α.[1] 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 will discuss all equations and quantities in atomic units unless further specified otherwise.

---

[1]More on this will be discussed in Sec. 3.6.3

2.3   One-electron Schrödinger equation

Discovered by Schrödinger in 1926, the Schrödinger equation is a non-relativistic solution to any quantum-mechanical system [23]. Consider the two-body problem with a nucleus and a single orbiting electron[2]. The electron interacts with the nucleus via the Coulomb interaction described by the following potential

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

(7)

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

$$H = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0\vec{r}} \, .$$

(8)

All observable quantities correspond to hermitian operators that act on the wavefunction ψ. The wavefunction ψ is described as 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 following eigenvalue problem

$$\hat{H}|\psi\rangle = E_n|\psi\rangle$$

(9)

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

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

(10)

---

[2]It is assumed here that the nucleus is a point particle with infinite mass.

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

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

For a two body atomic system the solutions for each can be written in terms of Laguerre polynomials and Spherical Harmonics. The radial equation has the following solutions [8]

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

Where Z is the nuclear charge atomic number, l is the angular momentum quantum number, n is the principle quantum number, and $L_{n-l-1}^{(2l+1)}(2Zr/n)$ is the generalized Laguerre polynomial (which is defined in Appendix D.3). Additionally, the spherical harmonics can be written as

$$Y_l^m(\theta,\phi) = (-1)^m\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi} \tag{13}$$

Where l is the angular momentum quantum number, m is the magnetic quantum number, and $P_l^m(\cos\theta)$ is the associated Legendre polynomial (which will be discussed further in Appendix D.4). A key feature of the spherical harmonics which will be 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 independant parts plays a crucial role in simplifying the task at hand and will be exploited when evaluating integrals involving these wavefunctions in Chapter 3.

2.4 Integration Techniques

In this section of the dissertation, standard approach to solving the integrals pertaining to the various matrix elements required throughout will be discussed. A matrix element is an operator - usually a perturbed Hamiltonian, that is used to approximate the behaviour of quantum systems under small disturbances. Calculating thier expectation values 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 can be split into two steps which can be calculated independantly.

$$\langle \psi^n | V | \psi^m \rangle = \int_0^\infty r^2 \, \psi^n(r) V_r \psi^m(r) \, dr \int_\Omega \sin\theta \, \psi^n(\theta, \phi) V_\Omega \psi^m(\theta, \phi) \, d\Omega \qquad (14)$$

Where Ω represents the solid angles for θ and ϕ. The total problem can then be solved with the simple combination of calculated integrals.

$$\langle \psi^n | V | \psi^m \rangle = I_{\text{radial}} \cdot I_{\text{angular}} \qquad (15)$$

The section serves as a general introduction to the process of calculating matrix elements, but Sec. 2.4.1 and Sec. 2.4.2 will 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 as follows

$$I_{\text{angular}} = \int_{\Omega} \sin\theta \; \psi^n(\theta, \phi) V_{\Omega} \psi^m(\theta, \phi) \; d\Omega \tag{16}$$

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

$$\int_0^{\pi} \int_0^{2\pi} Y_l^m(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) \; d\theta d\phi = \delta_{ll'}\delta_{mm'} \; . \tag{17}$$

For all angular integrals where the spherical harmonics contain different angular momentum or magnetic quantum numbers, the result will be zero. If given a scenario where three angular momenta are coupled together (i.e, there are three spherical harmonic functions to integrate), the Wigner 3j symbols can be used to couple the angular momenta in replacement of the integral. The Wigner 3j symbols are defined as [?]

$$\int_0^\pi \int_0^{2\pi} \sin\theta \, d\theta d\phi \, Y_{l_1}^{m_1}(\theta,\phi) Y_{l_2}^{m_2}(\theta,\phi) Y_{l_3}^{m_3}(\theta,\phi) = \tag{18}$$

$$\sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

Where the set of 6 parameters inside the brackets at the end of the expression is called a 3j Symbol, which has the following definiton [15]:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} (2j_2+1)^{\frac{1}{2}} \langle j_1, m_1, j_2, m_2 | j_1, j_2, j_3-m_3 \rangle \tag{19}$$

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 [15]

$$\langle j_1, m_1, j_2, m_2 | j_1, j_2, j, m \rangle = \delta(m_1+m_2+m) \times \tag{20}$$

$$\sqrt{\frac{(2j+1)(j_1+j_2-j)!(j_1-j_2+j)!(-j_1+j_2+j)!}{(j_1+j_2+j+1)!}} \times$$

$$\sqrt{(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!} \times$$

$$\sum_z \frac{(-1)^z}{z!(j_1+j_2-j-z)!(j_1-m_1-z)!(j_2+m_2-z)!(j-j_2+m_1+z)!(j-j_1-m_2+z)!}$$

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 can be written by substituting linear combinations of spherical harmonics for the angular parts of the integral. The $3-j$ symbols can be applied to such a system allowing us to avoid the integral and replace it with the closed form solution in equations (19) and (20).

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 $R_{nl}(r)$, stated in equation (12). The perturbed wavefunctions will thus also resemble a similar form since they serve as small corrections to the original solution[3]. 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[4]

$$I_{\text{radial}} = \int_0^\infty r^j e^{-\alpha r} \tag{21}$$

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[5], $\Gamma(z)$. The Gamma function integral has the following solution

$$\int_0^\infty r^j e^{-\alpha r} = \frac{\Gamma(j+1)}{\alpha^{j+1}} \tag{22}$$

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

$$\int_0^\infty r^j e^{-\alpha r} = \frac{j!}{\alpha^{j+1}} \ . \tag{23}$$

---

[3]See Sec. 2.5 for more details.

[4]This is shown explicitly in Sec. D.3.

[5]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. D.2.

Fitting the integrals to the Gamma function not only makes the task of computing 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 [22]. While these methods are powerful, they do have significant drawbacks compared to the derived analytical solutions due to error propagation and machine-precision.

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[6].

2.5   Perturbation Theory

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

perturbed Hamiltonian can be written as a sum of two terms;

$$\hat{H} = H^0 + \lambda H' . \tag{24}$$

Where H^0 is the standard Hamiltonian and H' is the perturbation. λ is a small weighting coefficient which keeps the perturbation small. expanding the wavefunction and the energy of the system as a power series in λ gives [19]

---

[6]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.

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \ldots \tag{25}$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots \ . \tag{26}$$

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 λ) but still contributes a small amount. The first order perturbation equation can be described as the following;

$$\left(H^0 - E^0\right)|\psi^1\rangle = \left(V - E^1\right)|\psi^0\rangle \ . \tag{27}$$

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

$$\langle\psi^0|H^0 - E^0|\psi^1\rangle = \langle\psi^0|V|\psi^0\rangle - E^1\langle\psi^0|\psi^0\rangle \ . \tag{28}$$

Which by orthogonality, makes the first term 0, and the last term 1. This is because of the normalization condition for the fully perturbed wavefunction. The normalization condition states that for each order of the perturbation

$$\langle\psi^n|\psi^n\rangle = 1 \ . \tag{29}$$

But since $|\psi^0\rangle$ is already normalized, the first order correction must then also satisfy

$$\langle\psi^0|\psi^1\rangle = 0 \ . \tag{30}$$

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

$$E^1 = \langle \psi^0 | V | \psi^0 \rangle . \tag{31}$$

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.

$$E^n = \langle \psi_{n-1} | V | \psi_0 \rangle . \tag{32}$$

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 inhomogenous terms, meaning separation of variables cannot be used. To solve this, one can assume that the higher order wavefunction is of the form of a power series, and use the method of Frobenius to check if a solution of this form exists. This will be discussed further 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

$$\left(H^0 - E^0 \right) | \psi^2 \rangle = \left(V - E^1 \right) | \psi^1 \rangle + E^2 | \psi^0 \rangle . \tag{33}$$

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 computationlaly will be discussed in Sec. A.

2.6 Recursion relations

When solving the perturbation equation, you end up with an inhomogeneous second order partial differential equation. To solve for the radial piece of the corrected wavefunction, one must 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 [25]:

$$\frac{d^2u}{dx^2} + \frac{d^2u}{dy^2} + k^2u = 0 \ . \tag{34}$$

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 solution exists. The method of solving these recurrence relations is what will be highlighted in the section below.

A recurrence relation is an equation where the nth 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 [17].

$$F_n = F_{n-1} + F_{n-2} \ . \tag{35}$$

But these equations can only be solved if there is a base case. A base case is the condition that somewhere, the sequence stops, or is no longer defined by its previous term. A good example of this is the factorial function. The nth factorial number is determined by

$$n! = n(n-1)! \tag{36}$$

Where 0! is not dependant on $-1!$, but is equivalent to 1. The recurrence relation

stops here. If the recurrence relation did not have a base case, 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 recurrence relation has a similar but less common form, where the $n-1^{\text{th}}$ term depends on the nth term. In this case, the recurrence can still be solved, but you must show that the base case lies somewhere above the current index of your recurrence, or you need to show that the sequence terminates. This means that after a certain point, you can prove that the series is equal to zero for every future term. This is best shown by the following recurrence relation

$$\sum_{j=0}^{\infty} \left[Z(j-1)a_{j-1} - \frac{j(j+1)}{2}a_j \right] r^{j-2} = - \left(\frac{1}{r} + Z \right) . \tag{37}$$

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

$$
\begin{aligned}
j &= 0 & -Za_{-1} &= 0 & (38)\\
j &= 1 & a_1 &= -1 \\
j &= 2 & Za_1 - 3a_2 &= -Z \\
& & -Z + 3a_2 &= -Z \\
& & a_2 &= 0 \\
j &= 3 & 2Za_2 + 6a_3 &= 0 \\
& & a_3 &= 0 \\
&\;\vdots & \vdots &
\end{aligned}
$$

$$\tag{39}$$

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 base case 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 setup for solving 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 required. 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 follows:

$$\left(H^0 - E^0\right)\psi^1 + V\psi^0 = E^1\psi^0 \tag{40}$$

$$\left(H^0 - E^0\right)\varphi^1 + W\psi^0 = F^1\psi^0 \ . \tag{41}$$

Multiplying equation (40) by φ^1 and equation (41) by ψ^1 and then subtracting (40) from (41) gives

$$\langle\psi^0|V|\psi^1\rangle - \langle\psi^0|W|\varphi^1\rangle = 0 \ . \tag{42}$$

Therefore

$$\langle\psi^0|V|\psi_1\rangle = \langle\psi^0|W|\varphi^1\rangle \ . \tag{43}$$

So given any two perturbations, the respective perturbation equations can be solved to retrieve φ^1 and ψ^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 magnetic dipole operator and the relativistic correction have been calculated, the Dalgarno Interchange theorem can be used to verify that the calculations were successful.

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 $\frac{1}{r}$ (The nuclear charge perturbation), and for the cubic Zeeman effect, the r^2 matrix element for relativistic 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.

CHAPTER 3

The Higher Order Zeeman Effect

3.1 Overview

Now that the proper theory has been introduced, we now move to the main section of
the thesis. Here the Zeeman Effect will be introduced, and the motivation and direct
applications will be discussed. Then, the higher order Zeeman Effect will be analyzed.
The main focus of this chapter is to show the effect of the quadratic Zeeman Effect,
and show how using the magnetic dipole operator in conjunction with the relativistic
corrections to $^3\text{He}^+$ can yield a cubic Zeeman Effect. The effects of both the quadratic
and cubic corrections will be discussed in great detail, and the impact of the effect
on high precision measurements will be displayed for various magnetic field strengths.

Sec. 3.2 will start with the history of the Zeeman effect, its origins and discovery.
Afterwards the motivation for the project in Sec. 3.3 will be discussed. Here, some
current experiments in the field such as the $g - 2$ experiment being conducted at the
Max Planck Institute by Klaus Blaum's research group as well as the applications to
high-precision magnetometry will be highlighted. Some additional applications in the
field of atomic physics such as . . . will be introduced as well. In Sec. 3.4, the ordi-
nary Zeeman effect will be discussed, introducing its theory and application to atomic
systems such as $^3\text{He}^+$. After introducing the ordinary Zeeman effect the quadratic
Zeeman effect will be introduced, where it will be derived using the canonical mo-
mentum and a description of its impact on an atom subjected to a magnetic field will
be given. Moving towards higher order systems, the cubic Zeeman effect of this thesis

will be introduced. Starting with the effects that contribute to the cubic Zeeman effect such as the magnetic dipole operator in Sec. 3.6.2 and relativistic corrections to the ^{3}He$^+$ ion in Sec. 3.6.3, these effects will be combined to yield a B^3 contribution to the energy splitting within the presence of an external magnetic field. Afterwards, Sec. 3.7 will discuss the results of the calculation and its applications.

3.2 History

3.3 Motivation

3.3.1 The $g - 2$ experiment

3.3.2 High-precision magnetometry

3.3.3 Connection to Atomic Physics

3.4 The Zeeman effect in Hydrogen

3.5 The Zeeman effect in Helium-3

3.6 The higher-order Zeeman effect

3.6.1 The quadratic Zeeman effect

The non-relativistic Hamiltonian for an n electron system in atomic units can be expressed as follows

$$\hat{H} = \sum_{i=1}^{n} \frac{\left(\vec{p}_i - e\vec{A}_i\right)^2}{2m} + V \tag{1}$$

using the cannonical momentum instead of the classical momentum is essential to account for electromagnetic interactions. The vector potential $\vec{A}$ can be described in

terms of the magnetic field

$$\vec{A} = \frac{B}{2}\left(y\hat{x} - x\hat{y}\right) \tag{2}$$

which when expanded gives us the operator corresponding to the quadratic Zeeman effect

$$\hat{H}_Z^{(2)} = \frac{B^2 e^2}{8m} \sum_{i=1}^{n} (x_i^2 + y_i^2) \tag{3}$$

This operator can be expressed in spherical coordinates, written in terms of Legendre Polynomials

$$\hat{H}_Z^{(2)} = \frac{B^2 e^2}{12m} \sum_{i=1}^{n} r_i^2 \left(P_0(\cos\theta) - P_2(\cos\theta)\right) \tag{4}$$

^{3}He$^+$ is a system which contains only one electron, so we can drop the summation which accounts for all electrons to get our final quadratic Zeeman operator

$$\hat{H}_Z^{(2)}(^3\text{He}^+) = \frac{B^2 e^2}{12m} r^2 \left(P_0(\cos\theta) - P_2(\cos\theta)\right) \tag{5}$$

3.6.2   The magnetic dipole moment operator

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

$$Q_{M1} = \mu_B \left(1 - \frac{2p^2}{3m^2c^2} + \frac{Ze^2}{3mc^2 r}\right) \vec{\sigma} \cdot \vec{B} \tag{6}$$

Where μ_B is the Bohr magneton

$$\mu_B = \frac{e\hbar}{2mc} \tag{7}$$

The second term in the brackets of the magnetic dipole moment operator 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 ^3He, the ordinary Zeeman effect will not contribute.

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

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

$$C_{\text{rel}}^{(2)} = \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} \frac{\langle \psi_0 | H_Z^{(2)} | \psi_n \rangle \langle \psi_n | Q_{M1} | \psi_0 \rangle}{E_0 - E_n} \tag{8}$$

3.7 Results

CHAPTER 4

Conclusion and Future Work

4.1   Overview

4.2   Consolidation of Results

4.3   Synthesis of Conclusions

4.4   Future Work

4.5   Theoretical and Practical Impact

APPENDIX A

Methods of solving for higher-order perturbations programmatically

APPENDIX B

Derivation of the Hydrogen Atom

APPENDIX C

Derivation of the Recursion Relations

APPENDIX D

Special Functions

D.1   Overview

D.2   Gamma Function

D.3   Laguerre Polynomials

D.4   Legendre Polynomials

D.5   Spherical Harmonics

REFERENCES

[1] Codata value: atomic unit of magnetic flux density.

[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.

[8] *Springer Handbook of Atomic, Molecular, and Optical Physics*. Springer Handbooks. Springer New York, New York, NY, 2006.

[9] DP Aguillard, T Albahri, D Allspach, A Anisenkov, K Badgley, S Baeßler, I Bailey, L Bailey, VA Baranov, E Barlas-Yucel, et al. Measurement of the positive muon anomalous magnetic moment to 0.20 ppm. *Physical review letters*, 131(16):161802, 2023.

[10] John M. Anthony and Kunnat J. Sebastian. Relativistic corrections to the zeeman effect in hydrogenlike atoms and positronium. *Physical Review A*, 49(1):192–206, Jan 1994.

[11] G. W. F. Drake. New variational techniques for the $1snd$ states of helium. *Physical Review Letters*, 59(14):1549–1552, Oct 1987.

[12] G. W. F. Drake and A. J. Makowski. High-precision eigenvalues for the $1s2p\,^1p$ and ^3p states of helium. *Journal of the Optical Society of America B*, 5(10):2207, Oct 1988.

[13] G. W. F. Drake and Zong-Chao Yan. Energies and relativistic corrections for the rydberg states of helium: Variational results and asymptotic analysis. *Physical Review A*, 46(5):2378–2409, Sep 1992.

[14] G.W.F. Drake. High precision variational calculations for the $1s21s$ state of h- and the $1s21s$, $1s2s\ 1s$ and $1s2s\ 3s$ states of helium. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 31(1):7–13, 1988.

[15] A. R. Edmonds. *Angular Momentum in Quantum Mechanics*. Investigations in Physics. Princeton University Press, Princeton, NJ, 2016.

[16] Midhat Farooq, Timothy Chupp, Joe Grange, Alec Tewsley-Booth, David Flay, David Kawall, Natasha Sachdeva, and Peter Winter. Absolute magnetometry with he-3. *Physical Review Letters*, 124(22), Jun 2020.

[17] L. Fibonacci. *Liber Abaci*. 1202.

[18] Daniele Fontanari and Dmitriĭ A Sadovskiĭ. Perturbations of the hydrogen atom by inhomogeneous static electric and magnetic fields. *Journal of Physics A: Mathematical and Theoretical*, 48(9):095203, Feb 2015.

[19] David J. Griffiths. *Introduction to Quantum Mechanics*. Cambridge University Press, Cambridge, 3rd ed edition, 2018.

[20] D. R. Hartree. The wave mechanics of an atom with a non-coulomb central field. part i. theory and methods. *Mathematical Proceedings of the Cambridge Philosophical Society*, 24(1):89–110, January 1928.

[21] A. A. Michelson and E. W. Morley. On the relative motion of the earth and the luminiferous ether. *American Journal of Science*, s3-34(203):333–345, November 1887.

[22] W.H. Press. *Numerical recipes: the art of scientific computing.* Cambridge University Press, Cambridge, UK; New York, 3rd ed edition, 2007.

[23] E. Schrödinger. An undulatory theory of the mechanics of atoms and molecules. *Physical Review*, 28(6):1049–1070, December 1926.

[24] A. Sommerfeld. Zur quantentheorie der spektrallinien. *Annalen der Physik*, 356(17):1–94, January 1916.

[25] H. Weber. Ueber die integration der partiellen differentialgleichung:. *Mathematische Annalen*, 1:1–36, 1869.

[26] Qixue Wu and G. W. F. Drake. Precision Hyperfine Structure of $2;\hat{3}$P State of $\hat{3}$He with External Magnetic. 38:R1.060, June 2007.

[27] Zong-Chao Yan and G. W. F. Drake. High-precision calculations of the zeeman effect in the 2^3p_j, 2^1p_1, 2^3s_1, and 3^3p_j states of helium. *Phys. Rev. A*, 50:R1980–R1983, Sep 1994.

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