



# **UNIVERSITY OF NAIROBI**

## **INVESTIGATION ON RADIATIVE CORRECTIONS RELATED TO THE FINE STRUCTURE AND HYPERFINE STRUCTURE**

By

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## DECLARATION AND CERTIFICATION

This research project is my own work and has never been submitted for examination in any other University or Research Institution for work leading to award of a degree

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## Abstract

Radiative corrections related to the fine structure, Lamb shift and hyperfine structure of atomic energy levels are studied. Since the perturbation Hamiltonian is very small compared to zero order Hamiltonian first order perturbation is used theory to find the respective corrections. The expressions obtained for the fine structure of hydrogen atom using the relativistic approach coincides with those obtained using the Dirac equation and the fine structure correction is proportional to  $\alpha^2 E_n^o$ , which is a small fraction of the Bohr energy. The Lamb shift correction is proportional to  $\alpha^3 E_n^o$ . While the hyperfine structure correction is proportional to  $10^{-3} \alpha^2 E_n^o$ . The implications of fine structure and hyperfine structure are seen as an outcome of very small corrections. Coincidence of this result with spectroscopic measurements will be a welcome confirmation.

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## **Dedication**

I dedicate my dissertation work to my family and many friends. A special feeling of gratitude to my grandmother Ebisiba Nyakerario whose words of encouragement ring in my ears. My sister Ruth has been with me in prayer and is very special.

I dedicate this work and give special thanks to my best friends Japheth Marine, Elizabeth Moiruri and Mark Context for being there for me throughout the entire master's program. Both of you have been my greatest companions. May God bless you all.

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## List of symbols

A	Magnetic potential
a	acceleration
B	Magnetic flux density
c	speed of light
$E_n^0$	Bohr energy
e	elementary charge
F	the total atomic angular momentum quantum number
H	Hamiltonian
h	Planck's constant
$\hbar$	reduced Planck's constant
j	total electron angular momentum quantum number
l	electron orbital angular momentum quantum number
n	principal quantum number
Z	atomic number
s	electron spin quantum number
I	nuclear spin quantum number
$\mu_s$	electron spin magnetic moment
$\mu_I$	nuclear spin magnetic moment
$\mu_B$	Bohr magneton
$\mu_N$	nuclear magneton
$a_0$	the radius of the first Bohr orbit
$e^-e^+$	electron positron pair
$E_n^0$	Bohr energy



# CHAPTER ONE: INTRODUCTION

## 1.1 Background to the study

The understanding of the atomic structure has been a concern to chemists and physicists especially in the twentieth century when the existence of atoms became universally accepted [Jones and Childers, 1999]. Earlier, Dalton (1800s) had introduced the idea that elements are made of small particles called atoms. Ever since, researchers have been in the quest to understand the full nature of the atom.

J.J. Thomson gave the first atomic model which he conceptualized to be a sphere of size  $10^{-10}$  m and of positively charged matter in which electrons were embedded. This model failed to explain optical spectra of hydrogen and other compounds [Chand, 2003]. Rutherford's scattering experiment of alpha particles by thin metal foils led to our present concept of the nuclear atom [Jones and Childers, 1999]. He proposed that all the positive charge of the atom was concentrated in a tiny nucleus at its center surrounded by a cloud of electrons [Halliday et al., 2002]. The Rutherford model failed to explain the stability of an atom in spite of the revolving electrons around the nucleus. Niels Bohr (1913) gave an explanation of the atomic spectral lines which, apparently, whose wavelength was explained by an equation suggested by Rydberg in which the reciprocal wavelength of a spectral line is given as the difference between two terms [Chand, 2013]. He formulated his model based on the Rutherford model of a central nucleus.

Bohr considered electron as revolving round the nucleus in stationary circular orbits for which the angular momentum of the electron is an integral multiple of  $\hbar$ . He also postulated that an atom radiates energy only when an electron jumps from a stationary orbit of higher energy to one of lower energy. The model failed to explain the fine structure of spectral lines, intensities of spectral lines and violated the uncertainty principle by the treating the electron as a miniature planet with definite radius and momentum. Sommerfeld (1916) refined the theory to consider elliptical orbits thus permitting an explanation of the fine structure of spectral lines [Semat, 1962]. With this refinement, the theory could only predict the correct spectra for hydrogen atom or hydrogen-like atoms. It fails to explain or predict the energy levels and spectra of many-electron atoms, in part, because it does not include the repulsive interaction between electrons and the spin-orbit interaction. Even the simplest many-electron atom, that is, neutral helium

atom, with 2 electrons has energy levels at values different from those predicted by the Bohr Theory. It also can't predict transition probabilities. For a given element, not all spectral lines possess the same intensity; a correct theory could enable calculation of the relative strength of lines [Brensdén and Joachain, 2003]

The Schrödinger theory (1926) successfully eliminates these fundamental problems. It extends to the de Broglie matter waves by providing a formal method of treating the dynamics of physical particles in terms of associated waves [Peebles, 2003]. It relies in interpretation of the wave function in terms of associated probabilities. The Schrödinger equation does not include electron spin. The spin appears only in relativistic treatments. The Dirac theory, which does take spin into consideration, predicts the fine structure of energy levels.

The Stern-Gerlach experiment (1942) showed [Chand, 2001] that the angular momentum is quantized, and in particular, that the intrinsic angular momentum of the electron (spin) was quantized. Orbiting electrons produce a magnetic moment independent of the intrinsic magnetic moment of the electron; the system may be regarded as two bar magnets having different orientations.

The spin of the electron was postulated for the first time by two Dutch graduate students Uhlenbeck and Goudsmit in 1924, with an associated magnetic moment,  $\mu_s$ , and enabled physicists to explain the fine structure of energy levels and spectral lines as well the anomalous Zeeman Effect [Chand, 2003].

The fine structure of energy levels and associated spectral lines can be viewed as coming from differences in energy of an electron's spin magnetic moment  $\mu_s$  in the magnetic field produced by the nucleus in the electron's rest reference frame. The dependence of the mass of the electron on its velocity leads to energy corrections (relativistic corrections) of the same order of magnitude as those due to spin - orbit interaction and also contribute to the observed fine structure of energy levels and associated spectral lines.

In 1938, deviations for H $\alpha$  fine structure observed by Houston and Williams Pasternak suggested that these results could be interpreted in terms of  $2S_{1/2}$  being higher by a wave number  $0.03\text{cm}^{-1}$  relative to  $2P_{1/2}$ . The discrepancies were first attributed to impurities of the source. Lamb and Retherford [Phys. Rev. 72, 241 (1947)], stimulated the development of Quantum

Electrodynamics (QED) based on the quantization of the electromagnetic field. The quantization involves assimilating the electromagnetic field to a set of simple quantum harmonic oscillators. The interaction of the zero point energy of the quantized field causes it to execute rapid oscillations [Burkhardt and Levental, 2006]. In his Nobel Prize acceptance speech, Bethe said "It is very important that this problem should receive further experimental and theoretical attention. When an accuracy of comparison of 0.1 Mc/sec has been reached, it will mean that the energy separations of the 2S and 2P states of hydrogen agree with theory to a precision of few parts in  $10^9$  of their binding energy or that the exponent in Coulomb law of force is two with comparable accuracy"[Bjorken and Drel, 1976].

The spin idea of the electron was also extended to the nucleus. The original indication that nuclei have spin is from atomic spectroscopy. Many lines in atomic spectra when examined with spectroscopes of very high resolution are found to consist of several lines very close together. Such lines are said to exhibit hyperfine structure.

The hyperfine structure of energy levels results from the interaction between the magnetic moment,  $\mu_I$  of the nucleus with the magnetic field produced by the electrons at the location of the nucleus. The electron magnetic field consists of two parts; one is the field produced by the spin magnetic moment and the other is the magnetic field produced by the orbital motion of the electron's charge. For non spherically symmetric nuclei, with nuclear spin  $I \geq 1$ , the interaction between electric quadrupole of the nucleus and the gradient of the electric field produced by the electrons at the location of the nucleus also contribute to the observed hyperfine structure splitting. The expectation value of the hyperfine Hamiltonian in the various atomic (and nuclear spin) states yield the hyperfine energy shifts [Ghoshal, 2006]. For spherically symmetric  $s$  states the expectation value comes from the Fermi contact term. For  $l \neq 0$ , the hyperfine energy comes entirely from the second term because the wave functions for  $l \neq 0$  vanish at the origin [Cohen-Tannoudjiet *al.*, 1977].

In this research project, we first briefly review the problem of the hydrogen atom or hydrogen-like atoms without spin, focusing on the gross energy levels, that is, Bohr's energies or Coulomb's energies. Secondly, we examine the hydrogen fine structure, which contains three first – order relativistic corrections, the relativistic correction to the kinetic electronic energy, the spin-orbit coupling and the so-called Darwin term. Thirdly, we briefly discuss the theory of

Lamb shift which enable to lift the  $j$  degeneracy inherent to the fine structure. Finally we explore the quantum theory of the hyperfine structure of the hydrogen atom, which results from the interaction between proton magnetic dipole moment and the magnetic field generated by the electron at the location of the proton.

## 1.2 Problem Statement

The understanding of the atomic structure has been a concern to chemists and physicists especially in the twentieth century when the existence of atoms became universally accepted [Jones and Childers, 1999]. In this project the focus is on the radiative corrections related to the fine structure and hyperfine structure of spectral lines of the hydrogen atom or hydrogen-like ions. For many reasons, it is important to understand the basic level – structure of the hydrogen atom or hydrogen-like atoms [Moore, 2009]. Since hydrogen is the simplest atom, not only the quantum study of the hydrogen atom or hydrogen-like ions is more or less complete but also the results obtained from the study of these systems can serve as a basis to tackle the quantum theory of many electron – atoms. Early atomic physics was focused on measuring and explaining the various atomic spectra [Moore, 2009].

The use of the Schrodinger equation without spin was a first key step in understanding and explaining atomic spectra. The considerable accuracy of spectroscopic experiments made it possible to observe effects which cannot be explained just by the gross energy levels or Bohr's energy levels [Haken and Wolf, 2005]. The theory has been improved by considering the interactions between internally generated fields with the electronic and nuclear spins. Effects involving the relativistic correction to the kinetic energy of the electron due to the increase in mass with the electron's velocity, the spin-orbit coupling and the so-called Darwin term determine the fine structure of the hydrogen atom [Burkhardt and Leventhal, 2006]. Effects related to the interaction of the nuclear multipole moments with internally generated field are termed the hyperfine structure. Observing these line splitting and shifts requires the ability to measure atomic spectral lines with spectroscopes of high resolving power. Thus, as the resolution is increased, first the fine structure will be observed, and then at a higher resolution one would finally resolve the hyperfine structure [Moore, 2009].

## **1.3 Objectives of the study**

### **1.3.1 Main objective**

The aim of the study is to investigate the effect of radiative corrections related to the fine and hyperfine structure splitting of atomic energy levels.

### **1.3.2. Specific objectives**

The specific objectives are:

- i) To evaluate relativistic corrections to the fine structure coupling constant.
- ii) To explore the use of Feynman diagram technique on the Lamb shift
- iii) To determine the effect of electron-proton magnetic moments interaction on atomic energy levels.

## **1.4 Justification and significance of the study**

The main concern for scientists is to understand the atomic structure. With improving spectroscopic techniques which have made it possible to observe effects which go beyond Bohr's predictions, theoretical approach has equally improved with the inclusion of the spin of the electron and that of the nucleus. This has provided a reliable explanation for the observed complex atomic spectra. In view of these observations, calculations have been done to a minimum order. Consequently, effects of higher order calculations have not been accounted for. Therefore, this study aims at shedding additional light on the theory of fine structure, lamb shift and hyperfine structure and the associated radiative effects with a conviction that we can contribute to a better understanding of atomic spectra.

The theory has been done for the hydrogen atom and hydrogen-like atoms. Being the simplest atom, the hydrogen problem can be solved completely not only without considering the spin of the electron, but also for the fine structure which involves relativistic corrections and the hyperfine structure resulting from the interaction of the nuclear multipole moments with internally generated fields.

It is anticipated that the results obtained from hydrogen atom can be used to study more complex atoms quantum mechanically. A deep understanding of the quantum theory of the hydrogen atom can form a basis to explain these spectral lines. The results can also be generalized to alkali since their optical properties are governed by the behavior of a single valence electron. Singly-ionized group two elements are also hydrogen-like and can be described by the same quantum theory. In addition, measurements of the spectral lines of hydrogen atom can act as a source of astronomical data in stellar spectroscopy.

## CHAPTER TWO: LITERATURE REVIEW

### 2.1 Introduction

This section reviews relevant studies on the fine structure, the lamb shift and the hyperfine structure of spectral lines by different researchers. The section is therefore intended to capture some major results pertaining to atomic spectra. In particular, the understanding of the atomic structure has been a concern to chemists and physicists especially in the twentieth century when the existence of atoms become universally accepted [Jones and Childers, 1999].

The nuclear model of the atom, as we know it presently, that is, the positive charge of the atom is concentrated in a tiny nucleus at its center surrounded by a cloud of electrons, was proposed by Rutherford and his co-workers in 1911 as an explanation to their scattering experiment of alpha particles by thin metal foils [Halliday *et al.*, 2002]. This put an end to the Thomson's model which assumed that the positive charge of the atom was spread out through the entire volume of the atom [Chand, 2003].

The energy levels of the hydrogen atom or hydrogen-like atoms, were derived for the first time by Bohr using his semi-classical approach (Bohr's postulates) [Haken and Wolf, 2005] and thirteen years later, they were confirmed by solving the Schrodinger equation. This achievement enabled scientists to explain the atomic spectral lines of hydrogen atom and other elements including many-electron atoms. The formulation of quantum theory managed to overcome some of the challenges faced by the Bohr's theory by predicting the energy levels and spectra of many-electron atoms and to calculate the intensity of spectral lines.

### 2.2. Fine structure of spectral lines

Many lines in atomic spectra when examined with spectroscopes of high resolution are found to consist of several lines very close together. Bohr's energy terms of one – electron atoms (with exceptions of the s states) are split into two sub-states [Haken and Wolf, 2005]. Such lines are said to exhibit fine structure. In 1921, Stern and Gerlach performed a deflection experiment of atomic beams of silver in inhomogeneous magnetic fields and came up with the conclusions of

space quantization for the intrinsic magnetic moments and the existence of two unique orientations of the atomic magnetic moments relative to the direction of the magnetic field [Jones and Childers, 1999].

Electron spin was introduced by Uhlenbeck and Goudsmit in 1925 to explain the fine structure of spectral lines and the anomalous Zeeman Effect [Subrahmanyam and BrijLal, 1984]. The discovery of the electron spin and the associated magnetic moment when introduced in the Schrodinger equation, as a correction term together with the relativistic correction in the electron kinetic energy, give an explanation of the fine structure of spectral lines [Barchewitz, 1997; Burkhardt and Leventhal, 2006].

The fine structure Hamiltonian can be separated into three corrective terms: the kinetic energy term ( $H_{kin}$ ), the spin-orbit interaction term ( $H_{so}$ ), and the Darwinian term ( $H_{Darwin}$ ). The atomic Hamiltonian including fine structure corrections is given by [Wikipedia, 2015]:

$$H = H_0 + H_{kin} + H_{so} + H_{Darwin} \quad (2.1)$$

The fine structure can be described completely using the Dirac equation. Equation (2.1) can be seen as a non-relativistic approximation of the Dirac equation [Burkhardt and Leventhal, 2006].

The scale of the fine structure splitting relative to the gross structure splitting is of the order of  $(Z\alpha)^2$ , where  $Z$  is the atomic number and  $\alpha = (e^2/\hbar c)$  is the fine structure constant, which has an approximate value of  $(\frac{1}{137})$ . Therefore, the fine structure splitting is a small effect, but it can be observed with the aid of spectroscopes of high resolution [Chandra, 2010]. The expression of the energy levels for one-electron atoms taking into account the above fine structure corrections have been derived by many authors among them; [ Barchewitz, 1997; Burkhardt and Leventhal, 2006; Bransden and Joachain, 2002] to obtain the following result:

$$E_{n,j} = -|E_n| \left[ 1 + \left( Z^2 \frac{\alpha^2}{n} \right) \left( \frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \right] \quad (2.2)$$

Where  $E_n$  is the Bohr energy,  $n$  the principal quantum number and  $j$  is the total angular momentum quantum number.



## 2.3 The Lamb shift

According to Equation (2. 2) states with the same  $n$  and  $j$  quantum numbers but different orbital quantum numbers ought to be degenerate. Therefore, fine structure terms with the same value of  $j$  (assuming  $n$  fixed) will be at the same level even if they have different values of  $l$ . In the years 1947 – 1952, Lamb and Retherford in their experiment showed that even the Dirac theory did not accurately describe the hydrogen atom [Hakin and Wolf, 2005]. In their findings, they showed that the  $2S_{1/2}$  and  $2P_{1/2}$  states of the hydrogen atom were not degenerate, but that the  $s$ -state had slightly higher energy than that of the  $p$  state [Davydov, 1962 ]. This is due to the fact that the ground state of the electromagnetic field is not zero, but the field undergoes “vacuum fluctuations” which interact with the electron [Bethe, 1947].

There is a self interaction of the electron by exchange of a photon as sketched in the Feynman diagram (fig.2). This "smears out" the electron position over a range of distance about the nucleus. There is a slight weakening of the force on the electron when it is very close to the nucleus, causing the  $2s$  electron (which has penetration all the way to the nucleus) to be slightly higher in energy than the  $2p_{1/2}$  electron. Simply stated, random electric fields push the electron and thereby they move it slightly further away from the proton than it would otherwise be.

For the hydrogen atom, with one electron, there is no shielding from inner electrons when in the  $2s$  or  $2p$  excited states. In the absence of this effect, the  $2s$  and  $2p$  would have identical energies since there is no shielding by the presence of other electrons. The "self-interaction" of the electron when near the proton causes the effective "smearing" of the electron charge so that its attraction to the proton is slightly weakened than it otherwise would have been. This means it has encountered an interaction which makes it slightly less tightly bound than a  $2p$  electron, hence higher in energy. The lamb shift is a very small effect; a small change of energy levels than they should. It is the energy of interaction between hydrogen and empty space. It is easily observed in the excited states of the hydrogen atom. [Bjorken and Drel, 1964].

## 2.4 Hyperfine structure of energy levels

The atomic nucleus influences the electronic spectra. The three most influences of the nucleus on electronic spectra , aside from the effect of the Coulomb field of the nuclear charge ( $+Ze$ ), are

the isotopic effect, the differing volumes of isotopic nuclei and most importantly, the interaction of the nuclear multipole moments with internally generated fields [Hakin and Wolf, 2005]. If the different physical properties of the nucleus are considered in the Schrodinger equation as correction terms, energy shifts smaller than those due to fine structure are obtained. This effect is called hyperfine structure [Peebles, 2003]. The optical hyperfine structure was already observed in 1881 by Albert Abraham Michelson [Wikipedia, 2015]. The presence of spins and magnetic moments of the atomic nuclei was first postulated by Wolfgang Pauli in 1924 and this enabled him to explain spectroscopic observations in terms of quantum mechanics [Hakin and Wolf, 2005]. In the year 1935, H. Schuler and Theodor Schmidt further proposed the existence of a nuclear electric quadrupole moments to explain the anomalies in the hyperfine structure [Wikipedia, 2015]. In this study, only the atomic hyperfine structure is considered.

Hyperfine structure occurs due to the energy of interaction between the nuclear magnetic dipole moment with the magnetic field generated by the electrons at the site of the nucleus, and the energy of interaction between the nuclear electric quadrupole moment with the electric field gradient produced by atomic electrons [Brandsen and Joachain, 2002; Chandra, 2010].

For spherically symmetric nuclei, the electric quadrupole moment is equal to zero, and therefore, only the magnetic hyperfine Hamiltonian is significant [Cohen – Tannoudjiet *al.*, 1977].

For non spherically symmetric nuclei, with nuclear spin  $I \geq 1$ , the interaction between the electric quadrupole of the nucleus and the gradient of the electric field produced by the electrons at the site of the nucleus also contribute to the observed hyperfine structure splitting [Hakin and Wolf, 2005]. However, the contribution of the electric hyperfine structure is much smaller than that of the magnetic HFS [Chandra, 2010]

Two approaches have been used in order to compute the magnetic hyperfine Hamiltonian, which include the electromagnetic approach [Wikipedia, 2015], and the quantum approach [Cohen – Tannoudjiet *al.*, 1977]. In the electromagnetic approach, the magnetic field produced, at the location of the nucleus, by the orbital motion of the electron is calculated using the Biot & Savart law [Wikipedia, 2015]. The magnetic field generated at the site of the nucleus by the electron spin magnetic moment is calculated using the classical formula of electromagnetism [Jackson, 1999]:

$$B_s(r) = \frac{1}{r^5} (3\mu_s \cdot r)r - \left(\frac{\mu_s}{r^3}\right) + \frac{8\pi}{3}\mu_s\delta(r) \quad (2.3)$$

Using the electromagnetic analogy, the Magnetic hyperfine Hamiltonian is given by:

$$\mathbf{H}_{\text{hf}} = -\boldsymbol{\mu}_s \cdot \mathbf{B}_{\text{tot}} \quad (2.4)$$

Where  $\mathbf{B}_{\text{tot}} = \mathbf{B}_l + \mathbf{B}_s$ , with  $\mathbf{B}_l$  and  $\mathbf{B}_s$  the magnetic field produced by the orbital angular momentum and the electron spin magnetic moment, respectively. For a many–electron atom, the expression of  $\mathbf{B}_{\text{tot}}$  is written in terms of the total angular momentum and the spin angular momentum, by summing over all the electrons and using an ad hoc projection operator [Wikipedia, 2015].

The determination of the magnetic hyperfine Hamiltonian using a quantum approach is based on the Schrodinger equation for the electron in the presence of the electromagnetic field produced by the nuclear spin magnetic moment. Many authors, among them Cohen – Tannoudjiet *al.* (1977) and Hetch, (2000) have shown that

$$\mathbf{H}_{\text{HF}} = 2\mu_B \left[ \frac{L}{r^3} - \frac{S}{r^3} + \frac{3r(S \cdot r)}{r^5} + \frac{8\pi}{3} S\delta(r) \right] \cdot g_I \mu_N I \quad (2.5)$$

Where the first term of  $\mathbf{H}_{\text{HF}}$  represents the interaction of the nuclear magnetic dipole moment  $\mu_I$  with the magnetic field created at the nucleus by the rotation of the electronic charge. The second and third terms represent the dipole-dipole interaction between the electronic and nuclear magnetic moment at a distance. The last term known as “the Fermi contact term” arises from the singularity at  $r = 0$  of the magnetic field produced by the electron at location of the nucleus. This term describes the interaction of the magnetic moment of the electron spin with the magnetic field inside the nucleus. The delta function expresses the fact that this contact term exists only when the wave functions of the electron and proton overlap, that is, for an s – orbital ( $l=0$ ) for which  $\Psi_{n00}(0)$  is different from zero.

The expectation values of the hyperfine structure Hamiltonian in the various atomic (and nuclear spin) states yield the hyperfine energy shifts [Jackson, 1967].

For spherically symmetric s–states, the expectation value comes from the Fermi contact term. In this case, the energy difference between the triplet and singlet states of the 1s state of atomic hydrogen is the source of the famous 21 cm line used in astrophysics [Peebles, 2003].

In an atom with nuclear spin  $I = 1$ , the nucleus can have an electric quadrupole moment which adds a contribution to the Coulomb's potential energy. In addition to the magnetic hyperfine Hamiltonian, there is an electric quadrupole term which contributes to the hyperfine structure splitting of energy levels. Since an electrical interaction does not directly affect the electron spin, the quadrupole term only modifies the orbital variables of the electron [Peebles, 2003]. If  $I > 1$ , other nuclear electric and magnetic multipole moments can exist, increasing in number as  $I$  increases, leading to the complexity of the hyperfine Hamiltonian [Cohen – Tannoudjiet *al.*, 1977]. However, for the great majority of cases, one can limit the hyperfine Hamiltonian to magnetic dipole and electric quadrupole terms, the other terms making extremely small contributions to the hyperfine structure splitting of spectral lines.

Some authors have also used the vector model to illustrate hyperfine structure splitting. In this model, there is coupling between the nuclear angular momentum,  $\mathbf{I}$ , and the electron's total angular momentum,  $\mathbf{J}$ , giving the total angular momentum of the atom,  $\mathbf{F}$  as

$$\mathbf{F} = \mathbf{I} + \mathbf{J} \quad (2.6)$$

and for one-electron atom,  $J = j$ . For an atom having two or more valence electrons, then  $J$  is obtained either through the LS coupling or the jj coupling.

The interaction energy between  $\mathbf{I}$  and  $\mathbf{J}$ , (hyperfine-structure energy), is given by

$$E_{nf} = \beta' \langle \mathbf{I} \cdot \mathbf{J} \rangle \quad (2.7)$$

where  $\beta'$  is the measure of the strength of coupling between  $\mathbf{I}$  and  $\mathbf{J}$ . using the rule of addition of angular momenta the hyperfine quantum number  $F$  can take the values ranging from  $|J - I|$  to  $J + I$  in steps of unity. Thus, each fine structure energy splits into  $(2I + 1)$  levels when  $J > I$  or into  $(2J + 1)$  when  $J < I$ .

## CHAPTER THREE: THEORETICAL BACKGROUND

### 3.1 BOHR'S ENERGY

In 1911, Rutherford and his co-workers studied the scattering of alpha particles by thin metal foils and concluded that all the positive charge of the atom was concentrated in a tiny nucleus at the center surrounded by a cloud of electrons [Halliday *et al.*, 2002]. They came up with the planetary model of the atom. Electrons were considered to be orbiting a static nucleus. However, this model meant the atom had a very short lifetime. According to classical electromagnetic theory, an accelerating charged particle should emit electromagnetic radiation (Jackson, 2001). Electrons being charged and moving in circular paths (accelerating) should spiral into the nucleus in  $10^{-8}$  seconds as predicted by  $(R = \frac{2}{3} \frac{e^2 a^2}{c^3})$  [Jackson, 2002]. Bohr amended the view of planetary motion of electrons to bring the model in line with the regular patterns (spectral series) of light emitted by real Hydrogen atoms. By limiting the orbiting electrons to a series of circular orbits having discrete radii, Bohr could explain for the series of discrete wavelengths in the emission and absorption spectrum of hydrogen. In this model, light is radiated from hydrogen atoms only when an electron made a transition from an outer orbit to one closer to the nucleus. The energy lost by the electron in the abrupt transition is precisely the same as the energy of the quantum of emitted light.

The structure of the atom will be well understood by studying the radiation emitted and absorbed by the atoms of a given element. Atomic spectroscopy of an element is the study of the radiation emitted and absorbed by the element. Analyzing light from the element in gas vapor using a spectroscope, it is found to consist of a series of very sharp lines of definite wavelength characteristic of the element emitting the radiation. In spite of their complex spectra, many of the spectral lines of each element were found to be related in a simple manner expressed by a simple equation suggested by Rydberg [Jones and Childers, 1999]. Balmer had earlier on obtained a simple relationship among the wave numbers in the visible light region of the hydrogen spectrum:

$$\frac{1}{\lambda} = \bar{\nu} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad (n = 3, 4, 5 \dots) \quad (3.1)$$

where  $\lambda$  is the wavelength,  $\nu$  the wave number of the spectral line,  $R_H$  is the Rydberg constant for hydrogen and  $n$  is an integer greater than 2-the principal quantum number. Substituting for  $n$  in equation (3.1) the successive values 3, 4, 5... we obtain the wave numbers of the lines in the Balmer series.

Bohr was the first to obtain a qualitative correct derivation of the Balmer's empirical formula for an atomic model, in his theory of the hydrogen atom. He adopted Rutherford's nuclear model of the atom; the hydrogen atom should consist a singly charged positive nucleus and an electron outside the nucleus, since the atomic number is equal to unity.

Assuming that the Coulomb's law and Newton's second law of motion were applicable in the atomic domain, the path of the electron around the nucleus should be a conic section [Semat, 2006]. A first approximation is to assume that this conic section is circle of radius  $r$  with nucleus fixed at the center of the circle. From coulomb's law, the force of attraction between the nucleus and the electron is

$$F = -\frac{Ze^2}{r^2} \quad (3.2)$$

Where  $Ze$  is the charge on the nucleus and  $e$  is the electronic charge. From Newton's second law of motion, we have:

$$F = ma = -\frac{mv^2}{r} \quad (3.3)$$

where  $m$  is the mass of the electron,  $a$  is its centripetal acceleration, and  $v$  is its velocity. The minus sign indicates that the acceleration is directed towards the center. Using equations (3.2) and (3.3) we get

$$\frac{ze^2}{r^2} = \frac{mv^2}{r} \quad (3.4)$$

Using Bohr's quantization of the orbital angular momentum:

$$mv_n r_n = \frac{nh}{2\pi} \quad (3.5)$$

From equation (3.4) and (3.5), the expression for the total energy is obtained as

$$E_n = -\frac{Z^2 m_e e^4}{2n^2 \hbar^2} = -\frac{13.6Z^2}{n^2} \text{ (eV)}. \quad (3.6)$$

By solving the Schrodinger equation for Hydrogen atom and hydrogen-like atoms in spherical coordinates, one can confirm the Bohr's energies in equation 3.6 [Chan, 2001]. The separation between the Bohr's energy levels is in the order of a few electron-volts and can be measured using ultra-violet and visible spectroscopy.

## 3.2 The Fine structure

When a spectral line of hydrogen spectrum is observed using a high resolution spectroscope, it is found to be a closely-spaced doublet [Akhezer, 1965]. This phenomenon is known as fine structure splitting of spectral lines. It is attributed to the relativistic correction to the kinetic energy of the electron, to the spin-orbit correction and the so-called Darwin term [Burkhardt and Leventhal, 2006].

### 3.2.1 The relativistic correction

The relativistic correction is related to the variation of mass of the electron with its velocity. Starting with the relativistic expression for the energy of a classical particle of rest mass  $m_e$  and momentum  $\mathbf{p}$

$$E = c\sqrt{\mathbf{p}^2 + m_e^2 c^2} \quad (3.6)$$

Performing a Taylor series expansion of E in powers of  $|p|/m_e$ ,

$$E^2 = m_e^2 c^4 \left(1 + \frac{p^2 c^2}{m_e^2 c^4}\right) \quad (3.7)$$

$$E(p) = \pm m_e c^2 \left(1 + \frac{p^2}{m_e^2 c^2}\right)^{1/2} \quad (3.8)$$

or

$$E(p) = m_e c^2 (1 + X)^{1/2}, \quad (3.8a)$$

where 
$$X = \frac{p^2}{m_e^2 c^2}.$$

Equation (3.7) can be expanded using Taylor series expansion

$$f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \dots + a_n x^n \quad (3.8b)$$

and performing an expansion about  $p = 0$ . In particular, when  $p = 0$ , equation 3.8b gives

$$f(0) \equiv E(0) = a_0$$

From Equation (3.7) if  $p = 0$ ,  $E(0) = m_0 c^2$ . This implies  $a_0 = m_e c^2$ .

To find the coefficients  $a_1, a_2, \dots, a_n$ , we take the derivatives of  $E(p)$  with respect to  $p$  and expand around  $p = 0$ :

$$E(p) = m_e c^2 \left(1 + \frac{p^2}{m_e^2 c^2}\right)^{1/2}$$

$$E'(p) = \frac{1}{2} m_e c^2 \left(1 + \frac{p^2}{m_e^2 c^2}\right)^{-1/2} \cdot \frac{2p}{m_e^2 c^2}$$

$$E'(0) = 0 \Rightarrow a_1 = 0$$

$$E''(p) = \frac{1}{m_e} \left(1 + \frac{p^2}{m_e^2 c^2}\right)^{-1/2} + \frac{p}{m_e} \cdot \left(-\frac{1}{2}\right) \left(1 + \frac{p^2}{m_e^2 c^2}\right)^{-3/2} \cdot \left(\frac{2p}{m_e^2 c^2}\right) \quad (3.9)$$

$$E''(p) = \frac{1}{m_e} \Rightarrow 2a_2 = \frac{1}{m_e}$$

We write:



$$E = m_e c^2 + \frac{\mathbf{p}^2}{2m_e} - \frac{\mathbf{p}^4}{8m_e^3 c^2} + \dots \quad (3.10)$$

In addition to the rest mass energy (first term), and the non-relativistic kinetic energy (second term), we find the term  $-\frac{\mathbf{p}^4}{8m_e^3 c^2}$ , which represents the first-order correction to the Hamiltonian.

The relativistic correction to the energy is the expectation value of this term:

$$E_{rel}^{(1)} = -\frac{1}{8m_e^3 c^2} \langle \hat{\mathbf{p}}^4 \rangle \quad (3.11)$$

The Hamiltonian of relativistic correction,  $\hat{H}_{rel}$ , contains only  $\hat{\mathbf{p}}^4 = \hat{p}^2 \hat{p}^2$ , and  $\hat{p}^2$  appears in the unperturbed Hamiltonian so that

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{r} \quad (3.12)$$

Since  $\hat{p}^2$  is present in  $\hat{H}_{rel}$ , then  $\hat{H}_{rel}$  is diagonal in the  $\langle nlm \rangle$  basis set and the first-order correction to the energy is given by [Burkhardt and Leventhal, 2006]:

$$E_{rel}^{(1)} = -\frac{1}{8m_e^3 c^2} \langle nlm | \hat{p}^2 \hat{p}^2 | nlm \rangle \quad (3.13)$$

From Equation (3.13), we have

$$\hat{p}^2 = 2m_e \left( \hat{H}_0 + \frac{e^2}{r} \right) \quad (3.13a)$$

so that

$$\begin{aligned} E_{rel}^{(1)} &= -\frac{1}{8m_e^3 c^2} \langle nlm | \left( \hat{H}_0 + \frac{e^2}{r} \right)^2 | nlm \rangle \\ &= -\frac{1}{2m_e c^2} \left[ \left( E_n^{(0)} \right)^2 + 2E_n^{(0)} (e^2) \left\langle \frac{1}{r} \right\rangle_{nl} + (e^2)^2 \left\langle \frac{1}{r^2} \right\rangle_{nl} \right] \end{aligned} \quad (3.14)$$

where  $E_n^{(0)}$  is the Bohr energy.

With the following expectation values (Barchewitz, 1997):

$$\left\langle \frac{1}{r} \right\rangle_{nl} = \frac{1}{a_0 n^2} \quad (3.15a)$$

and

$$\langle \frac{1}{r^2} \rangle_{nl} = \frac{1}{a_0^2} \cdot \frac{2Z}{n^3(l+1/2)} \quad (3.15b)$$

where  $a_0 = \frac{\hbar^2}{m_e e^2}$  is Bohr radius for the first orbit,  $n$  is the principal quantum number and  $l$  is the orbital angular momentum quantum number.

These expectations values may be expressed in terms of  $E_n^{(0)}$  giving,

$$\langle \frac{1}{r} \rangle_{nlm} = 2 \left( \frac{1}{e^2} \right) E_n^{(0)} \quad (3.16)$$

and

$$\langle \frac{1}{r^2} \rangle_{nlm} = \frac{4n}{(l+1/2)} \left( \frac{1}{e^2} \right)^2 (E_n^{(0)})^2 \quad (3.17)$$

Notice that the first expectation value, multiplied by  $-(e^2)$ , is the average value of the potential energy.

Using equations (3.16) and (3.17) in equation (3.13), we then have

$$E_{rel}^{(1)} = - \frac{(E_n^{(0)})^2}{2m_e c^2} \left[ -3 + \frac{4n}{(l+1/2)} \right] \quad (3.18)$$

We can express the relativistic energy in terms of the fine structure constant,  $\alpha = (e^2/\hbar c)$ . From equation (3.11), the zero order energy can be expressed in terms of  $\alpha$  by  $E_n^{(0)} = -\left(\frac{1}{2}\right) m_e c^2 \alpha^2 / n^2$ , giving, after substitution and rearrangements:

$$E_{rel}^{(1)} = \left[ -\frac{3}{4} + \frac{n}{(l+1/2)} \right] \frac{Z^2 \alpha^2}{n^2} E_n^{(0)} \quad (3.19)$$

From equation (3.19), we can see that  $|E_{rel}^{(1)} / E_n^{(0)}|$  is of the order of  $\alpha^2$ , which is approximately  $10^{-5}$ .

### 3.1.2 Spin-orbit correction

The spin-orbit correction is associated with the interaction between the spin of the electron with its orbital motion. A non-relativistic particle moving in an electric field  $\mathbf{E}$  with velocity  $\mathbf{v}$  experiences an effective magnetic field according to magnetic field theory. The electric field which is due to the charge of the nucleus is

$$\mathbf{E} = \frac{er}{r^3} \quad (3.20)$$

and the magnetic field  $\mathbf{B}$  is

$$\vec{B} = -\frac{\vec{V} \times \vec{E}}{c^2} \quad (3.21)$$

In the electron reference frame, the proton seems to be rotating about it and since its speed is high, it can be considered to be a steady current loop generating a magnetic field  $\mathbf{B}$  such that

$$\mathbf{B} = \frac{Ze_0}{m_e c r^3} \mathbf{I} \hat{z} \quad (3.22)$$

We can then put an additional correction term to the Hamiltonian of a Hydrogen atom of the form

$$\begin{aligned} H_{s.o} &= -\boldsymbol{\mu}_s \cdot \mathbf{B} \\ &= -\frac{Ze^2}{m_e c^2 r^3} \mathbf{V} \times \mathbf{r} \cdot \mathbf{S} \\ &= \frac{Ze^2}{m_e^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S} \end{aligned} \quad (3.23)$$

where  $\mathbf{L} = \mathbf{r} \times m_e \mathbf{v}$

Introducing the Thomas precession term, which is a purely relativistic correction term, we have:

$$H_{s.o} = \boldsymbol{\mu}_s \cdot \mathbf{B} = \frac{Ze^2}{2m_e^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S} \quad (3.24)$$

Equation (3.23) gives the spin-orbit correction/interaction Hamiltonian, for the hydrogen atom or hydrogen-like ion. Using  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , where  $\mathbf{J}$  is the total angular momentum, we have:

$$\mathbf{L} \cdot \mathbf{S} = 1/2 (J^2 - L^2 - S^2)$$

$H_{s,o}$  commutes with both  $L^2$  and  $S^2$  but not with  $S_z$  and  $L_z$ . This means that the simultaneous Eigen states of the unperturbed and perturbing Hamiltonian are the same as the simultaneous Eigen states of  $L^2$ ,  $S^2$  and  $J^2$ . We then have

$$L^2 \varphi_{l,s,j,m_j} = l(l+1) \hbar^2 \varphi_{l,s,j,m_j} \quad (3.25a)$$

$$S^2 \varphi_{l,s,j,m_j} = s(s+1) \hbar^2 \varphi_{l,s,j,m_j} \quad (3.25b)$$

$$J^2 \varphi_{l,s,j,m_j} = j(j+1) \hbar^2 \varphi_{l,s,j,m_j} \quad (3.25c)$$

$$L \varphi_{l,s,j,m_j} = m \hbar \varphi_{l,s,j,m_j} \quad (3.25d)$$

and

$$\begin{aligned} \Delta E &= \left\langle l, \frac{1}{2}, j, m_j \left| \hat{H} \right| l, \frac{1}{2}, j, m_j \right\rangle \\ &= \frac{e^2 \hbar^2}{4m_e^2 c^2} \left\langle l, \frac{1}{2}, j, m_j \left| \frac{J^2 - L^2 - S^2}{r^3} \right| l, \frac{1}{2}, j, m_j \right\rangle \\ &= \frac{e^2 \hbar^2}{4m_e^2 c^2} \left[ j(j+1) - l(l+1) - \frac{3}{4} \right] \left\langle \frac{1}{r^3} \right\rangle \\ &= \frac{e^2 \hbar^2}{4m_e^2 c^2 a_0^3 n^3} \left[ \frac{\{j(j+1) - l(l+1) - \frac{3}{4}\}}{l(l+\frac{1}{2})(l+1)} \right] \end{aligned} \quad (3.26)$$

where  $n$  is the principal quantum number and

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{Z^2}{a_0^3 n^3 l(l+1)(l+1/2)}$$

(Bransden and Joachain, 2003). In addition,

$$\Delta E = E_n \frac{Z^2 \alpha^2}{n^2} \left[ \frac{n\{\frac{3}{4} + l(l+1) - j(j+1)\}}{2l(l+\frac{1}{2})(l+1)} \right] \quad (3.27)$$

where  $\alpha = \frac{e^2}{\hbar c}$  and is the fine structure constant.

The magnitude of the correction is  $\alpha^2$  times the unperturbed hydrogen energy, which is very small since  $\alpha = \frac{1}{137}$ .

### 3.1.3 The Darwin Term

This term does not act on the spin variable. It is diagonal in  $l$ ,  $m_l$  and  $m_s$ . It applies to the case when  $l = 0$ . The energy correction to this term is given by

$$\begin{aligned}
 \Delta E &= \frac{\hbar^2 Z e^2}{2m^2 c^2} \langle \Psi_{n00} | \delta(r) | \Psi_{n00} \rangle \\
 &= \frac{\hbar^2 Z e^2}{2m^2 c^2} |\Psi_{n00}(0)|^2 \\
 &= \frac{1}{2} m c^2 \frac{(Z\alpha)^2}{n^2} \frac{(Z\alpha)^2}{n} \\
 &= -E_n \frac{(Z\alpha)^2}{n}, \quad l = 0
 \end{aligned} \tag{3.28}$$

Since the energy shift due to spin-orbit coupling (including the limit  $l=0$ , which represents the Darwin term) has the same order of magnitude as that due to the relativistic correction, we combine the two corrections to obtain the total energy correction due to the fine structure. Adding together these two corrections and using  $j = l \pm \frac{1}{2}$  for a hydrogen atom the energy shift is given by:

$$\Delta E = E_n \frac{Z^2 \alpha^2}{n^2} \left( \frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \tag{3.29}$$

This is the modification of energy levels of a hydrogen atom or a hydrogen-like atom due to spin-orbit coupling and relativistic correction. The set of values corresponding to different values of  $\Delta E_{nj}$  but the same value of  $E_n$  is called fine structure.  $|\Delta E|$  becomes smaller as  $n$  or  $j$  increases, and larger as  $Z$  increases.

The total width of the fine structure for a given principal quantum number,  $n$  i.e. between levels with  $j = l - \frac{1}{2}$  and  $j = l + \frac{1}{2}$  is equal to

$$D = \Delta E_{nj1} - \Delta E_{nj2} = \frac{R_H \alpha^2 Z^4}{2n^3} \quad (3.30)$$

We can see that the fine structure shift is proportional to  $n^{-3}$ .

### 3.2 Lamb Shift

The lamb shift is an electrodynamic phenomenon that is due to the interaction between matter and empty space. The ‘empty’ space is regarded as an electron-positron vacuum and the electromagnetic vacuum. The electromagnetic vacuum interaction with the electron is strong that it causes the shifting of the  $2S_{1/2}$  and  $2P_{1/2}$  levels. Performing the expansion of the electromagnetic field in Fourier series and considering the zeroth energy, the coordinate displacement of the electron can be written as [Sokolov, *et al.*, 1962]

$$r = -\frac{e}{m_0} \sum_w E(w) \cos wt \quad (3.31)$$

with a variation

$$\overline{(\Delta r)^2} = \frac{2}{\pi} \alpha \left( \frac{\hbar}{m_0 c} \right)^2 \ln \frac{2n^2}{\alpha^2} \quad (3.32)$$

This is Brownian motion of pseudo photons [Beck, 1976]. This means that vacuum waves destroy the point electron making the electron become a geometrical mean between the classical radius and the Compton wavelength:

$$r_{pp} = \sqrt{\alpha} \frac{\hbar}{m_0 c} \quad (3.33)$$

This changes the interaction of the electron with nuclear charge leading to additional interaction energy–level shift. This means that the potential energy of the electron in the nuclear field will have a different form i.e. putting into consideration the Poisson equation, the energy shift is:

$$\Delta E_{pp} = \frac{4}{3} e_0^2 \left( \frac{\hbar}{m_0 c} \right)^2 |\Psi(0)|^2 \ln \frac{2n^2}{\alpha^2} \quad (3.34)$$

The shift is valid only for the s-state ( $l=0$ ) where

$$|\Psi(0)|^2 = \frac{1}{\pi n^3 a_0^3}$$

For  $a_0 = \frac{\hbar^2}{m_0 a_0^3}$ , the first Bohr radius for hydrogen,

$$\Delta E_{pp} = \frac{8}{3\pi} \alpha^3 \frac{R\hbar}{n^3} \ln \frac{2n^2}{\alpha^2} \quad (3.35)$$

Substituting for the values of the 2S-state, we obtain

$$\Delta E_{pp} = 17.8R = 1040\text{MHz}$$

and the experimentally accepted value is as given below:

$$\Delta E_{pp} = 1057.77\text{ MHz}$$

This is a semi-classical approach for electrons interacting with electron-positron vacuum. We now check for the relativistic quantum theory and check how the value obtained therein compares with the experimental one. Essentially, the electrons are scattered by a relatively static nucleus as shown below:

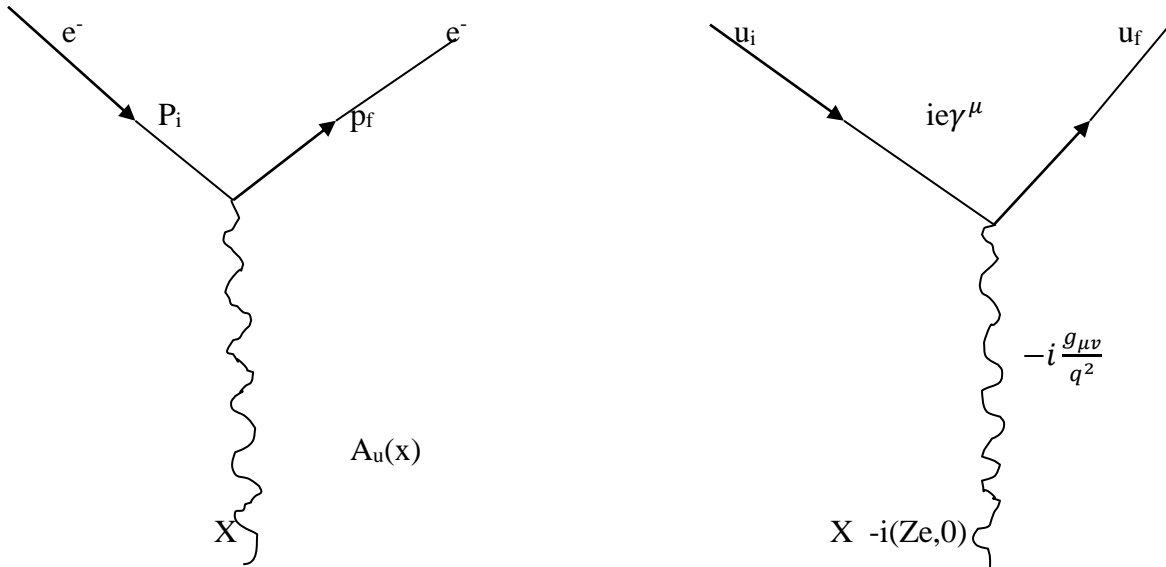


Figure 1. Feynman rules for Rutherford scattering of electrons off a static charge  $Ze$ , for instance a nucleus.

The scattering amplitude for the above processes is defined as

$$T_{fi} = -i \int d^4x J_\mu^{fi}(x) A^\mu(x) \quad (3.36)$$

where  $J_\mu^{fi}(x) = -e\bar{u}_f \gamma_\mu u_i e^{-iq \cdot x}$ ,  $A^\mu(x)$  is a four-vector potential associated with static charge and  $q$  is the change in momentum given as  $q = p_i - p_f$ . Hence, equation 3.36 becomes

$$T_{fi} = ie\bar{u}_f \gamma_\mu u_i A^\mu(q) \quad (3.37)$$

where  $A^\mu(q) = \int d^4x A^\mu(x) e^{-iq \cdot x}$ . For a static charge  $A^\mu(x)$  is time independent, thus we have

$$\begin{aligned} A^\mu(q) &= \int dt e^{-i(E_i - E_f) t} \int d^3x e^{-iq \cdot x} A^\mu(\bar{x}) \\ &= (2\pi) \delta(E_i - E_f) A^\mu(q) \end{aligned} \quad (3.38)$$

Therefore,  $A^\mu(q) = (2\pi) \delta(E_i - E_f) \frac{J^\mu(q)}{|q|^2}$ ,

where we use Maxwell's equations and the time-independence of the potential  $A^\mu(q)$  to arrive at

$$A^\mu(q) = \frac{J^\mu(q)}{|q|^2}$$

and

$$T_{fi} = i(2\pi) \delta(E_i - E_f) e \bar{u}_f \gamma_\mu u_i \frac{1}{|q|^2} J^\mu(\bar{q}) \quad (3.39)$$

The scattering amplitude is thus given by:

$$-iM = ie\bar{u}_f \gamma_\mu u_i \frac{1}{|q|^2} J^\mu(\bar{q})$$

When there is energy conservation, we have:

$$-iM = ie\bar{u}_f \gamma_\mu u_i \left( \frac{-g_{\mu\sigma}}{q^2} \right) (-ij^\sigma(q)) \quad (3.40)$$

$-ij^\sigma$  is associated with the source such that

$$\bar{j}(\bar{x}) = 0 \text{ and } j^o(x) = \rho(\bar{x}) = Ze \delta(\bar{x}) \quad (3.41)$$



This implies that

$$-iM = (ie\bar{u}_f \gamma_\mu u_i) \left( \frac{-i}{|q|^2} \right) (-iZe)$$

and

$$\begin{aligned} q^2 &= (p_i - p_f)^2 = -2K^2 (1 - \cos\theta) \\ &= -16\text{Sin}^2\frac{\theta}{2} \end{aligned} \tag{3.42}$$

where we have used  $K \equiv |p_i| = |p_f|$  and  $M$  is the scattering amplitude whose square gives

$$\frac{d\delta}{d\Omega} \sim |M|^2 \sim \frac{1}{-16\text{Sin}^2\frac{\theta}{2}} \tag{3.42a}$$

In equation (3.42a),  $\theta$  is the scattering angle. The exchange photon fluctuates to an  $e^- e^+$  pair as in figure 2 below

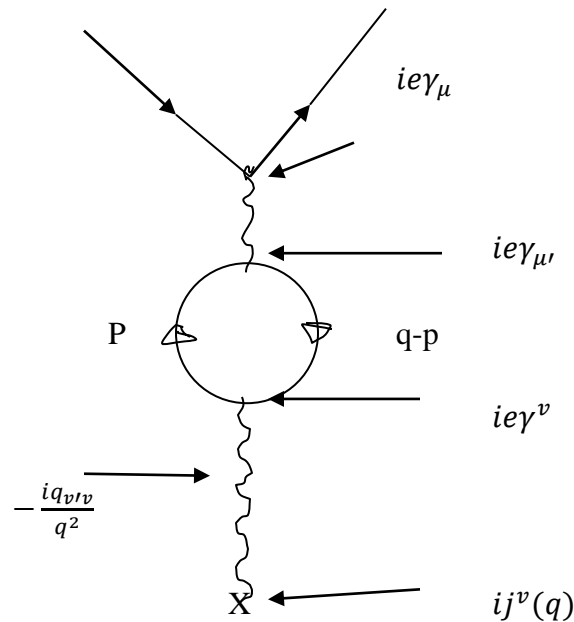


Figure 2. Feynman diagram for Rutherford scattering in which the exchanged photon fluctuates into an  $e^- e^+$  pair.

The exchanged photon spends time as a virtual  $e^-e^+$  pair and this will lead to a modification of coulomb's law which results from the lowest order diagram. Using

$$iM = (ie\bar{u}_f\gamma_0u_i) \left(\frac{-i}{|q|^2}\right) \left(1 - \frac{\alpha}{3\pi} \log\left(\frac{M^2}{m^2}\right) - \frac{\alpha}{15\pi} \frac{q^2}{m^2} + O(e^4)\right) (-iZe) \quad (3.43)$$

which becomes

$$-iM = (ie_R\bar{u}_f\gamma_0u_i) \left(\frac{-i}{|q|^2}\right) \left(1 - \frac{e_R^2}{60\pi^2} \frac{q^2}{M^2}\right) (-iZe_R) \quad (3.44)$$

where  $e_R = e \left(1 - \frac{e^2}{12\pi^2} \log\frac{M^2}{m^2}\right)^2$ . Suppose  $e_R$  is the electric charge, i.e.,

$$\frac{e_R^2}{\hbar c} = \frac{1}{137},$$

then, if there is an infinity associated with  $M_n \rightarrow \infty$ , it will be 'absorbed' by  $e_R$ . Therefore this factor contributes to the invariant amplitude  $M$  becoming finite.

For the scattering amplitude representing the Fourier transform of the potential, the first term in  $(-iM)$  is considered proportional to the potential  $|q|^{-2}$  associated with the coulomb potential. Since

$$V_0(r) = \frac{-Ze_R^2}{(2\pi)^3} \int d^3q e^{-iqr} \frac{1}{|q|^2} = -\frac{Ze^2}{4\pi r}, \quad (3.45)$$

then the second term represents the quantum effect of the virtual  $e^-e^+$  loop in the propagator of the exchanged photon. It contains an extra term  $|q|^2$  in relation to the first. In coordinate space  $|q|^2 \rightarrow \nabla^2$

$$\frac{1}{(2\pi)^3} \int d^3q e^{iqr} = \delta(r) \quad (3.46)$$

The  $\delta(r)$  implies that there is a conservation

From equation 3.44,  $(-iM)$  corresponds to an interaction between the electron and the charge  $Ze_R$  of the form

$$V(r) = - \left(1 - \frac{e_R^2}{60\pi^2 M^2} \nabla^2\right) \frac{Ze^2}{4\pi r}$$

$$= -\frac{Ze^2}{4\pi r} - \frac{e_R^4}{60\pi^2 M^2} \delta(r) \quad (3.47)$$

The extra interaction and its sign is due to the screening by the  $e^-e^+$  pair.

- i) The first term in (3.43) is such that when  $q^2 \rightarrow 0$ , the  $e^-$  probes the static charge  $Ze_R$  from a large distance and interacts via the coulomb interaction
- ii) By definition  $e_R$  is the usual electron charge, the one measured in any long-range electromagnetic interaction.
- iii) When the electron comes closer to the nucleus (i.e.  $-q^2$  increases) it penetrates the cloud of virtual  $e^-e^+$  pairs which surround it. This leads to an increase in the effective interaction. The presence of the loop, thus, leads to an additional attractive force between the electrons and the nucleus.

This effect, represented to the lowest order by the  $\delta(r)$  potential contributes to the energy levels of the hydrogen atom. Treating the second term as a perturbation, a contribution to the lamb shift is obtained thus:

$$\Delta E_{nl} = \frac{e_R^4}{60\pi^2 M^2} |\Psi_{nl}(0)|^2 \delta_{l0} \quad (3.48)$$

where  $\Psi_{nl}$  are hydrogen wave functions.  $\delta_{l0}$  imply that the  $\delta(r)$  potential can only perturb wave functions which are finite at the origin, i.e. those with  $l = 0$ . These can be established experimentally by measuring the lamb shift between  $2S_{1/2}$  and  $2p_{1/2}$ . These levels are degenerate if the loop contributions are not included. The changes depend on their separation.

For instance, the hydrogen atom is bound by the exchange of photons between the electrons and protons. The Coulomb force leads to a separation of a Bohr radius on the average. The electron can deviate from its Bohr orbit due to the fluctuation of the exchange photons into  $e^-e^+$  pairs.

This quantum screening reduces the attraction when the electron is far from the proton and increases the force when it approaches the nucleus. These competing effects don't cancel since the Coulomb force falls with  $r$ . The net force is an additional attraction over and above the coulomb potential  $-\frac{e_R}{r}$  given by the second term in (3.40) as:

$$-iM = (ie_R \bar{u}_f \gamma_0 u_i) \left( \frac{-i}{|q|^2} \right) \left[ 1 - \frac{e_R^2}{60\pi^2} \frac{q^2}{M^2} \right] (-i Ze_R) \quad (3.43)$$

The second term in the square bracket modifies the  $\gamma_\mu$  Lorentz structure of the current. This means that the electron interacts via both its charge  $-e_m$  and its magnetic moment  $-e/2m$ . With

$$-e_R \bar{u}_f \gamma_0 u_i = -\frac{e}{2m} \bar{u}_f [p_f + p_i - i\delta_{\mu\nu} q^\nu]_\mu u_i, \quad (3.49)$$

we can identify the magnetic moment from the interaction energy  $(-\mu \cdot B)$  using the relation

$$\int \left[ -\frac{e}{2m} \bar{\Psi}_f [p_f + p_i - i\delta_{\mu\nu} q^\nu]_\mu \Psi_i \right] A^\mu d^3x = \int \Psi_A^f \left( \frac{e}{2m} \delta \cdot B \right) \Psi_A^i d^3x \quad (3.49a)$$

$\Psi_A$  denotes the upper two large components of  $\Psi$  and, hence,  $\bar{\mu} = -\frac{e}{2m} \bar{\delta}$ .

Since  $\bar{\mu} = -g \frac{e}{2m} \bar{s}$ , then  $S \equiv \frac{1}{2} \delta$  for gyromagnetic ratio  $g = 2$ . This therefore, implies from equation (3.49) that

$$\mu = -\frac{e}{2m} \left( 1 + \frac{\alpha}{2\pi} \right) \delta$$

or

$$g = \left( 1 + \frac{\alpha}{2\pi} \right)$$

The electron, thus, has an anomalous magnetic moment given as [Chand, 2001]

$$\begin{aligned} \frac{g-2}{2} &= \frac{1}{2} \left( \frac{\alpha}{\pi} \right) - 0.32848 \left( \frac{\alpha}{\pi} \right)^2 + (1.49) \left( \frac{\alpha}{4\pi} \right)^3 + \dots \\ &= (116955.4) \times 10^{-19} \end{aligned} \quad (3.50)$$

This compares with the experimental value

$$\frac{g-2}{2} = (1159657.7 \pm 3.5) \times 10^{-19} \quad (3.51)$$

### 3.3 The Hyperfine structure

The interaction between the nuclear magnetic moment and the magnetic field produced by the electrons at the position of the nucleus perturbs the energy levels of an atom [Peebles, 1992]. For nuclei with nuclear spin  $I \geq 1$ , the hyperfine structure splitting involves another term associated with the interaction between the nuclear electric quadrupole and the gradient of the electric field

generated by the electrons at the position of the nucleus [Wikipedia, 2015]. Since the effect is very small compared to the separation between Bohr's energies and fine-structure energies, it is named hyperfine structure. The hyperfine splitting of the ground state level of the hydrogen atom is equivalent to a wavelength of 21.1 cm [Cohen-Tannoudji *et al.*, 1977]. This is the famous line used to derive the most stable atomic clocks, and used in radio astronomy to map out the distribution and motion (through the Doppler Effect) of neutral gas in galaxies, the bulk of the gas being atomic hydrogen.

### 3.3.1 The Magnetic Hyperfine Hamiltonian

The term in the Hamiltonian that represents the interaction between the proton dipole moment and magnetic field produced by the electron at the position of the nucleus is derived from classical electromagnetism.

#### 3.3.1.1 Magnetic field of a magnetic dipole

It is often convenient to consider a loop of wire to be magnetic dipole. In the case of atoms, the current loop is due to the circulation of electrons about the nucleus.

Just as electric behavior of many molecules can be characterized in terms of their electric dipole moment, the magnetic behavior of atoms can be characterized in terms of their magnetic dipole moment [Halliday *et al.*, 2003]. The vector potential produced by a circular loop of radius  $a$  at a distance  $r$  from its center is given by [Lorrain and Corson, 1970; Perez *et al.*, 2002]

$$\vec{A} = \frac{\vec{M} \times \vec{r}}{r^3} \quad (3.52)$$

where  $|\mathbf{M}| = I(\pi a^2)$  is the magnitude of the magnetic dipole. By definition,

$$\mathbf{B} = \nabla \times \mathbf{A}$$

From the theory of vectors, if  $f$  is a scalar function and  $\vec{C}$  is a vector, then

$$\nabla \times (f\vec{C}) = \nabla f \times \vec{C} + f(\nabla \times \vec{C}) \quad (3.53)$$

Taking  $\vec{C} = \mathbf{m} \times \mathbf{r}$  and  $f = \left(\frac{1}{r^3}\right)$ , we then have:

$$\mathbf{B}(\mathbf{r}) = \frac{3(\mathbf{m} \cdot \mathbf{r})\mathbf{r}}{r^5} - \frac{\mathbf{m}}{r^3}$$

If we replace  $m$  by the nuclear magnetic dipole moment ( $\mu_I$ ), we obtain the magnetic field produced by  $\mu_I$  at the position of the nucleus as

$$\mathbf{B}(\mathbf{r}) = \frac{3(\mu_I \cdot \mathbf{r})\mathbf{r}}{r^5} - \frac{\mu_I}{r^3} \quad (3.54)$$

The energy of interaction between the electron magnetic moment ( $\mu_e$ ) in this magnetic field is

$$V = - \boldsymbol{\mu}_e \cdot \mathbf{B} = \left\{ \frac{\mu_e \mu_p}{r^3} - 3 \frac{(\mu_e \cdot \mathbf{r})(\mu_p \cdot \mathbf{r})}{r^5} \right\} \quad (3.55)$$

In Equation (3.55),  $\mu_e$  is the electron magnetic dipole moment and  $\mathbf{r}$  is the separation between the electron and nucleus. Note that the equation is symmetric in the electron and nucleus variables.

We will use the classical equation (3.55) for  $V$  as a guide to writing down the magnetic hyperfine Hamiltonian for a hydrogen atom.

The proton and electron magnetic dipole moments are defined respectively by [Peebles, 1992]

$$\boldsymbol{\mu}_p = (g_p e / 2M_p c) \mathbf{I}, \quad g_p \approx 5.6 \quad (3.56a)$$

$$\boldsymbol{\mu}_e = - (g_e e / 2m_e c) \mathbf{S}, \quad g_e \approx 2 \quad (3.56b)$$

In equation (3.65),  $M_p$  and  $m_e$  are the proton mass and the electron mass, respectively. The magnetic moment of the negatively charged electron is antiparallel to the spin, and the magnetic moment of the positively charged proton is parallel to the spin.

The classical approach above enables one to determine the magnetic hyperfine Hamiltonian for the hydrogen atom (one electron–atom). The results obtained can be extended to any atom.

### 3.3.1.2 Quantum Approach for Determining the magnetic hyperfine Hamiltonian

The magnetic hyperfine Hamiltonian originates from the coupling between the electron and the electromagnetic field created by the nucleus [Cohen-Tannoudjiet *al.*, 1977]. To show this, we let  $\mathbf{A}(\mathbf{r}, t)$  and  $\phi(\mathbf{r}, t)$  be the vector and the scalar potentials associated with the electromagnetic field of the nucleus. Then, for the hydrogen atom in which the sole electron is interacting with the proton through the Coulomb's potential energy and the binding energy of the electron being much smaller than its rest energy, one can predict the properties of the atom from the non-relativistic quantum theory. The fields  $\mathbf{B}$  and  $\mathbf{E}$  are calculated from the known relations of classical electromagnetism (Gauss system)

$$\mathbf{B} = \vec{\nabla} \times \mathbf{A} \quad (3.57a)$$

$$\mathbf{E} = \vec{\nabla} \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \quad (3.57b)$$

The quantum Hamiltonian for an electron in an electromagnetic field with vector and scalar potentials  $\mathbf{A}$  and  $\phi$  is obtained by replacing in the zero-order Hamiltonian  $V(\mathbf{r})$  by  $V(\mathbf{r}) + q\phi(\mathbf{r}, t)$  and the momentum  $\mathbf{p}$  by  $[\mathbf{p} - (q/c)\mathbf{A}] = [\mathbf{p} + (e/c)\mathbf{A}]$ , where  $\vec{p} = -i\hbar\vec{\nabla}$ . The time-dependent Schrodinger equation is then given by:

$$i\hbar \frac{\partial \phi}{\partial t} = H\phi \quad (3.58)$$

where the Hamiltonian  $H$  is given, in the presence of an electromagnetic field, by

$$\hat{H} = \frac{1}{2m} (\mathbf{p} + e/c \mathbf{A})^2 + V(\mathbf{r}) + e\phi(\mathbf{r}, t) - \mu_s \cdot \mathbf{B} \quad (3.59)$$

For static magnetic fields, the most convenient gauge is the Coulomb's gauge for which  $\phi = 0$  and  $\vec{\nabla} \cdot \mathbf{A} = 0$ . Taking into account equation (3.57a), equation (3.59) becomes

$$H = \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e}{2mc} [\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}] + \left(\frac{e^2}{2m^2 c^2}\right) A^2 + 2\mu_B \mathbf{S} \cdot (\vec{\nabla} \times \mathbf{A}) \quad (3.60)$$

In equation (3.60), the term

$$H_{\text{HF}} = \frac{e}{2mc} [\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}] + \left( \frac{e^2}{2m^2 c^2} \right) A^2 + 2\mu_B \mathbf{S} \cdot (\vec{\nabla} \times \mathbf{A}) \quad (3.61)$$

represents the magnetic hyperfine Hamiltonian. Since the hyperfine structure brings a very small correction to the Bohr energies, it is legitimate to ignore the second term proportional to  $A^2$ .

We then calculate the term  $(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p})$ , where  $\vec{A} = \frac{\vec{\mu}_I \times \vec{r}}{r^3}$  is the vector potential produced by the nuclear magnetic dipole moment at the position of the electron so that

$$(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) = \left[ \mathbf{p} \cdot (\boldsymbol{\mu}_I \times \mathbf{r}) \frac{1}{r^3} + \frac{1}{r^3} (\boldsymbol{\mu}_I \times \mathbf{r}) \cdot \mathbf{p} \right] \quad (3.62)$$

We apply the rules for a mixed vector product to the vector operators provided that we do not change the order of two non-commuting operators. Since the components of  $\mu_I$  commute with  $\mathbf{r}$  and  $\mathbf{p}$ , we have:

$$(\boldsymbol{\mu}_I \times \mathbf{r}) \cdot \mathbf{p} = (\mathbf{r} \times \mathbf{p}) \cdot \boldsymbol{\mu}_I = \hbar \mathbf{L} \cdot \boldsymbol{\mu}_I \quad (3.63)$$

where  $(\mathbf{r} \times \mathbf{p}) = \hbar \mathbf{L}$  is the electron's orbital angular momentum operator. It can be shown easily that  $\left[ L, \frac{1}{r^3} \right]$ . Therefore,

$$\frac{1}{r^3} (\boldsymbol{\mu}_I \times \mathbf{r}) \cdot \mathbf{p} = \frac{(\mathbf{r} \times \mathbf{p}) \cdot \boldsymbol{\mu}_I}{r^3} = \frac{\hbar \mathbf{L} \cdot \boldsymbol{\mu}_I}{r^3} \quad (3.64)$$

$$\text{Similarly, } \mathbf{p} \cdot (\boldsymbol{\mu}_I \times \mathbf{r}) \frac{1}{r^3} = -\boldsymbol{\mu}_I \cdot (\mathbf{p} \times \mathbf{r}) \cdot \left( \frac{1}{r^3} \right) = \frac{\hbar \mathbf{L} \cdot \boldsymbol{\mu}_I}{r^3} \quad (3.65)$$

Substituting equations (3.64) and (3.65) into equation (3.62), we find that

$$(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) = 2 \frac{\hbar \mathbf{L} \cdot \boldsymbol{\mu}_I}{r^3} \quad (3.66)$$

$$\left( \frac{e}{2mc} \right) (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) = \frac{e\hbar}{mc} \frac{\boldsymbol{\mu}_I \cdot \mathbf{L}}{r^3} = 2\mu_B \frac{\boldsymbol{\mu}_I \cdot \mathbf{L}}{r^3} \quad (3.67)$$

$$H_{\text{HF}} = 2\mu_B \left\{ \frac{\boldsymbol{\mu}_I \cdot \mathbf{L}}{r^3} + \mathbf{S} \cdot (\vec{\nabla} \times \mathbf{A}) \right\} \quad (3.68)$$

To write the explicit expression of  $\mathbf{S} \cdot (\vec{\nabla} \times \mathbf{A})$ , we use the following property from theory of vector analysis. The expression for the vector potential is equivalent to



$\vec{\nabla} \times \frac{\mu_I}{r}$ . This then becomes

$$\vec{\nabla} \times \left( \frac{\mu_I}{r} \right) = \frac{1}{r} (\nabla \times \mu_I) - \mu_I \times \vec{\nabla} \left( \frac{1}{r} \right) = \mu_I \times \frac{\mathbf{r}}{r^3} \quad (3.69)$$

The first term on the right hand side of equation (3.69) is equal to zero since  $\mu_I$  is a constant vector (depending only on the coordinates of the nucleus) and does not depend on the coordinate of the “field - point”. Hence,

$$\mathbf{S} \cdot (\vec{\nabla} \times \mathbf{A}) = \mathbf{S} \cdot \left[ \nabla \times \left( \nabla \times \frac{\mu_I}{r} \right) \right] \quad (3.70)$$

Substituting equation (3.70) into equation (3.68), we have:

$$H_{\text{HF}} = 2\mu_B \left\{ \frac{\mu_I \cdot \mathbf{L}}{r^3} + \mathbf{S} \cdot \left[ \nabla \times \left( \nabla \times \frac{\mu_I}{r} \right) \right] \right\} \quad (3.71)$$

The first term in equation (3.71) is called the orbital term and the second term containing the electron spin ( $\mathbf{S}$ ) and nuclear spin ( $\mathbf{I}$ ) is the spin–spin interaction term ( $H_{\text{SS}}$ ). We can calculate explicitly the spin–spin interaction term ( $H_{\text{SS}}$ ) for  $r$  different from zero and for  $r$  equal to zero as follows:

(i)  $r \neq 0$

In this case, we consider equation (3.71) and use the following vector identity:

$$\nabla \times \nabla \times \vec{C} = \nabla(\nabla \cdot \vec{C}) - \nabla^2 \vec{C}$$

so that,

$$H_{\text{SS}} = 2\mu_B \left[ \mathbf{S} \cdot \vec{\nabla} \left( \nabla \cdot \frac{\mu_I}{r} \right) - \nabla^2 \left( \frac{\mu_I}{r} \right) \right] \quad (3.72a)$$

$$H_{\text{SS}} = 2\mu_B \left[ \mathbf{S} \cdot \left[ -\nabla \left( \mu_I \cdot \frac{\mathbf{r}}{r^3} \right) \right] - \nabla^2 \left( \frac{\mu_I}{r} \right) \right] \quad (3.72b)$$

$$\text{But } \nabla^2 \left( \frac{\mu_I}{r} \right) = \mu_I \nabla^2 \left( \frac{1}{r} \right) = 0 \quad (3.72c)$$

On the other hand,

$$-\nabla \left( \mu_I \cdot \frac{\mathbf{r}}{r^3} \right) = -\frac{1}{r^3} \nabla(\mu_I \cdot \mathbf{r}) - (\mu_I \cdot \mathbf{r}) \nabla \left( \frac{1}{r^3} \right) = \frac{3r(\mu_I \cdot \mathbf{r})}{r^5} - \frac{\mu_I}{r^3} \quad (3.73)$$

Substituting equations (3.72c) and (3.73) into equation (3.72b), we then have

$$H_{ss} = 2\mu_B \left[ \frac{3(\mathbf{S}\cdot\mathbf{r})(\boldsymbol{\mu}_I\cdot\mathbf{r})}{r^5} - \frac{\mathbf{S}\cdot\boldsymbol{\mu}_I}{r^3} \right] \quad (3.74)$$

Equation (3.74) represents the Hamiltonian of spin-spin interaction for  $r \neq 0$ :

(ii) For  $r = 0$ , we have

$$H_{ss} = 2\mu_B \left[ \frac{8\pi}{3} (\mathbf{S}\cdot\boldsymbol{\mu}_I) \delta(\mathbf{r}) \right] \quad (3.75)$$

Considering equations (3.74) and (3.75), the Hamiltonian of spin-spin interaction for any value of  $r$  is given by the sum of equations (3.73) and (3.75) as

$$H_{ss} = 2\mu_B \left[ \frac{8\pi}{3} (\mathbf{S}\cdot\boldsymbol{\mu}_I) \delta(\mathbf{r}) + \frac{3(\mathbf{S}\cdot\mathbf{r})(\boldsymbol{\mu}_I\cdot\mathbf{r})}{r^5} - \frac{\mathbf{S}\cdot\boldsymbol{\mu}_I}{r^3} \right] \quad (3.76)$$

In equation (3.76), the first term in bracket represents the “contact Hamiltonian” and the second and third terms represent the Hamiltonian of spin – spin interaction at a distance. The contact Hamiltonian will give a contribution only for  $r = 0$  and for  $\Psi(0) \neq 0$ , that is, for s-states for which  $l = 0$ .

In equation (3.76), we use the relation  $\boldsymbol{\mu}_I = g_I \mu_N \mathbf{I}$  and taking into account equation (3.71), the hyperfine magnetic Hamiltonian can be written as

$$H_{HF} = 2\mu_B \left[ \frac{L}{r^3} - \frac{\mathbf{S}}{r^3} + \frac{3r(\mathbf{S}\cdot\mathbf{r})}{r^5} + \frac{8\pi}{3} \mathbf{S} \delta(\mathbf{r}) \right] \cdot g_I \mu_N \mathbf{I} \quad (3.77)$$

Under this form of Equation (3.77), the magnetic hyperfine Hamiltonian can be interpreted easily by writing the equation as

$$H_{HF} = -\boldsymbol{\mu}_I \cdot \mathbf{B}_e \quad (3.78)$$

where  $\mathbf{B}_e$  is the magnetic field generated by the electron(s) at the position of the nucleus (proton) and

$$\mathbf{B}_e = \mathbf{B}_L + \mathbf{B}_S \equiv \mathbf{B}_J \quad (3.79)$$

where  $\mathbf{B}_J$  is the magnetic field produced by the electrons at the position of the nucleus,  $\mathbf{B}_L$  is the magnetic field produced by the orbital motion of the electron and  $\mathbf{B}_S$  is the magnetic field produced by the spin magnetic dipole moment.

### 3.3.1.3 Magnetic hyperfine energy for one-electron atoms

The magnetic hyperfine energy for one electron-atom can be written as

$$E_{HF}^m = \langle -\mu_{\mathbf{I}} \cdot \mathbf{B}_e \rangle = \langle -g_I \mu_N \mathbf{I} \cdot \mathbf{B}_J \rangle \quad (3.80)$$

Introducing the coefficient of hyperfine energy, Equation (3.80) becomes:

$$E_{HF}^m = \beta \langle \mathbf{I} \cdot \mathbf{J} \rangle \quad (3.81)$$

where  $\beta = -\frac{g_I \mu_N}{\langle J^2 \rangle} \langle \mathbf{B}_J \cdot \mathbf{J} \rangle$  is the coefficient of magnetic hyperfine energy which measures the strength of the coupling between  $\mathbf{I}$  and  $\mathbf{J}$ .

At the position of the nucleus, there is a magnetic field  $\mathbf{B}_J$  which interacts with the nuclear magnetic moment and orients the nuclear spin. The result of this interaction is a coupling of the electron's angular momentum ( $\mathbf{J}$ ) and that of the nucleus ( $\mathbf{I}$ ) to give a total angular momentum of the atom ( $\mathbf{F}$ ). In analogy to the coupling for electrons, we have

$$\mathbf{F} = \mathbf{J} + \mathbf{I} \quad (3.82a)$$

$$F^2 = J^2 + I^2 + 2 \mathbf{J} \cdot \mathbf{I} \quad (3.82b)$$

$$\langle \mathbf{J} \cdot \mathbf{I} \rangle = \frac{1}{2} [F(F + 1) - J(J + 1) - I(I + 1)] \quad (3.83)$$

According to the atom vector model, the quantum number  $F$  has values ranging from  $J+I$  to  $|J - I|$ . Substituting equation (3.83) into equation (3.81), the hyperfine magnetic energy becomes

$$E_{HF}^m = \frac{\beta}{2} [F(F + 1) - J(J + 1) - I(I + 1)] \quad (3.84)$$

### 3.3.1.4 Expression of the coefficient of hyperfine magnetic energy

We do a calculation for  $L \neq 0$  and since we are dealing with one-electron atoms,  $L \equiv l$ . Therefore, the contact Hamiltonian will not be considered here because  $r \neq 0$ . Hence, for  $L \neq 0$ , the coefficient of hyperfine magnetic energy is given by:

$$\beta = -\frac{g_I \mu_N}{\langle J^2 \rangle} \langle H_J \cdot J \rangle \quad (3.85)$$

where:  $\mathbf{J} = \mathbf{L} + \mathbf{S}$

$$\mathbf{B}_J = \mathbf{B}_e = -\frac{2\mu_B}{r^3} \left[ -\mathbf{L} + \mathbf{S} - \left( \mathbf{S} \cdot \frac{\mathbf{r}}{r} \right) \frac{\mathbf{r}}{r} \right] \quad (3.86)$$

Substituting for  $\mathbf{B}_J$  into  $\beta$  we have

$$\beta = \frac{2}{J(J+1)} \frac{g_I \mu_B \mu_I}{\langle r^3 \rangle} \langle \left[ -\mathbf{L} + \mathbf{S} - \left( \mathbf{S} \cdot \frac{\mathbf{r}}{r} \right) \frac{\mathbf{r}}{r} \right] \cdot (\mathbf{L} + \mathbf{S}) \rangle$$

Since the angular momentum is perpendicular to  $\mathbf{r}$ , we have  $\vec{L} \cdot \vec{r} = 0$ . Therefore,

$$\begin{aligned} \beta &= \frac{2}{J(J+1)} \frac{g_I \mu_B \mu_I}{\langle r^3 \rangle} \langle [-L^2 + S^2 - (\mathbf{S} \cdot \mathbf{r}/r)^2] \rangle \\ &= \frac{2}{J(J+1)} g_I \mu_B \mu_I \langle \frac{1}{r^3} \rangle \left[ -L(L+1) + S(S+1) - 3 \langle \left( \mathbf{S} \cdot \frac{\mathbf{r}}{r} \right)^2 \rangle \right] \end{aligned} \quad (3.87)$$

For an electron,  $s = \frac{1}{2} \therefore s(s+1) = \frac{3}{4}$  and  $(\mathbf{S} \cdot \frac{\mathbf{r}}{r})$  is the projection of  $\mathbf{S}$  along the direction of the radial unit vector. The  $3 \langle \left( \mathbf{S} \cdot \frac{\mathbf{r}}{r} \right)^2 \rangle$  is obtained thus:

$$\begin{aligned} \langle S_z \rangle &= m_s = \frac{1}{2} \\ \langle \mathbf{S} \cdot \frac{\mathbf{r}}{r} \rangle &= m_s = \frac{1}{2} \\ -3 \langle \left( \mathbf{S} \cdot \frac{\mathbf{r}}{r} \right)^2 \rangle &= -3 \times \left( \frac{1}{2} \right)^2 = -\frac{3}{4} \end{aligned}$$

The value of  $\langle \frac{1}{r^3} \rangle$  is given by (Zettili, 2009) :

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3 n^3 l(l+1)(L+\frac{1}{2})}$$

where  $Z$  is the atomic number  $a_0 = \frac{h^2}{\mu e^2}$  is the radius of Bohr's first orbit for the reduced mass  $\mu$ ,  $n$  is the principal quantum number  $l$  is the orbital quantum number

Therefore for  $l \neq 0$ ,

$$\beta = \frac{Z^3 g_I \mu_B \mu_N}{a_0^3 n^3 (l+1/2) J(J+1)} \quad (3.88)$$

### 3.3.1.5 Calculation of the coupling constant for $L = 0$

To calculate the coupling constant for  $L = 0$ , we use

$$E_{contact} = \frac{16\pi}{3} \mu_B \langle \mathbf{S} \cdot \boldsymbol{\mu}_I \rangle |\varphi(0)|^2 \quad (3.89)$$

For  $L = 0$ ,  $\mathbf{J} \equiv \mathbf{S}$ ;  $\boldsymbol{\mu}_I = g_I \mu_B \mathbf{I}$

so that

$$E_{contact} = \frac{16\pi}{3} g_I \mu_I \mu_B |\varphi(0)|^2 \langle \mathbf{J} \cdot \mathbf{I} \rangle = \beta' \langle \mathbf{J} \cdot \mathbf{I} \rangle$$

where  $\langle \mathbf{J} \cdot \mathbf{I} \rangle = \frac{1}{2} [F(F+1) - J(J+1) - L(L+1)]$

$\varphi_{n00}(0) = Y_{00} R_{n0}$  is given by (Zettili, 2009):

$$|\varphi_{n00}(0)|^2 = \frac{1}{4\pi} \left( \frac{2Z}{na_0} \right)^3 \frac{1}{2n(n!)^3} \frac{(n!)^4}{(n-1)!}$$

$$|\varphi_{n00}(0)|^2 = \frac{1}{8\pi} \left( \frac{2Z}{na_0} \right)^3 = \frac{Z^3}{\pi n^3 a_0^3}$$

$$\beta' = \frac{16Z^3}{3} \frac{g_I \mu_I \mu_B}{n^3 a_0^3}$$

$$E_{contact} = \frac{\beta'}{2} [F(F+1) - J(J+1) - I(I+1)] \quad (3.90)$$

Using equation (3.90), we can show that the hyperfine structure of the ground state of the Hydrogen atom is given by:

$$E_{hf} = \frac{\beta'}{2} [F(F+1) - J(J+1) - I(I + 1)]$$

The ground state level  $1^2S_{1/2}$ ;  $n=1$ ,  $l=0$ ,  $J = \frac{1}{2}$  and  $I = \frac{1}{2}$ .

Since  $F$  is the total angular momentum quantum number of the atom, ranging from  $I + J$  to  $|I - J|$ . for  $J = I = \frac{1}{2}$ , we have,  $F: 1, 0$ .

Equation (3.90) becomes, in this case,

$$\begin{aligned} \text{for } F = 0; E_0 &= \frac{\beta'}{2} \left[ 0 - \frac{3}{4} - \frac{3}{4} \right] \\ &= -\frac{3\beta'}{4} \end{aligned}$$

$$\text{For } F = 1; E_1 = \frac{\beta'}{2} \left[ 1.2 - \frac{3}{4} \right] = \frac{\beta'}{4}$$

This implies, that the  $E_{hf}$  splits the  $1S_{1/2}$  level into two hyperfine levels separated by energy as:

$$\begin{aligned} \Delta E &= E_1 - E_0 = \beta' \\ &= \frac{16Z^3}{3} \frac{g_I \mu_N \mu_B}{n^3 a_0^3} \end{aligned} \quad (3.91)$$

Substituting for  $Z = n = 1$ ,  $\mu_N = 5.0584 \times 10^{-24} \text{ erg/G}$ ,  $\mu_B = 9.274 \times 10^{-21} \text{ erg/G}$ ,  $a_0 = 0.529 \times 10^{-8} \text{ cm}$ ,  $g_I = 5.58569$ , we find:

$$\Delta E = 1424.7 \text{ MHz}$$

This corresponds to a wavelength of 20.986 cm

### 3.3.2 Quadrupolar hyperfine Hamiltonian and energy of quadrupolar interaction

The hyperfine splitting between levels with the same value of  $J$ , expressed in units of frequency, are in general of the order of  $10^9$  Hz [ Hakin and Wolf, 2005; Chandra, 2010]. Compared with the distance between the ground state level and various excited levels of the hydrogen atom, for example, the hyperfine structure splitting represent very small corrections (the relative correction being of order of  $10^{-5}$ ). For these corrections to be meaningful, it is necessary that the general study of the atom be done with sufficient rigor; in particular, one must take into account the extension of the nucleus, that is, one must consider the electric quadrupole moment ( $Q$ ) of the nucleus. If the nucleus were comparable to a point or had a spherical symmetry, its electric quadrupole moment would be equal to zero. Nuclei whose nuclear spin is equal to 0 or to 1/2 are spherically symmetric and their electric quadrupole moment,  $Q = 0$ . Helium atom ( ${}^4\text{He}$ ) with  $I = 0$  and Hydrogen atom ( ${}^1\text{H}$ ) with  $I = 1/2$  are some examples of atoms for which  $Q = 0$ .

In many cases, when  $I > 1$ , the distribution of the nuclear charge ( $q_N$ ) inside the nucleus is not spherically symmetric. We take into account this gap to spherical symmetry by introducing the nuclear electric moments. Since the nuclear charge is positive, its electric dipole moment is equal to zero. The deformation of the nucleus leads to an electric quadrupole moment.

The electric quadrupole moment is defined as follows:

$$Q_e = \langle 3Z^2 - r^2 \rangle = \int (3Z^2 - r^2) \rho_N(r) d\tau \quad (3.92)$$

In Equation (3.92), the average is calculated around the configuration of the nucleus. It is assumed that the distribution of nuclear charge has symmetry of revolution around the OZ axis, which is parallel to the nuclear angular momentum operator  $\vec{J}$ ). From equation (1), it is clear that  $Q = 0$  for a sphere. In fact,  $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = (1/3) \langle r^2 \rangle$ .

The electric quadrupolar hyperfine effect is associated with the interaction between the electric quadrupole moment and the gradient of the electric field generated by the electrons in the neighborhood of the nucleus [Wikipedia, 2015]. Assuming that the distribution of the nuclear

charge has a symmetry of revolution about the OZ axis, that is, the nuclear spin  $\vec{I}$  is parallel to OZ axis, and that the electronic cloud has a symmetry of revolution about the oz axis, that is, the electronic total angular momentum  $\vec{J}$  is parallel to oz, it is shown that the gradient of the electric field is given by [Hakin and Wolf, 2005]:

$$\varphi_{zz} = \frac{-\partial E_z}{\partial z} = \frac{\partial^2 V}{\partial z^2} \quad (3.93)$$

The additional energy resulting from the quadrupolar coupling is given by:

$$\Delta E_Q = \frac{eQ\langle\varphi_{zz}\rangle}{4} \left[ \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2} \right] = \frac{eQ}{4} \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle \left[ \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2} \right] \quad (3.94)$$

In Equation (3),  $\theta$  is the angle between the OZ and oz axes (i.e., the angle between  $\vec{I}$  and  $\vec{J}$ ); therefore, Equation (3) is equivalent to:

$$\Delta E_Q = \frac{eQ}{4} \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle \left[ \frac{3}{2} \langle \cos^2 \mathbf{I} \cdot \mathbf{J} \rangle - \frac{1}{2} \right] \quad (3.95)$$

The calculation of  $\cos^2(\mathbf{I}, \mathbf{J})$  can be done using the atom vector model:

$$\mathbf{F} = \mathbf{I} + \mathbf{J}$$

$$\mathbf{F}^2 = \mathbf{I}^2 + \mathbf{J}^2 + 2 \mathbf{I} \cdot \mathbf{J} \cos(\mathbf{I} \cdot \mathbf{J})$$

$$\langle \cos(\mathbf{I} \cdot \mathbf{J}) \rangle = \frac{\langle F^2 \rangle - \langle I^2 \rangle - \langle J^2 \rangle}{2\sqrt{\langle I^2 \rangle} \sqrt{\langle J^2 \rangle}} = \frac{F(F+1) - I(I+1) - J(J+1)}{2\sqrt{I(I+1)} \sqrt{J(J+1)}} \quad (3.96)$$

However, the expression of  $\Delta E_Q$  obtained by substituting Equation (3.96) into Equation (3.95) is imperfect. The correct result was obtained by CASIMIR using a quantum mechanical approach:

$$\Delta E_Q = \frac{eQ}{4} \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle \frac{3}{2} \frac{C(C+1) - 2I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \quad (3.97)$$

where  $C = F(F+1) - I(I+1) - J(J+1)$ . Introducing the quadrupolar coupling constant,  $B = \frac{eQ}{4} \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle$ , we have:

$$\Delta E_Q = \frac{B}{4} \frac{3}{2} \frac{C(C+1) - 2I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \quad (3.98)$$



The quadrupolar hyperfine Hamiltonian is an effect of second order compared to the magnetic hyperfine Hamiltonian [Hakin and Wolf, 2005].

Considering both the magnetic hyperfine structure effect and the electric quadrupolar interaction, the hyperfine structure energy splitting is described by the following expression [Chandra, 2010]:

$$E_{J,I} = \frac{A'}{2}C + \frac{B}{4} \frac{3C(C+1) - 2I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \quad (3.99)$$

In Equation (3.99),  $A'$  is the hyperfine structure energy constant; the constants  $C$  and  $B$  have the same meaning as in equation (3.97).

## CHAPTER FOUR: RESULTS AND DISCUSSIONS

In this section, the results and discussions involving the fine structure, the lamb shift and the hyperfine structure of spectral lines splitting are presented. In particular, from the expression (3.27) of the spin-orbit coupling correction, it is evident that the interaction between the electron spin with the orbital angular momentum splits each level of a hydrogen-like atom into two resulting doublet levels. For instance, the upper state of sodium D lines, the 3P state is split into the  $3P_{1/2}$  and the  $3P_{3/2}$  states. From the expression (3.28) of fine structure, it can also be deduced that the splitting is proportional to the fourth power of the atomic number,  $Z$  and therefore, the splitting is easily observable for heavy atoms. However, the values of fine structure splitting of the various lines of hydrogen ( $Z=1$ ) are comparatively small. For the  $H_{\alpha}$ , line of the Balmer series ( $6560.98\text{\AA}$ ), the splitting in wave numbers calculated using the spin-orbit correction is approximately  $0.2217\text{ cm}^{-1}$  which is comparable to the value  $0.33\text{cm}^{-1}$  obtained spectroscopically [Haken and wolf,2004]. This lies in the microwave range.

Observations of optical spectral lines are, however, affected by Doppler broadening of spectral lines, implying that these splitting may be temperature dependent. From the fourth power dependence on the atomic number of the fine structure splitting, it follows that heavier elements may have a larger magnitude of splitting.

It can also be noticed that the splitting is greatest for the smallest principal quantum number,  $n$ .

From Equation (3.35), it can be deduced that the lamb shift is proportional to the third power of the fine structure constant and it decreases with increasing principal quantum number. The electron emission/absorption has given us a method by which it is possible to accurately calculate a value for the electron spin g-factor.

The hyperfine structure of energy levels resulting from the interaction between the nuclear multipole moments and the internally generated field was determined using the electromagnetic approach and the quantum approach. It can be deduced from equation (3.88) that the hyperfine structure corrections are proportional to approximately  $10^{-8}E_n^0$ . In addition, the hyperfine splitting for the ground state of the hydrogen was calculated and a value of  $\lambda = 20.986\text{ cm}$  was obtained. This value is close to the accepted value of  $21\text{cm}$ .

## CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

From our study we have seen that all the fine-structure terms, that is, the relativistic correction to the electronic kinetic energy term, the spin – orbit interaction term and the Darwin term (for  $l = 0$ ), are proportional to  $\alpha^2 E_n^0$ , where  $\alpha$  is the fine – structure constant. Since  $\alpha^2$  is about  $10^{-5}$ , the fine -structure correction is a small fraction of the Bohr energy,  $E_n^0$ . The energy shift between fine-structure states (the fine-structure interval) decreases as  $1/n^3$ , where  $n$  is the principal quantum number. For a hydrogen-like atom with atomic number  $Z$ , the fine structure correction increases rapidly as  $Z^4$ . This implies, that the fine - structure correction becomes easier to observe as the atomic number  $Z$  increases. The fine - structure correction for the hydrogen atom can also be obtained by solving the Dirac equation for an electron placed in the Coulomb potential created by the proton.

Since the quantum electrodynamical result closely compares to the experimental result than the semi-classical result, the quantum electrodynamics proves to be more reliable and an extended study to higher order corrections seems compelling.

We have developed the quantum theory of atomic hyperfine structure and have applied this theory to the description of the hyperfine structure splitting of the ground state of the hydrogen atom. In the ground state of the hydrogen atom, the proton and electron spin can only be oriented parallel or antiparallel to one another. This corresponds to two possible values of the total angular momentum quantum number  $F$  ( $F = 1$  or  $0$ ). From the theory that we have developed, using the values of the nuclear gyromagnetic ratio, the radius of Bohr's first orbit, the Bohr magneton and the nuclear magneton, we have calculated the energy difference between these two states and found a wave number of  $0.0475 \text{ cm}^{-1}$ . This was found to correspond to a frequency of  $1424.7 \text{ MHz}$  or  $\lambda = 20.984 \text{ cm}$ . Since its discovery in 1951, the 21 cm line of hydrogen has played an important role in radio – astronomy. For the hydrogen-like atoms, the hyperfine splitting increases with the cubic power of the atomic number and therefore, in such heavy ions, the hyperfine splitting should be many times larger than in the hydrogen atom. Also, in such heavy ions, the electric quadrupolar effect may contribute to the observed hyperfine structure splitting.

## RECOMMENDATIONS

Future studies on the theory of fine structure could focus on solving the Dirac equation for an electron placed in the Coulomb potential created by the proton and consider the limits of the weak relativistic system such as the hydrogen atom to obtain the three fine structure correction terms.

In addition, a consideration on higher order loops in the Feynman diagrams could help improve the accuracy of a theoretical prediction on the Lamb shift splitting.

Also, future studies should focus on developing the theory of molecular hyperfine structure and carry out measurements of hyperfine structure interaction in atomic and molecular spectra and in electron paramagnetic resonance spectra of free radicals and transition metal ions.

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