



Review Article

Determination of Nuclear Structure Effects on Atomic Spectra by Applying Rayleigh–Schrödinger Perturbation Theory

Aliyu Adamu^{1,*}, Muhammad Hassan¹, Mohammed Kyari Dikwa², Salamatu Ahmad Amshi³

¹Department of Physics, University of Maiduguri, Borno, Nigeria

²Department of Physical Science, School of Health Technology Maiduguri, Borno, Nigeria

³Department of Pharmaceutical Chemistry, University of Maiduguri, Borno, Nigeria

Email address:

aliyuadamu703@gmail.com (A. Adamu), muhammad59@hotmail.com (M. Hassan), mkyari@gmail.com (M. K. Dikwa),

salmaamshi@gmail.com (S. A. Amshi)

*Corresponding author

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Abstract: In this work, we applied the first order time independent Rayleigh–Schrödinger Perturbation Theory, as an approximation method to calculate numerically the corrections in atomic spectra due to nuclear structure effects. The results showed that the nuclear structure effects distort the atomic spectra in different ways: The combined fine structure effect which decreases with increasing values of n , split the quantum number n into $l \pm \frac{1}{2}$ and the magnitude of the energy levels shift is of order of 10^{-6} eV relative to the energy levels calculated from the non-relativistic Schrodinger equation. An energy level determined by the total angular momentum j of the orbiting electron are found to split further due to hyperfine structure effects with the energy difference of 5.9×10^{-6} eV. This corresponds to a wavelength is 21 cm. The energy shift between $2s_{1/2}$ and $2p_{1/2}$ states due to the effects of vacuum fields on orbiting electron was calculated as 5.52×10^{-6} eV. We then continue to investigate the change in atomic spectra caused by the finite size nuclear structure effects. The finite-size nuclear structure effect on atomic spectra computed is of order of the scaling factors, ξ , ξ^2 and ξ^3 for $n = 1$, $n = 2$ and $n = 3$ atomic energy levels respectively. This showed that as the energy levels increased the effects of the finite – size nucleus on the orbiting electron is diminishing. Therefore the concept of finite nuclear size model has an extremely small impact on atomic spectra. These theoretical findings revealed some of the behavior of atomic spectra which may develop the understanding of spectroscopy and spectroscopic methods.

Keywords: Spectroscopy, Electron Transitions, Schrödinger Equation, Quantum Numbers, Energy Shift, Finite – Size Nucleus

1. Introduction

The investigation of the radiation emitted or absorbed by atoms or molecules is called spectroscopy [1, 2]. The spectrum is the intensity of the emitted radiation as a function of its frequency, f or its wavelength, λ [3]. Spectroscopy can be categorized in to atomic spectroscopy, ultraviolet and visible spectroscopy, fluorescence spectroscopy, x-ray fluorescence spectroscopy, infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance spectroscopy, electron spin spectroscopy and mass

spectroscopy [4, 5]. Atomic spectra arise from electron quantum leaps between orbits. The difference in energy between the orbits jumped by the electron comes out of the atom as spectral lines. These lines depend on the orbital from which the electron jumped [6, 7]. The internal molecular structure may respond to radiant energy in addition to electron transitions. In some molecules the bonding electrons also have natural resonant frequencies, giving rise to molecular vibration, while others exhibit a rotation. The differences in energy levels associated with vibration and rotation are much smaller than those involved in electron transitions, therefore excitation resulting from these

phenomena will occur at comparatively longer wavelengths; vibrational excitation is typically associated with infrared radiation, while rotational excitation are associated with far-infrared or even microwave radiation. Despite vibrational and rotational excitation being primarily associated with spectral regions other than ultraviolet-visible, they do have an effect on electron transitions within this range. The principal effect is of 'broadening', that is the deviation of an observed absorption region from its predicted region.

For most species, especially in solution, excitation does not appear as sharp absorbance points at highly differentiated wavelengths, but rather as bands of absorbance over a range of wavelengths. A principal reason is that absorbance at the electron transition level are frequently accompanied by smaller structures at the vibrational level. In the same way each vibrational structures may have even smaller associated structures at the rotational level, so an absorbance spectrum due to electron transitions may display far more complex structures than expected [3].

It is observed that the frequencies of the spectral lines of the atoms or molecules are not exactly as predicted by Schrödinger equation. Certain splitting in the spectrum appears when observed using a high-resolution spectrometer [8]. The observed splitting in the spectral lines is due to the structure of the atomic nucleus. The nuclear structure affects atomic spectra in many ways. For example the hyperfine interaction between electrons and the nuclear magnetic moment, this results in a small splitting of spectral lines. Electrons are also sensitive to other properties of the nucleus they are bound to, such as nuclear mass, charge distribution or spin. These nuclear properties which act simultaneously, distort the atomic spectra in different ways. Small distortions in the atomic spectra can give insight into the structure of the atom [9], molecules or other chemical species. To account for these nuclear effects, one must often applied nuclear theory and any additional experimental information which may provide useful calibration for the calculated values.

The description of atomic or molecular spectra is important tools in understanding spectroscopy and spectroscopic methods [10]. Spectroscopy is a widely used and accepted technique capable of determining trace (μgdm^{-3}) and ultra trace ($< \mu\text{gdm}^{-3}$) levels of elements (or) metals in a wide variety of samples with good accuracy and acceptable precision [11]. It Spectroscopy applied across research, quality, and manufacturing, with continuing focus on life science and pharmaceutical environments, they are equally as relevant in agriculture, food safety, inorganic and organic chemistry, biochemistry, clinical chemistry, geochemistry, geological exploration, environmental sciences (air, soil and water pollutions), industrial control processes, and many manufacturing industries to name a few [12-17]. In this study, we investigated the change in atomic spectra cause by the nuclear structure effects.

2. Theoretical Procedures

The road to understanding the origins of atomic spectra began with Johann Balmer in 1885, when he noticed the regularities in the wavelengths of the spectrum and described

it with the formula:

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad (1)$$

where n is an integer and takes on the values 3, 4, 5,... and λ_0 is a constant wavelength of 364.56 nm. He denoted the *Balmer series* by $H_\alpha, H_\beta, H_\gamma, \dots$, starting at the long wavelength end in the visible region of the electromagnetic spectrum. The empirical result equation (1) was later generalized by Johannes Rydberg in 1900, to describe the entire observed spectrum by the formula:

$$\frac{1}{\lambda} = \mathcal{R} \left(\frac{1}{m^2} - \frac{1}{n^2} \right), m = 1, 2, 3, \dots, n > m \quad (2)$$

where \mathcal{R} , known as the Rydberg constant, has the value $1.097 \times 10^7 \text{m}^{-1}$. Later, a similar series named the *Lyman series* was discovered in the ultraviolet, and several similar series were found in the infrared, named after *Paschen, Brackett, Pfund, Humphreys, Hansen* and *Strong*, and successively less famous people. Neil Bohr made an assumption that all these spectral lines arise from electron quantum leaps between orbits, $n = 1, 2, 3, \dots$. The increasing values of n represent higher energy levels or greater distance from the nucleus. The difference in energy, ΔE between the orbits jumped by the electron is related to the wavelength, according to the following equation [18, 19]:

$$\Delta E = E_n - E_m = \frac{hc}{\lambda} \quad (3)$$

where $h = 6.62 \times 10^{-34} \text{Js}$ is the Plank's constant and c is the speed of light in a vacuum. This energy comes out of the atom as light of a specific color which depends on the orbital from which the electron jumped [20]. The energies E_m and E_n can be found from quantum mechanics by solving the Schrodinger wave equation:

$$E\psi(r) = -\frac{\hbar^2}{2m_e} \nabla^2 \psi(r) + U(r)\psi(r) \quad (4)$$

using electrostatic potential [21,22] of a fixed charge $+Ze$:

$$U(r) = -\frac{Zke^2}{r} \quad (5)$$

where $m_e, k = (4\pi\epsilon_0)^{-1}$ and e are the electronic mass and charge, respectively [23]. According to equation (4), the allowed energies E_n of an electron are given by:

$$E_n = -\frac{ke^2 Z^2}{2a_0 n^2}, n = 1, 2, 3, \dots \quad (6)$$

Where $a_0 = \hbar^2/m_e e^2 = 5.29 \times 10^{-11} \text{m}$ is the Bohr radius. Comparing (6) and (3) and using the relation: $h = 2\pi\hbar$, we find that the spectral lines of atoms occur at wavelengths:

$$\frac{1}{\lambda} = -\frac{ke^2}{4\pi\hbar c a_0} Z^2 \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

The series can be obtained in terms of wave number: $\bar{\nu}_{m,n}$ as:

$$\bar{\nu}_{m,n} = \mathcal{R} Z^2 \left(\frac{1}{m^2} - \frac{1}{n^2} \right), n = 1, 2, 3, \dots, n > m \quad (7)$$

Equation (7) can be used to generate the wave numbers of the lines in each of these series; $n = 1, 2, 3, 4, 5, 6 \dots$ for the *Lyman, Balmer, Paschen, Brackett, Pfund, Humphreys...* series respectively.

When the lone orbiting electron is solely subject to the electrostatic influence of the nucleus, its energy level depends exclusively on the principal quantum number, n [24-26]. It is clearly observed that the frequencies of the spectral lines of the atoms or molecules are not exactly as predicted by equation (7). Other splitting in the spectrum appears when observed using a high-resolution spectrometer [27]. This is due to the following nuclear structure effects:

- a. Fine Structure Splitting
 - i. Relativistic motion
 - ii. Spin – orbit interaction
 - iii. Quantization of electric fields
- b. Nuclear Contributions
 - i. Hyperfine splitting
 - ii. Finite – size nuclear effects
- c. Lamb Shifts
 - i. Vacuum fields fluctuations
 - ii. Vacuum polarization

These nuclear structures affect the atomic spectra in many ways and as a result distort the atomic spectra obtained using (7) [28]. The corrections to the spectra obtained from (7) due to nuclear structure, can be corrected by adding a small change $\lambda U(r)$, in potential (5) caused by these effects:

$$U(r) = U(r) + \lambda U(r) \quad (8)$$

This small change in potential will also produce a small change in the Hamiltonian. The new Hamiltonian can be written as the sum of two terms:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H} \quad (9)$$

where $\lambda \hat{H}$, is the perturbation and λ is taken to be dimensionless small number, $\lambda \ll 1$, so that the perturbation $\lambda \hat{H}$ is small compared to the original Hamiltonian \hat{H}_0 . We will seek to calculate the change in energy E_n and wave function ψ_n produced by an arbitrary small change in the Hamiltonian \hat{H} , by solving a new eigen functions ϕ_n and eigen values \hat{E}_n as

$$(\hat{H}_0 + \lambda \hat{H})\phi_n = \hat{E}_n \phi_n \quad (10)$$

Where the energy eigenstates $\phi_n^{(0)}$ could correspond to the hydrogen wave function, the spin eigenfunction of electron in a magnetic field or any other set of wavefunction that are exact solutions of Schrödinger's equation. Written ϕ_n and \hat{E}_n as

$$E = mc^2 \sqrt{1 + \left(\frac{\vec{p}}{mc}\right)^2} = mc^2 \left[1 + \frac{1}{2} \left(\frac{\vec{p}}{mc}\right)^2 - \frac{1}{8} \left(\frac{\vec{p}}{mc}\right)^4 + \dots \right] = mc^2 + \frac{\vec{p}^2}{2m} - \frac{(\vec{p}^2)^2}{8m^3 c^2} + O(p^6) \quad (14)$$

The first term in (14) is interpreted as the rest energy of the electron; the second term is the non-relativistic kinetic energy that we are familiar with in everyday life. Hence, we use the third term in writing the perturbed Hamiltonian:

$$H_{rc} = -\frac{(\vec{p}^2)^2}{8m^3 c^2} = -\frac{1}{2mc^2} \left(H_0 + \frac{Zke^2}{r} \right)^2 \quad (15)$$

power series in λ , we have

$$\left. \begin{aligned} \hat{E}_n &= \hat{E}_n(\lambda) = \hat{E}_n^{(0)} + \lambda \hat{E}_n^{(1)} + \lambda^2 \hat{E}_n^{(2)} + \dots \\ \phi_n &= \phi_n(\lambda) = \phi_n^{(0)} + \lambda \phi_n^{(1)} + \lambda^2 \phi_n^{(2)} + \dots \end{aligned} \right\} \quad (11)$$

Here $\hat{E}_n^{(0)}$ is the 0th order correction to the n^{th} eigen value, and $\phi_n^{(0)}$ is the 0th order correction to the n^{th} eigen function; $\hat{E}_n^{(1)}$ and $\phi_n^{(1)}$ are the 1st order corrections; $\hat{E}_n^{(2)}$ and $\phi_n^{(2)}$ are the 2nd order corrections and so on. Substituting (11) into (10) and doing some algebra (see Ref [29]), the generalized eigen value of the energy is obtained using Rayleigh – Schrödinger perturbation theory as:

$$\hat{E}_n^{(N)} = \langle \phi_n^{(0)} | \lambda \hat{H} | \phi_n^{(N-1)} \rangle \quad (12)$$

3. Derivation and Discussion

Equation (12) allowed us to compute the approximate solutions of the energy eigenvalue to any desired accuracy. The 1st order ($N = 1$) perturbative corrections is be given by

$$\Delta E_n^{(1)} = \langle \phi_n^{(0)} | \lambda \hat{H} | \phi_n^{(0)} \rangle \quad (13)$$

Equation (13) can be applied to calculate the splitting of the spectral line caused by the nuclear structure effects.

3.1. The Fine Structure Corrections

The fine structure was known experimentally long before a proper theoretical understanding was achieved, and it was an important driving force in theoretical developments at a certain stage in the history of atomic physics. In addition to its intrinsic interest and importance in atomic spectra, the fine structure is interesting as a window on relativistic quantum mechanics.

3.1.1. The Relativistic Corrections to the Kinetic Energy of the Electron

In relativistic classical mechanics, the total energy of an electron is is

$$E = \sqrt{(pc)^2 + (mc^2)^2}$$

Now we are interested only in the case where the particle is only slightly relativistic so that $v < c$. In this limit we can expand the square root to obtain

Using the Perturbation Theory (15), the relativistic correction for a new state $|nl\rangle$ can be expressed as:

$$\langle nl|H_{rc}|nl\rangle = -\frac{1}{2mc^2}\left\langle nl\left|\left(H_0 + \frac{Zke^2}{r}\right)\left(H_0 + \frac{Zke^2}{r}\right)\right|nl\right\rangle = -\frac{1}{2mc^2}\left[E_n^{(0)2} + 2E_n^{(0)}Zke^2\langle r^{-1}\rangle_n + (Zke^2)^2\langle r^{-2}\rangle_{nl}\right]$$

Using the following equation,

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

We obtain

$$\langle H_{rc}\rangle_{nl} = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n \frac{Zke^2}{n^2 a_0} + \frac{(Zke^2)^2}{n^3 a_0^2 \left(l + \frac{1}{2}\right)}\right] = \frac{E_n}{2mc^2} \frac{Zke^2}{2a_0 n^2} \left[\frac{4n}{\left(l + \frac{1}{2}\right)} - 3\right] = -E_n \left(\frac{Z\alpha}{n}\right)^2 \frac{n}{4} \left\{ \begin{array}{l} -\frac{4}{j} + \frac{3}{n}, \left(j = l + \frac{1}{2}\right) \\ -\frac{4}{j+1} + \frac{3}{n}, \left(j = l - \frac{1}{2}\right) \end{array} \right\} \quad (16)$$

The number j in (16) represents the total angular momentum of the electron, and can take on the values $j = 1/2, 3/2, \dots, n/2$.

3.1.2. Spin-Orbit Coupling of Electron

From relativity, an electron moving in an electric field \vec{E} , feels a small magnetic field in its reference frame given by

$$\vec{B} = \frac{1}{c^2} \vec{v} \times \vec{E} + O\left(\frac{v}{c}\right)^2$$

where velocity \vec{v} [30]. For a central field the corresponding electric field due to potential (5) can be determined by

$$\vec{E} = \frac{\vec{r}}{r} \frac{dU(r)}{dr} = -Zke \frac{\vec{r}}{r^3} \quad (17)$$

However, there is another contribution to the effective magnetic field arising from the relativistic effect connected with the precession of axes under rotation, called Thomas precession. This suggests multiplying (17) further by a factor of 1/2 and gives rise to total spin-orbit interaction energy:

$$\langle njlm_j|H_{LS}|njlm_j\rangle = \frac{Zke^2}{2m^2c^2} \frac{\hbar^2}{2} \langle \frac{1}{r^3} \rangle_{nl} \times \left\{ \begin{array}{l} \left(j - \frac{1}{2}\right), \left(j = l + \frac{1}{2}\right) \\ \left(-j - \frac{3}{2}\right), \left(j = l - \frac{1}{2}\right) \end{array} \right\} \quad (19)$$

The expectation of r^{-3} for the dipole interaction was first estimated by Goldsmith and by Fermi and Segre by comparison with the hydrogenic wave functions:

$$\langle r^{-3} \rangle_{nl} = \left(\frac{Z}{na_0}\right)^3 \frac{1}{l\left(l + \frac{1}{2}\right)(l+1)}$$

We obtain

$$\langle H_{LS} \rangle = -E_n \left(\frac{Z\alpha}{n}\right)^2 \frac{n}{4} \times \left\{ \begin{array}{l} \frac{2}{j\left(j + \frac{1}{2}\right)}, \left(j = l + \frac{1}{2}\right) \\ -\frac{2}{\left(j + \frac{1}{2}\right)(j+1)}, \left(j = l - \frac{1}{2}\right) \end{array} \right\} \quad (20)$$

3.1.3. The Darwin Term

Schrödinger suggested [30] that the relativistic electron undergoes a Zitterbewegung motion due to the interference between positive and negative energy term in the solution [31-34]. The angular frequency at which an electron zitters is

$$H_{LS} = -\mu_s \cdot \vec{B} = \frac{Zke^2}{2(mc)^2} \frac{1}{r^3} [\vec{S} \cdot (\vec{p} \times \vec{r})]$$

$$= \frac{Zke^2}{2(mc)^2} \frac{1}{r^3} (\vec{L} \cdot \vec{S})$$

where the angular momentum $\vec{L} = \vec{r} \times \vec{p}$. The total angular momentum, $\vec{J} = \vec{L} + \vec{S}$. Taking their square

$$\vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S} \text{ or } \vec{L} \cdot \vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$$

Therefore, spin-orbit coupling

$$(\vec{L} \cdot \vec{S})|njlm_j\rangle = \frac{\hbar^2}{2} [j(j+1) - l(l+1) - \frac{3}{4}] \quad (18)$$

Since the unperturbed states are degenerate, it is easy to see that the spin-orbit coupling is diagonal in the eigenstates of the total angular momentum and hence the energy of a dipole moment in a magnetic field will be given as

given by

$$\omega = \frac{2mc^2}{\hbar}$$

This corresponds to a characteristic length of

$$\lambda = \frac{c}{\omega} = \frac{\hbar}{2mc} = \frac{\lambda_0}{2}$$

where $\lambda_0 = \hbar/mc$ is the Compton wavelength [35].

Therefore the potential energy the electron experience is not strictly at a particular position, but rather an “average” around that point, as illustrated in Figure 1. In order to quantify this correction we shall define an effective potential that is the average of the potential over a fuzzy ball about the size of λ_0 .

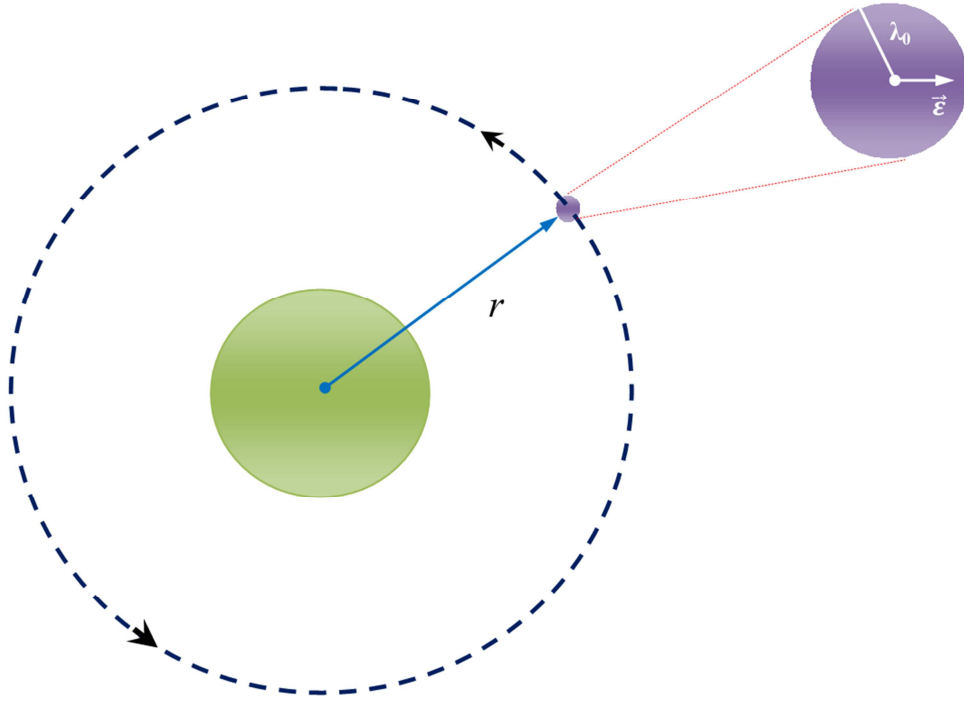


Figure 1. Set up of the Darwin correction.

$$U_{eff} = \frac{1}{Volume} \int U(\vec{r} + \vec{\epsilon}) d^3\epsilon$$

We shall perform the integration over a sphere of Volume:

$$V = \frac{4}{3}\pi\lambda_c^3 = \frac{4}{3}\pi\left(\frac{\hbar}{mc}\right)^3$$

The correction can be computed in a Taylor expansion around the average position $\vec{\epsilon}$:

$$U(\vec{r} + \vec{\epsilon}) = U(\vec{r}) + \vec{\epsilon} \cdot \nabla U + \sum_{i,j=1}^3 \frac{1}{2} \epsilon_i \epsilon_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} U + \dots$$

Let us perform the integration term by term for clarity.

$$V_e = \frac{1}{V} \left[\int U(\vec{r}) d^3\epsilon + \int \vec{\epsilon} \cdot \nabla U d^3\epsilon + \frac{1}{2} \int \epsilon_i \epsilon_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} U d^3\epsilon \right] \quad (21)$$

and the spherical symmetry of Zitterbewegung says

$$\int U(\vec{r}) d^3\epsilon = U(\vec{r}) \times Volume \quad (22)$$

$$\int \vec{\epsilon} \cdot \nabla U d^3\epsilon = \nabla U \cdot \int \vec{\epsilon} d^3\epsilon = 0 \quad (23)$$

Since there is no preferred direction and we are integrating over all directions. This is also the reason why

$$\int \epsilon_i \epsilon_j d^3\epsilon = A \delta_{ij} = \lambda_0^2 \delta_{ij} = \left(\frac{\hbar}{mc}\right)^2 \delta_{ij} \quad (24)$$

Putting (23) into the average of the third term in (21) we obtain

$$\int \epsilon_i \epsilon_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} U d^3\epsilon = \frac{1}{3} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 U \delta_{ij} \quad (25)$$

So in the end we have obtained an expression for the effective potential.

$$V_e = U(\vec{r}) + \frac{1}{6} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 U \delta_{ij} \quad (26)$$

This argument leads to the Darwin term,

$$H_{Darwin} = \frac{1}{6} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 U \delta_{ij} \quad (27)$$

A full relativistic calculation gives us our third perturbation given by:

$$H_{Darwin} = \frac{1}{8} \left(\frac{\hbar}{mc}\right)^2 \nabla^2 U \delta_{ij} \quad (28)$$

For the Coulomb potential (5) the Laplacian ∇^2 , is given by

$$\nabla^2 U(r) = \nabla^2 \frac{Zke^2}{r} = -4\pi Zke^2 \delta^3(\vec{r}) \quad (29)$$

Where $+Ze$ is the charge of the nucleus and $\delta(r)$ is the three-dimensional Dirac delta function and it is zero everywhere except at s states ($r=0$). Therefore,

$$H_{Darwin} = \frac{\hbar^2}{8m_e^2 c^2} 4\pi Zke^2 \delta^3(\vec{r}) \quad (30)$$

The Darwin term has an expectation value only for the s -states, because

$$\langle n | H_{Darwin} | n \rangle = \frac{\hbar^2}{8m_e^2 c^2} 4\pi Zke^2 |\psi_n(0)|^2 \quad (31)$$

The intensity of the wave function corresponding to s states is

$$|\psi_n(0)|^2 = \frac{Z^3}{\pi n^3 a_0^3} \quad (32)$$

The expectation value then is

$$\langle n | H_{\text{Darwin}} | n \rangle = \frac{4\pi Z k e^2 \hbar^2}{8m_e^2 c^2} \frac{Z^3}{\pi n^3 a_0^3} = -E_n \left(\frac{Z\alpha}{n} \right)^2 \frac{n}{4} \quad (33)$$

where the use of $\alpha = e^2/\hbar c$ have been made. When $l = 0, j = 1/2$ in (20), the expression (32) coincides with that of the

$$E_{FS}(n, j) = |E_n| \left(\frac{Z\alpha}{n} \right)^2 \frac{n}{4} \begin{cases} -\frac{4}{j} + \frac{3}{n} + \frac{2}{j(j+\frac{1}{2})}, & (j = l + \frac{1}{2}) \\ -\frac{4}{j+1} + \frac{3}{n} - \frac{2}{(j+\frac{1}{2})(j+1)}, & (j = l - \frac{1}{2}) \end{cases}$$

The Combination of the three Corrections gives rise to the fine structure for hydrogen atom:

$$E_{FS}(n, j) = \frac{|E_n|}{4} \left(\frac{Z\alpha}{n} \right)^2 \left[\frac{3}{4} - \frac{2n}{2j+1} \right] \quad (34)$$

Combining the spin and angular momentum, the total angular momentum takes values $j = l \pm 1/2$.

3.2. The Hyperfine Splitting

Taking into account the coupling between the nuclear spin I and the total angular momentum j of the orbiting electron, an energy level determined by j will be split further, forming a hyperfine structure. To determine the magnitude of hyperfine structure let us start by defining the magnetic moment of the nucleus as

$$\vec{\mu}_N = \frac{+Ze}{2m_N} g_N \vec{I} \quad (35)$$

where \vec{I} is the nuclear spin vector. The complete action from which the Maxwell's equations are derived for the Quantum Electrodynamics is

$$S = \int dt d^3x \left[\frac{1}{8\pi} (\vec{E}^2 - \vec{B}^2) - \phi \rho + \frac{1}{c} \vec{A} \cdot \vec{j} \right] \quad (36)$$

A magnetic moment couples to the magnetic field with the Hamiltonian $H_{HF} = -\vec{\mu}_e \cdot \vec{B}$, and therefore appears in the Lagrangian as $L = +\vec{\mu}_e \cdot \vec{B}$. We add this term to the above action

$$S = \int dt d^3x \left[\frac{1}{8\pi} (\vec{E}^2 - \vec{B}^2) - \phi \rho + \frac{1}{c} \vec{A} \cdot \vec{j} + \vec{\mu} \cdot \vec{B} \delta \vec{r} \right] \quad (37)$$

Where \vec{r} is the position of the magnetic moment. The equation of motion for the vector potential is obtained by varying the action with respect to \vec{A}

$$\vec{\nabla} \times \vec{B} = \frac{1}{c} \dot{\vec{E}} + \frac{4\pi}{c} \vec{j} - 4\pi\mu \times \vec{\nabla} \delta \vec{r} \quad (38)$$

In the absence of time-varying electric field or electric current, the equation is simply

$$\vec{\nabla} \times \vec{B} = -4\pi\mu \times \vec{\nabla} \delta \vec{r} \quad (39)$$

It is tempting to solve it immediately as

$$\vec{B} = -\mu \delta \vec{r} \quad (40)$$

spin-orbit coupling.

Thus, the Darwin term exactly compensates for the absence of the spin-orbit interaction [36]. Finally, putting (16), (20) and (33) together we obtained the fine structure correction as:

To solve it, we use Coulomb gauge and write (39) as

$$-\vec{\nabla}^2 \vec{A} = -4\pi\mu \times \vec{\nabla} \delta \vec{r} \quad (41)$$

Because $\vec{\nabla}^2 (\vec{r}^{-1}) = -4\pi\mu \delta \vec{r}$, we find

$$\vec{A}(\vec{r}) = -\vec{\mu}_N \times \vec{\nabla} \delta \vec{r} = \vec{\mu}_N \times \vec{\nabla} \frac{\vec{r}}{|\vec{r}|^2} \quad (42)$$

The magnetic field is its curl,

$$\vec{B}(\vec{r}) = \vec{\nabla} \times \vec{A} = -\left[\vec{\mu}_N \vec{\nabla}^2 \frac{1}{|\vec{r}|} - \vec{\nabla}(\vec{\mu}_N \cdot \vec{\nabla}) \frac{1}{|\vec{r}|} \right] \quad (43)$$

Finally the interaction of two magnetic moments, $\vec{\mu}_e$ and $\vec{\mu}_N$, is given by the magnetic field $\vec{B}(\vec{r})$ created by the second magnetic moment at \vec{r}

$$\begin{aligned} H_{HF} &= -\vec{\mu}_e \cdot \vec{B}(\vec{r}) = -\frac{e}{m_e} \vec{S}_e \cdot \left[\vec{\mu}_N \vec{\nabla}^2 \frac{1}{|\vec{r}|} - \vec{\nabla}(\vec{\mu}_N \cdot \vec{\nabla}) \frac{1}{|\vec{r}|} \right] \\ &= -\frac{e}{m_e} \vec{S}_e \cdot \left[\frac{Ze}{2m_N} g_N \vec{I} \vec{\nabla}^2 \frac{1}{|\vec{r}|} - \vec{\nabla} \left(\frac{+Ze}{2m_N} g_N \vec{I} \cdot \vec{\nabla} \right) \frac{1}{|\vec{r}|} \right] \\ &= -\frac{Ze^2 g_N}{2m_N m_e} \left[\vec{S}_e \cdot \vec{I} \vec{\nabla}^2 \frac{1}{|\vec{r}|} - S_i I_j \vec{\nabla}(\vec{\nabla}) \frac{1}{|\vec{r}|} \right] \quad (44) \end{aligned}$$

According to perturbation theory, the first order correction to the energy is the expectation value of the unperturbed Hamiltonian:

$$\begin{aligned} &\langle l s j | I F M_F | H_{HF} | l s j | F M_F \rangle \\ &= -\frac{Ze^2 g_N}{2m_N m_e} \left[\langle \vec{S}_e \cdot \vec{I} \vec{\nabla}^2 \frac{1}{|\vec{r}|} \rangle - \langle S_i I_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \frac{1}{|\vec{r}|} \rangle \right] \quad (45) \end{aligned}$$

where l , s and j are respectively the quantum numbers of orbital angular momentum, spin and total angular momentum of the electron, I is the quantum number of the nuclear spin, F is the quantum number of the total angular momentum of the atom and M_F is of its z -component quantum number. The second term in (45) can be simplified because of the spherical symmetry of s states. (Basically the derivative with respect to x is odd in x so when the integral is done, only the terms where $I = j$ are nonzero).

$$\int d^3 r |\psi_{n00}|^2 \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \frac{1}{|\vec{r}|} = \frac{\delta_{ij}}{3} \int d^3 r |\psi_{n00}|^2 \vec{\nabla}^2 \frac{1}{|\vec{r}|} \quad (46)$$

So we have

$$\langle H_{HF} \rangle = -\frac{2}{3} \frac{Ze^2 g_N}{2m_N m_e} \langle \vec{S}_e \cdot \vec{I} \nabla^2 \frac{1}{|\vec{r}|} \rangle \quad (47)$$

Now working out the ∇^2 term in spherical coordinates,

$$\nabla^2 = \left(\frac{\partial^2}{\partial r^2} - \frac{2}{r} \frac{\partial}{\partial r} \right) \frac{1}{r} = \frac{2}{r^3} + \frac{2}{r} \left(\frac{1}{r^2} \right) = 0$$

We find that it is zero everywhere but we must be careful at $r = 0$. To find the effect at $r = 0$ we will integrate.

$$\begin{aligned} \langle \nabla^2 \frac{1}{r} \rangle &= \int_{r=0}^{\epsilon} \nabla^2 \frac{1}{r} d^3r = \int_{r=0}^{\epsilon} \vec{\nabla} \cdot \left(\vec{\nabla} \frac{1}{r} \right) d^3r \\ &= \int \left(\vec{\nabla} \frac{1}{r} \right) \cdot d\vec{s} = \int \frac{\partial}{\partial r} \frac{1}{r} d\vec{s} \\ d\vec{s} &= \int_{r=0}^{\epsilon} \frac{-1}{r^2} d\vec{s} = (4\pi\epsilon^2) \frac{-1}{\epsilon^2} = -4\pi \end{aligned}$$

So the integral is non zero for any region including the origin. Therefore

$$\begin{aligned} \langle H_{HF} \rangle &= -\frac{2}{3} \frac{Ze^2 g_N}{2m_N m_e} \vec{S}_e \cdot \vec{I} (-4\pi |\psi_{n00}(0)|^2) \\ &= \frac{4}{3} (Z\alpha)^4 \left(\frac{m_e}{m_N} \right) (m_e c^2) g_N \frac{1}{n^3} \left(\frac{\vec{S}_e \cdot \vec{I}}{\hbar^2} \right) \quad (48) \end{aligned}$$

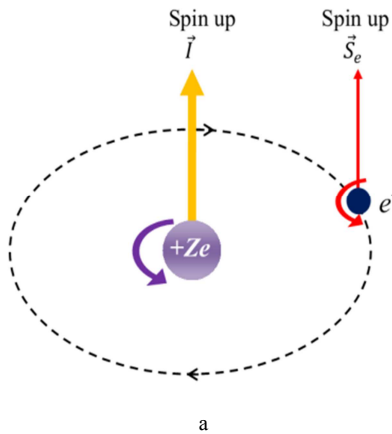
Now, just as in the case of the $\vec{S} \cdot \vec{L}$, spin-orbit interaction, to solve (48) it is convenient to define the total spin $\vec{F} = \vec{S} + \vec{I}$. Then we have

$$\vec{S} \cdot \vec{I} = \frac{1}{2} (\vec{F}^2 - \vec{S}^2 - \vec{I}^2) = \frac{1}{2} \hbar^2 \left[f(f+1) - \frac{3}{4} - \frac{3}{4} \right] \quad (49)$$

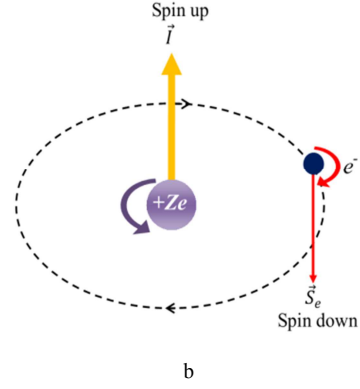
The energy of the electron in magnetic field, due to the proton's magnetic dipole moment, is

$$E_{HF} = -E_n \frac{4}{3} \left(\frac{Z\alpha}{n} \right)^2 n \left(\frac{m_e}{m_N} \right) g_N \left[f(f+1) - \frac{3}{2} \right] \quad (50)$$

If the spins are parallel (or, more precisely, if they are in the triplet state), the total spin is 1, and hence $f(f+1) = 2$, the energy is higher than it is when the spins are antiparallel (the single state) where the total spin is 0, and $f(f+1) = 0$.



a



b

Figure 2. (a) The triplet state (b) The singlet state.

Thus

$$\begin{aligned} E_{\text{triplet}} &= -E_n \frac{1}{3} \left(\frac{Z\alpha}{n} \right)^2 \left(\frac{m_e}{m_N} \right) n g_N \\ E_{\text{singlet}} &= -E_n \left(\frac{Z\alpha}{n} \right)^2 \left(\frac{m_e}{m_N} \right) n g_N \end{aligned} \quad (51)$$

The measured value of gyromagnetic ratio of proton g_N is 5.59. Therefore the energy difference is

$$\Delta E_{HF} = \frac{2}{3} E_n \left(\frac{Z\alpha}{n} \right)^2 \left(\frac{m_e}{m_N} \right) n g_N = 5.9 \times 10^{-6} \text{ eV} \quad (52)$$

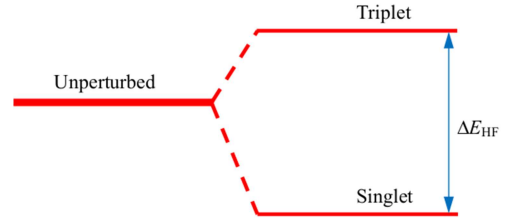


Figure 3. Hyper fine splitting in the ground state of hydrogen atom.

3.3. Vacuum Fields Fluctuations

As the electron moves through the vacuum fields, it jiggles slightly and as the result the coupling of the electron with the nucleus weakens and therefore the average value of its potential energy required additional displacement δr . Since δr is very small, the effective potential at point $U(r + \delta r)$ can be simplified using the Taylor expansion as:

$$U(r + \delta r) = U(r) + \delta r \cdot \vec{\nabla} U(r) + \frac{1}{2} (\delta r \cdot \vec{\nabla})^2 U(r) + \dots$$

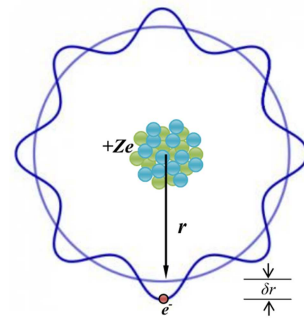


Figure 4. A cartoon depicting the jittery motion of a point – like electron due absorption and emission of virtual photons.

And therefore, the average modified potential can be written as:

$$\langle U(r + \delta r) \rangle = \langle U(r) \rangle + \langle \delta r \rangle \cdot \vec{\nabla} U(r) + \frac{1}{2} \langle (\delta r \cdot \vec{\nabla})^2 \rangle U(r) + \dots \quad (53)$$

Since δr is an oscillator, $\langle \delta r \rangle = 0$ but its average square value:

$$\langle (\delta r \cdot \vec{\nabla})^2 \rangle = \frac{1}{3} \langle \delta r^2 \rangle \vec{\nabla}^2 \quad (54)$$

Thus, equation (53) can take the form:

$$\langle U(r + \delta r) \rangle = \langle U(r) \rangle + \frac{1}{6} \langle \delta r^2 \rangle \vec{\nabla}^2 U(r) \quad (55)$$

The perturbed potential is therefore:

$$U'(r) = \frac{1}{6} \langle \delta r^2 \rangle \vec{\nabla}^2 U(r) \quad (56)$$

We can determine the displacement δr by considering the lowest (or zeroth) energy level of the electromagnetic field quantized as a harmonic oscillator is

$$E = \left(n + \frac{1}{2} \right) \hbar \omega$$

where $\hbar \omega$ is the quantum of energy and n the number of photons, $n = 0$ when there are no photons. Thus, there exists an energy given by

$$E_\omega = \frac{1}{2} \hbar \omega$$

But if we have fluctuating electric and magnetic fields \mathcal{E} and \mathcal{H} respectively, then the fluctuating electric field is

$$E_\omega = \frac{1}{8\pi} \int (\mathcal{E}^2 + \mathcal{H}^2) d\omega = \frac{\mathcal{E}_0^2}{4\pi} \Omega$$

where $\langle \mathcal{E}^2 \rangle_t = \langle \mathcal{H}^2 \rangle_t$ since we have a set of plane waves. From (54) and (55) we find:

$$\langle \mathcal{E}_0^2 \rangle = \frac{2\pi}{\Omega} \hbar \omega \quad (57)$$

To calculate the displacement δr of the electron motion, we consider the equation of motion of a simple harmonic oscillator of mass m and frequency ω , that is

$$\ddot{r} = -\omega^2 r \quad (58)$$

If it is assumed that the electron is bound to the atom harmonically, then

$$\begin{aligned} m\omega^2 \delta r &= -e\mathcal{E}_0 \\ \Rightarrow \delta r &= -\frac{e}{m\omega^2} \mathcal{E}_0 \end{aligned} \quad (59)$$

Since δr is an oscillation it means that $\langle \delta r \rangle_t = 0$. Therefore its mean square oscillation is

$$\langle \delta r^2 \rangle_t = \frac{e^2}{m^2 \omega^4} \langle \mathcal{E}_0^2 \rangle_t = \frac{2\pi}{\Omega} \frac{\hbar e^2}{m^2 \omega^3} \quad (60)$$

The full mean square fluctuation is the result of non-coherent action of all components of the field,

$$\langle \delta r_0^2 \rangle_t = \int \langle \delta r^2 \rangle_t \rho(\omega) d\omega \quad (61)$$

where $\rho(\omega)$ is the density of states for the field and has the value

$$\rho(\omega) d\omega = \frac{\Omega \omega^2 d\omega}{\pi^2 c^3}$$

Therefore,

$$\langle \delta r_0^2 \rangle_t = \frac{2\hbar e^2}{\pi m^2 c^3} \int_{\omega_0}^{\infty} \frac{d\omega}{\omega} \quad (62)$$

This result is formally divergent, but there are physical factors that cut off the integral. At large frequencies there occurs the relativistic growth of the electrons mass; for small frequencies, $\hbar \omega \ll$ distance to the first excited state, the perturbation does not work.

The divergence is only logarithmic so that it is sufficient to estimate those limits approximately, so we have

$$\hbar \omega_{\max} \sim mc^2; \hbar \omega_{\min} \sim \Delta E_{\text{Hydrogen}} \sim (Z\alpha)^2 mc^2$$

With these approximations we can evaluate the integral and have the mean square oscillation as

$$\langle r_0^2 \rangle = \frac{2\hbar e^2}{\pi m^2 c^3} \ln \left[\frac{f}{(Z\alpha)^2} \right] \quad (63)$$

where f is a numerical factor. Since the electron wave function varies slowly over the nuclear volume, the energy level ΔE_n of an electron in a state ψ_n will depend partly on the expectation of the perturbed potential:

$$\Delta E_n = \frac{1}{6} \int \vec{\nabla}^2 U(r) \langle r_0^2 \rangle |\psi_n|^2 d\tau$$

The intensity of the wavefunction corresponding to s states is

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

The Laplacian of a potential (5) corresponding to a nucleus of charge density ρ_0 is given by:

$$\vec{\nabla}^2 U(r) = 4\pi e \rho_0$$

Using equation (56), we can calculate the direct effect of vacuum fields' fluctuation as

$$\Delta E_n = |E_n| \frac{8}{3\pi} \alpha^3 \frac{Z^2}{n} \ln \left[\frac{f}{(Z\alpha)^2} \right] \quad (64)$$

where the use of equation (56) have been made.

The Quantum mechanics calculation of vacuum field fluctuations due to Bethe [37, 38] results in an energy shifts:

$$\Delta E_{nlm} = |E_n| \frac{8}{3\pi} \alpha^3 \frac{Z^2}{n} \ln \left[\frac{v_{\max}}{v_{\min}} \right] \quad (65)$$

By virtue of the modified Dirac equation, Das and Sidharth [39] obtained the energy shift ΔE of frequency $f \approx 1056 \text{ MHz}$

which is very nearly equal to the *Lamb shift*.

3.4. The Finite-Size Nucleus

The atomic spectra are slightly affected by the finite-size of atomic nucleus. If the nucleus is being described as a finite-size source with a uniform distribution of charges of radius R , then the electron wave function can penetrate to $r \leq R$, and thus the electron spends part of its time inside the nuclear charge distribution, there it feels a very different interaction and the potential for a finite-size nucleus is given as [9, 40, 41]:

$$U(R) = -\frac{Zke^2}{R} \left(\frac{3}{2} - \frac{1}{2} \frac{r^2}{R^2} \right) \quad (66)$$

where $R = r_0 A^{1/3}$, with $r_0 = 1.2 \times 10^{-15} m$. The magnitude of the nuclear size effect can be accurately calculated by the use of perturbation theory [42, 43].

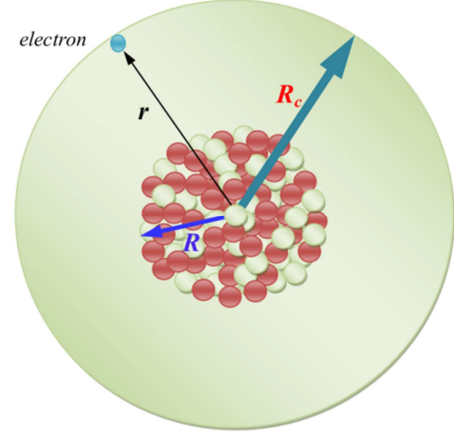


Figure 5. The Finite-Size Nucleus.

The energy level shifts ΔE_{nlm} of an electron in a state ψ_{nlm} due to the finite size of nucleus can be calculated using (13) as

$$\Delta E_{nlm} = \int \psi_{nlm}^* \{U(R) - U(r)\} \psi_{nlm} d\tau = \frac{Zke^2 4\pi}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{nlm}|^2 r^2 dr \quad (67)$$

The normalized wave function ψ_{nlm} is given by:

$$\psi_{nlm}(r, \theta, \phi) = \left[\left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!} \right]^{\frac{1}{2}} e^{-\frac{ar}{2}} (ar)^l L_{n-l-1}^{2l+1}(ar) Y_l^m(\theta, \phi) \quad (68)$$

Regular solutions exist for $n \geq l + 1$ and the lowest state with $l = 1$ (called a $2p$ state) occurs only with $n = 2$ [44, 45]. Thus, electrons can be grouped related to the quantum number n they occupy, as $1s, 2s, 2p, 3s, 3p, 3d$, and so on. Taking the approximation $r \ll a_0$, i.e., $e^{-Zr/a_0} \approx 1$ and for a constant wave function over the region of integration, the perturbative corrections in the states s, p and d can be obtain using the normalized wave function above as:

$$\Delta E_{100} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{100}|^2 d\tau = 0.8 |E_3| \xi^0$$

$$\Delta E_{200} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{200}|^2 d\tau = 0.2 |E_2| \xi^1$$

$$\Delta E_{210} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{210}|^2 d\tau = 0.008 |E_2| \xi^2$$

$$\Delta E_{21\pm 1} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{21\pm 1}|^2 d\tau = 0.008 |E_2| \xi^2$$

$$\Delta E_{300} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{300}|^2 d\tau = 0.23 |E_3| \xi^1$$

$$\Delta E_{310} = \frac{Zke^2}{R} \int \psi_{310}^* \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} \psi_{310} d\tau = |E_3| \xi^2$$

$$\Delta E_{31\pm 1} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{31\pm 1}|^2 d\tau = 0.01 |E_3| \xi^2$$

$$\Delta E_{320} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{320}|^2 d\tau = 0.00002 |E_3| \xi^3$$

$$\Delta E_{32\pm 1} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{32\pm 1}|^2 d\tau = 0.0001 |E_3| \xi^3$$

$$\Delta E_{32\pm 2} = \frac{Zke^2}{R} \int \left\{ \frac{r^2}{2R^2} - \frac{R}{r} - \frac{3}{2} \right\} |\psi_{32\pm 2}|^2 d\tau = 0.013 |E_3| \xi^3$$

This correction is therefore of order $\zeta = (R/a_0)^2 = 5 \times 10^{-10}$.

4. Results and Conclusions

Table 1 showed spectral lines calculated using equation (7). The spectrum depends exclusively on the principal quantum number n since an electron is solely subject to the electrostatic influence of the nucleus.

Table 1. The electromagnetic spectrum as described by Bohr.

| Transitions ($n \rightarrow m$) | λ (nm) | Spectrum |
|-----------------------------------|----------------|-------------|
| Layman Series ($n = 1$) | | |
| $2 \rightarrow 1$ | 122.324 | Ultraviolet |
| $3 \rightarrow 1$ | 103.209 | Ultraviolet |
| $4 \rightarrow 1$ | 97.859 | Ultraviolet |
| $5 \rightarrow 1$ | 95.565 | Ultraviolet |
| $6 \rightarrow 1$ | 94.366 | Ultraviolet |
| $7 \rightarrow 1$ | 93.653 | Ultraviolet |
| $8 \rightarrow 1$ | 93.206 | Ultraviolet |
| $9 \rightarrow 1$ | 92.895 | Ultraviolet |
| Balmer Series ($n = 2$) | | |
| $3 \rightarrow 2$ | 660.550 | Red |
| $4 \rightarrow 2$ | 489.296 | Violet |
| $5 \rightarrow 2$ | 436.872 | Violet |
| $6 \rightarrow 2$ | 412.844 | Violet |
| $7 \rightarrow 2$ | 399.578 | Violet |
| $8 \rightarrow 2$ | 391.562 | Violet |
| $9 \rightarrow 2$ | 386.124 | Violet |
| Paschen Series ($n = 3$) | | |
| $4 \rightarrow 3$ | 1887.718 | Infrared |
| $5 \rightarrow 3$ | 1290.339 | Infrared |
| $6 \rightarrow 3$ | 1101.359 | Infrared |
| $7 \rightarrow 3$ | 1011.500 | Infrared |
| $8 \rightarrow 3$ | 960.660 | Infrared |
| $9 \rightarrow 3$ | 928.950 | Infrared |
| Brackett Series ($n = 4$) | | |
| $5 \rightarrow 4$ | 4077.719 | Infrared |
| $6 \rightarrow 4$ | 2642.371 | Infrared |
| $7 \rightarrow 4$ | 2179.689 | Infrared |
| $8 \rightarrow 4$ | 1957.395 | Infrared |
| $9 \rightarrow 4$ | 1829.374 | Infrared |
| Pfund Series ($n = 5$) | | |
| $6 \rightarrow 5$ | 7507.620 | Infrared |
| $7 \rightarrow 5$ | 4683.161 | Infrared |
| $8 \rightarrow 5$ | 3764.592 | Infrared |
| $9 \rightarrow 5$ | 3320.417 | Infrared |
| Series ($n = 6$) | | |
| $7 \rightarrow 6$ | 12448.184 | Infrared |
| $8 \rightarrow 6$ | 7550.874 | Infrared |
| $9 \rightarrow 6$ | 5945.763 | Infrared |
| Series ($n = 7$) | | |
| $8 \rightarrow 7$ | 20969.855 | Infrared |
| $9 \rightarrow 7$ | 11986.297 | Infrared |
| Series ($n = 8$) | | |
| $9 \rightarrow 8$ | 27978.993 | Infrared |

It can be observed from our results (34), (52), (64) and (69) that there is a deviation in the atomic spectra calculated from equation (7). Equation (34) showed that the combined energy shifts due to fine structure effect yield one formula in which l

drops out. This showed that the fine structure effect depends on the principle quantum number, n and the total angular momentum, j and that the splitting between the $j = l + \frac{1}{2}$ and the $j = l - \frac{1}{2}$ states is of order $(Z\alpha)^2 E_n$.

Table 2 showed that with $l = 0$ and $j = -\frac{1}{2}$, both $1s_{1/2}$ and $2s_{1/2}$ states, experience a energy shift, while with $j = +\frac{1}{2}$, both the former $2s_{1/2}$ state, and the latter $2p_{1/2}$ states share the same shift in energy and the pairs of states $3s_{1/2}$ and $3p_{1/2}$, and $3p_{3/2}$ and $3d_{3/2}$ each remain degenerate while the state $3d_{5/2}$ is unique. The very small energy shift between the states: $2s_{1/2}$ and $2p_{1/2}$; $3s_{1/2}$ and $3p_{1/2}$; $3p_{3/2}$ and $3d_{3/2}$ is known as the Lamb shift.

The Lamb shift of $2s_{1/2}$ and $2p_{1/2}$ states for hydrogen atom ($Z = 1$) for $n = 2$ was measured from equation (64) as

$$\Delta E_n = 5.52 \times 10^{-6} \text{ eV}$$

And the corresponding frequency is $\approx 1023 \text{ MHz}$. Lamb and Retherford calculated the splitting using equation (65) and found that the $2s_{1/2}$ state is shifted by about 1000 MHz .

Table 2. The nuclear structure corrections to energies of $n = 1$, $n = 2$ and $n = 3$ states of hydrogen atom.

| Orbitals | Energy Shift (eV) | |
|------------|-------------------------|-----------------------|
| | Fine structure | The Lamb Shift |
| $1s_{1/2}$ | 1.8115×10^{-4} | 5.52×10^{-6} |
| $2s_{1/2}$ | 2.8305×10^{-6} | |
| $2p_{1/2}$ | 2.8305×10^{-6} | |
| $2p_{3/2}$ | 8.4898×10^{-6} | |
| $3s_{1/2}$ | 2.4843×10^{-7} | The Lamb Shift |
| $3p_{1/2}$ | 2.4843×10^{-7} | |
| $3p_{3/2}$ | 7.4543×10^{-7} | The Lamb Shift |
| $3d_{3/2}$ | 7.4543×10^{-7} | |
| $3d_{5/2}$ | 1.7393×10^{-6} | |

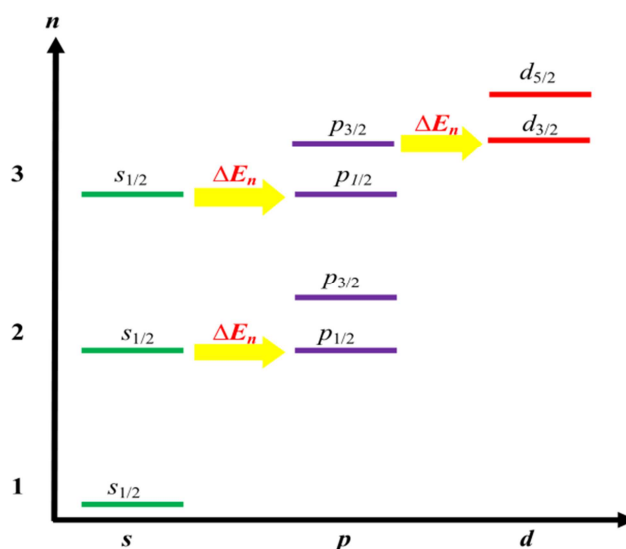


Figure 6. The Fine Structure splitting and the Lamb shift, ΔE_n .

Since the proton has spin $\frac{1}{2}$, the quantum number f has possible values $f = j + \frac{1}{2}$, $j - \frac{1}{2}$. Hence every energy level associated with a particular set of quantum numbers n , l , and j will be split into two levels of slightly different energy, depending on the relative orientation of the proton magnetic dipole with the electron state. The energy separation of the

hyperfine interaction is given by (52). Therefore, for ground state of the hydrogen atom ($n=1$), the energy separation between the states of $f=1$ and $f=0$ is $5.9 \times 10^6 eV$. The frequency of the photon emitted in a transition from the triplet to the singlet state is

$$f = \frac{\Delta E_{HF}}{h} = 1420 MHz$$

with a corresponding to a wavelength of

$$\lambda = \frac{c}{f} = \frac{3 \times 10^8 m/s}{1420 \times 10^6 Hz} = 21 cm$$

Thus, transitions between these levels occur at 21 cm.

The corrections to energies of $n=1$, $n=2$ and $n=3$ states of hydrogen atom due to finite – size charge distribution of nucleus were computed using the results obtained by equation (67) and the results are shown in Figure 7.

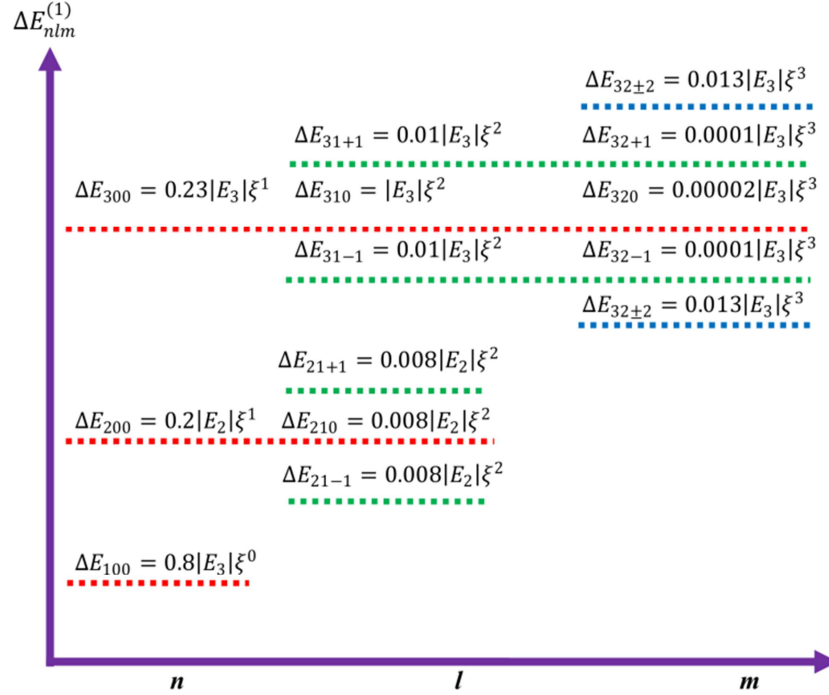


Figure 7. The finite nuclear size corrections $\Delta E_{nlm}^{(1)}$ to energies of $n=1$, $n=2$ and $n=3$ states of hydrogen atom with their corresponding values of l and m .

Figure 7 shows the corrections factor for the $1s$, $2s$ and $3s$ energy orbital is ξ and for the $2p$ and $3p$ energy orbital is ξ^2 while the $3d$ energy orbital has the correction factor of ξ^3 . Thus the effect of a finite size of the nucleus on energy level is largest in the lowest state, $1s$ electron than that in any other state. Next come $2s$, $3s$, $2p$, $3p$, $3d$, etc. Non- s orbitals have a much smaller fraction inside the nucleus and so cause smaller perturbation, the energy shift is much smaller. The finite-size nucleus gives an extremely small effect on the $3d$ orbitals.

The atomic spectra can be described in the first approximation by solving the Schrodinger equation for the electrons in the central potential which described the spectral terms by the principal quantum number n and the orbital angular momentum quantum number l . In the Schrödinger equation, the spin of the electron is not taken into consideration.

Dirac using his equation describes the relativistic effects which in which the orbital angular momentum quantum numbers are further split into $l \pm \frac{1}{2}$ states due to a coupling between the electron spin s and orbital angular momentum. Consequently the spectral lines arising from transitions between the energy levels are each split into several lines. These effects play a significant role in systems containing heavy atoms.

The solution of the Dirac version of Schrodinger equation

leaves several states degenerate. However, Lamb and Retherford showed that, there is an energy shift in the $2S_{1/2}$ and $2P_{1/2}$ caused by the interaction of the electron with the quantum radiation field and the corresponding frequency is measured as about 1000 MHz.

In the first approximation, both Schrödinger and Dirac equation was derived based on the assumptions that the atomic nucleus has a point-like charge of infinite mass. The results obtained from the proton and neutron investigations [46-51] have been interpreted as evidence that the atomic nucleus is not truly point-like, instead exhibits finite-size structure in both its mass and charge distribution. Although the results obtained from this correction (Figure 7), is very small as compared to other effects, it will reflect on the nature of the atomic spectra.

Atoms, molecules or ions absorb radiation in different regions of the electromagnetic spectrum in which the energy of such radiation is in proportion with its energy of wavelength. Thus, splitting or shifts in energy or wavelength will significantly alter the spectrum.

Correct identification of nuclear structure effects in atomic transitions is very important in connection with accurate theoretical atomic or molecular structure calculations involving quantum chemistry, quantum physics or quantum electrodynamics corrections. This can be tested in

high-precision experiments.

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