



Eigenvalues of the Hamiltonian Fine structure of the Hydrogen Like Systems: Semi-Relativistic Theory of Sakho vs Relativistic Theory of Dirac

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ABSTRACT

Purpose of the study: The goal of this work is to present a comparative study between the semi-relativistic theory of Sakho and the relativistic theory of Dirac applied to calculations of the eigenvalue of the Hamiltonian fine structure of the hydrogen like systems. The three small perturbative corrections (relativistic mass correction, spin-orbit coupling, and the Darwin term) of the Hamiltonian are considered.

Methodology: This research is based on correction of the semi-classical Bohr's theory on the hydrogen like systems considering the relativistic mass correction by ignoring the electron's spin. This approach referred to as semi-relativistic theory allows one to express the eigenvalues of the Hamiltonian fine structure to be compared to that from the relativistic wave function of Dirac

Main Findings: The research gives the first expression of the quantized energy of hydrogen like systems taking only into account, the relativistic mass correction. This result provides exactly the eigenvalues of the Hamiltonian fine structure predicted from Dirac's relativistic theory for all the non-degenerated quantum states n^2L_j ($j = l \pm s$) of the hydrogen like systems (i.e. $1^2s_{1/2}$, $2^2p_{3/2}$, $3^2d_{5/2}$, $4^2f_{7/2}$, and so on).

Novelty/Originality of this study: Theoretical determination of the eigenvalue of the Hamiltonian fine structure predicted from Dirac's relativistic theory for all the non-degenerated quantum states is obtained with a soft semi-relativistic theory without including in the calculations the spin-orbit coupling and the Darwin term corrections.

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1. INTRODUCTION

An atom is defined as a nucleus around which a cloud of electrons orbits according to the planetary atomic model [1-4] proposed by Ernest Rutherford in 1911. In 1913, Bohr formulated three postulates [5-7] explaining coherently the emission of spectral lines within his semi-classical approach [1, 2, 8]. One of the first relativistic corrections to Bohr's model was made by Arnold Sommerfeld in 1916 within the framework of the Bohr-Sommerfeld model allowing elliptical orbits of electrons around an atomic nucleus [1, 2, 9]. This model permits the discovery of the orbital quantum number. In 1928, Paul Dirac developed a fundamental relativistic wave equation describing spin-1/2 particles, such as the electron [4, 9, 10]. This relativistic model coherently interprets the fine structure of spectral lines in the hydrogen-like systems.

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In 1993, Ibrahima Sakho, planned to provide a semi-relativistic correction to the Bohr model by considering only the variation of the electron's mass with velocity [11]. The goal of this work is firstly to give an overview of the means relativistic theories devoted to the corrections of the semi-classical Bohr's theory on the hydrogen like systems and secondly, to present for the first time, a comparative study between the semi-relativistic theory of Sakho and the relativistic theory of Dirac applied to the calculations of the eigenvalues of the Hamiltonian fine structure of the hydrogen like systems. Section 2 gives an overview of the semi-classical Bohr's theory on the hydrogen like systems and of the means relativistic theories devoted to the corrections of the Bohr's model. Section 3 presents a comparison between the semi-relativistic theory of the relativistic theory of Dirac.

2. OVERVIEW OF THE MEANS RELATIVISTIC THEORIES ON THE HYDROGEN LIKE SYSTEMS

2.1. Semi-Classical Bohr's Theory

2.1.1. The Bohr's postulates

In 1913, two years after the first Solvay Congress, Bohr formulated two fundamental postulates to develop his semi-classical theory on the hydrogen atom:

First postulate: an atom (or an atomic system) cannot be in all states predicted by classical mechanics. Only certain quantum states characterized by well-defined discrete values of energy $E_1, E_2, E_3, \dots$, can be occupied by atomic systems. Contrary to the predictions of classical electrodynamics, an atom occupying these so-called stationary states emits no radiation. Second postulate: during the transition from a higher-energy stationary state E_n to another stationary state of lower energy E_p , the energy of the atom changes by the amount $\Delta E = E_n - E_p$. If this energy change is due to the emission of radiation, this process is then accompanied by the emission of a photon of pulsation ω and frequency $\nu = c/\lambda = \omega/2\pi$:

$$\Delta E = |E_n - E_p| = h\nu. \quad \dots (1)$$

Introducing the reduced Planck's constant $\hbar = h/2\pi$, ΔE is then given by :

$$\Delta E = |E_n - E_p| = \hbar\omega = \frac{hc}{\lambda}. \quad \dots(2)$$

The first postulate introduces the quantization of the energy E_n along with the notion of stationary states, explaining the fact that electrons in rotational motion around the nucleus do not emit energy. The second postulate indicates what happens when an atomic system transit from one stationary state to another one. This corresponds to the emission or absorption of a photon with energy $h\nu$ explaining then the origin of spectral lines (fig.1).

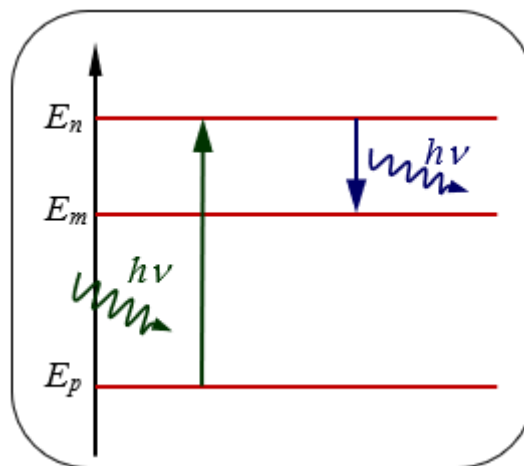


Figure 1. Electronic transitions.

- (a) Process of absorption of a photon $h\nu$; which corresponds to an excitation of the atom.
- (b) Process of emission of a photon $h\nu'$; which corresponds to a de-excitation of the atom.

2.1.2. The Bohr's Principle Quantization of the Angular Momentum

The Bohr's model of the quantized atom is based on two main approximations:

1. Approximation of circular electron orbits: the orbit of an electron is a circle of radius r centered on the nucleus;

2. Approximation of an infinitely heavy fixed nucleus: the reduced mass of the {nucleus-electron} system is equal to the rest mass $m = m_0$ of the electron.

The notion of an orbit is a purely classical concept. Quantum mechanics developed later (1926) rejects this notion. This justifies the semi-classical nature of the Bohr's theory applied to the hydrogen atom. Let's then consider an electron of mass m moving around the nucleus of the hydrogen atom of mass M as shown in Figure 2. Here, v denotes the value of the orbital speed of the electron orbiting the nucleus (here the proton).

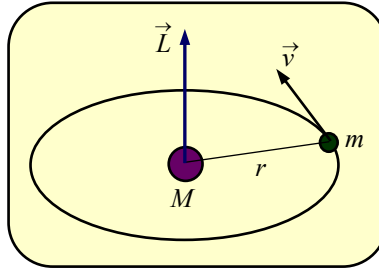


Figure 2. Angular momentum $\vec{L}$ of the electron

By definition, the angular momentum of the electron is the moment of its momentum $\vec{p} = \vec{m} \vec{v}$, so :

$$\vec{L} = \vec{r} \wedge \vec{p} = \vec{m} \vec{r} \wedge \vec{v} \quad \dots(3)$$

The direction of the angular momentum is such that the triad $(\vec{r} \vec{v} \vec{L})$ is right-handed. The speed vector and the position vector being perpendicular, then:

$$L = mrv \quad \dots(4)$$

To establish the quantized expression of the electronic orbit radius, Bohr stated the principle of quantization of the angular momentum. Only electronic orbits characterized by discrete values of angular momentum are allowed:

$$\vec{L} L = n \frac{h}{2\pi} = n \hbar \quad \dots(5)$$

It should be mentioned that, equation (5) is often considered as the third postulate of Bohr. But this is not correct since it is generally considered that a postulate cannot be demonstrated. Postulates are propositions that are accepted as true without proof, and that serve as a basis for establishing theorems or more complex demonstrations. It is the case of the two postulates of Bohr enounced above and the six postulates of quantum mechanics such as the famous Schrodinger's postulate in 1926 by the Austrian physicist Erwin Schrodinger's. Let's demonstrate Eq. (5) by two different ways.

First way: analogous to Planck's quantization condition of the linear harmonic oscillator in phase space

Within the framework of the Bohr-Sommerfeld model (see subsection 2.2), the quantization condition of the orbital angular momentum is analogous to Planck's quantization condition of the linear harmonic oscillator in phase space:

$$\oint p dq = nh \quad \dots(5)$$

Sommerfeld and Wilson applied the same form of quantization (5) to the radial vector and to the azimuthal angle (this condition was proposed independently by American chemist William Wilson and Germanic physicists Arnold Sommerfeld).

Thus, within the framework of the Bohr-Sommerfeld model, the quantization condition of angular momentum called the Wilson-Sommerfeld rule is written as:

$$\vec{L} \oint p_r dr = n_r h ; \oint p_\phi d\phi = n_\phi h \quad \dots(6)$$

In Eqs. (6), $p_r = mv$, v the orbital speed of the electron, and n_r is the radial quantum number and n_ϕ the azimuthal quantum number, n_r can be positive or zero while n_ϕ is strictly positive (the value $n_\phi = 0$ is forbidden since it would mean that the semi-minor axis b is zero giving an ellipse degenerated into a line).

Within the framework of the Bohr model, the radius r is constant (circular orbit) and the angular momentum $L = mrv$ is also constant. Using the second relation (6), we obtain (by replacing p_ϕ with L):

$$\oint L d\varphi = nh \Rightarrow \int_0^{2\pi} d\varphi = nh \quad \dots(7)$$

The integration of Eq. (7) provides the Bohr's principle quantization of the angular momentum (5).

$$L = n \frac{h}{2\pi} = n\hbar$$

Second way: De Broglie atomic model of wave electronic orbits

In 1923, French physicist Louis de Broglie hypothesized that all matter exhibits both wave and particle properties known as wave-particle duality [12, 13]. According to this hypothesis, the wavelength λ of a particle is inversely proportional to its momentum p , the constant of proportionality been equal to the Planck's constant h . So:

$$\lambda = \frac{h}{p} \quad \dots(8)$$

De Broglie argued that Bohr's quantization hypothesis could be explained if the electron was not considered as a particle, but rather as a circular standing wave, as shown in Figure 3.

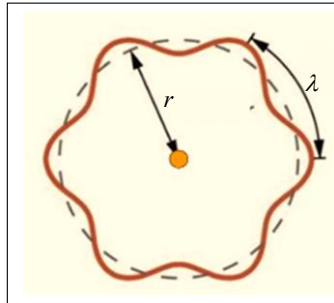


Figure 3. Wave electronic orbit according to the De Broglie's atomic model

For a circular orbit of radius r , the circumference is $2\pi r$, the de Broglie condition for constructive interference is:

$$2\pi r = n\lambda, n=1,2,3,\dots \quad \dots(9)$$

Let's use Eqs. (8) and (9). We find

$$2\pi r p = 2\pi m v r = nh \Rightarrow L = n \frac{h}{2\pi}$$

We obtain again equation (5).

2.1.3 Quantization of Electronic Orbits, Bohr Radius

Using Eqs. (4) and (5) we get:

$$mvr = nh. \quad \dots(10)$$

Let us now move on to the dynamic study of the circular motion of the electron of the hydrogen atom (fig.4).

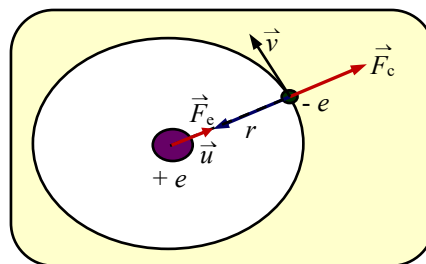


Figure 4. Forces applied to the electron of the hydrogen atom.

In the reference frame related to the nucleus, the total energy (potential and kinetic energies) of the {nucleus–electron} system is given by the relation:

$$E = \frac{1}{2}mv^2 - \frac{e^2}{r} \quad \dots(11)$$

On its circular orbit, the electron is subjected to the centripetal electric force $\vec{F}_e$ and the centrifugal force $\vec{F}_c$. These forces are given by the well-known expressions:

$$\vec{F}_e = -k \frac{e^2}{r^2} \vec{u} ; \vec{F}_c = m \vec{a}_n = m \frac{v^2}{r} \vec{u} \quad \dots(12)$$

The stability of the electron's orbit is expressed by the principle of inertia, namely:

$$\sum \vec{F}_{ext} = \vec{F}_e + \vec{F}_c = \vec{0}. \quad \dots(13)$$

So we get :

$$-k \frac{e^2}{r^2} \vec{u} + m \frac{v^2}{r} \vec{u} = \vec{0} \quad \dots(14)$$

Using Eq. (14), we find :

$$-k \frac{e^2}{r^2} = m \frac{v^2}{r} \Rightarrow mv^2 = k \frac{e^2}{r} \quad \dots(15)$$

Let's derive the square of the speed from relation (10), we get:

$$(mvr)^2 = n^2 \hbar^2 \Rightarrow v^2 = \frac{n^2 \hbar^2}{m^2 r^2} \quad \dots(16)$$

By substituting the expression of v^2 into the last of the equalities (15), we obtain:

$$m \frac{n^2 \hbar^2}{m^2 r^2} = k \frac{e^2}{r} \Rightarrow \frac{n^2 \hbar^2}{mr_n} = ke^2.$$

The quantified expression of the radius r_n is then written:

$$r_n = \frac{n^2 \hbar^2}{mke^2} = a_0 \times n^2. \quad \dots(17)$$

For $n = 1$, we obtain the radius of the first orbit: $r_1 = a_0$. By definition, a_0 is called the Bohr radius with :

$$a_0 = r_1 = \frac{\hbar^2}{mke^2}. \quad \dots(18)$$

2.1.4 The Bohr's Quantized Energy of the Hydrogen Atom, Rydberg Unit

Let's substitute the expression of mv^2 given by equation (15) into relation (11). The total energy of the {nucleus – electron} system is then written as:

$$E = -k \frac{e^2}{2r}. \quad \dots(19)$$

The radius of the electronic orbit being quantized according to (17), then:

$$E_n = -k \frac{e^2}{2r_n}. \quad \dots(20)$$

Hence the quantized expression of the energy of the hydrogen atom is written as:

$$E_n = -\frac{k^2 me^4}{2\hbar^2 n^2}. \quad \dots(21)$$

Major Contributions

Bohr was born on October 7, 1885, in Copenhagen (Denmark). He died on November 18, 1962, in Copenhagen (Denmark). In 1913, he published in the "Philosophical Magazine" a description of what the atomic structure is according to him. His theory earned the interest of great figures such as Albert Einstein and would later be experimentally confirmed. The two physicists would meet on multiple occasions between 1927 and 1935 to discuss their disagreements concerning quantum theory. These exchanges would form the basis of the "Philosophical Writings" published by Bohr.

2.2. Bohr-Sommerfeld Model

2.2.1. Description, Elliptical Orbits

The Bohr's model is based on the approximation of circular orbits. In 1916, German physicist Arnold Sommerfeld considered that electronic orbits are rather elliptical; the circular orbits adopted by Bohr being special cases (in fact, it's true only for the ns orbital for which the orbital quantum number is zero). Thus, within the framework of the Bohr-Sommerfeld model, the nucleus occupies one of the foci (here F) of the elliptical orbit, and the position of the electron on the orbital plane is identified by the radius r and the azimuthal angle φ (Figure 5).

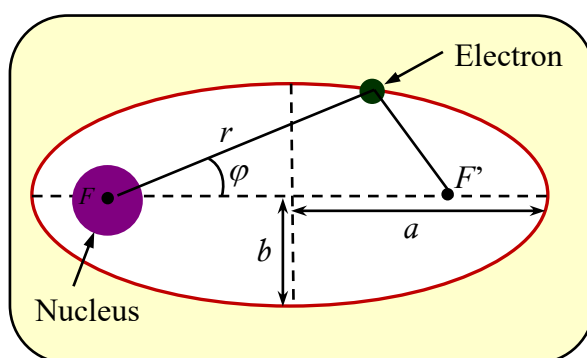


Figure 5. Bohr – Sommerfeld model of elliptical orbit

Just like Bohr's theory, Sommerfeld's theory is not a purely quantum theory since it is based on the notion of orbit, which was later rejected by the uncertainty principle formulated in 1927 (11 years later) by the German physicist Walter Heisenberg (1901-1979). However, the Bohr-Sommerfeld model allowed the correction of Bohr's model by notably showing that the energy of a hydrogen-like system depends on the orbital quantum number and explaining, among other things, the fine structure of the hydrogen atom spectrum.

2.2.2. Introduction of the Orbital Quantum Number

In the Sommerfeld's theory, the conditions satisfied by the energy of the hydrogen-like systems and the angular momentum are [14]:

$$E_k = -Z^2 \frac{Rhc}{n^2} \quad \dots(46)$$

$$L = -k\hbar. \quad \dots(47)$$

In this relationship, k is an integer satisfying the inequality $k \leq n$ with n the principal quantum number introduced in the Bohr's model.

Let's put $n_\varphi = k$. The semi-major axis a of the ellipse and the semi-minor axis b (see Figure 5) satisfy the relation [14]:

$$a = 4\pi\epsilon_0 \frac{n^2 \hbar^2}{Zme^2} = n^2 \frac{a_0}{Z} \quad ; \quad b = 4\pi\epsilon_0 \frac{nk\hbar^2}{Zme^2} = nk \frac{a_0}{Z}. \quad \dots(47)$$

In (47), a_0 is the Bohr's radius. Using (47), we get :

$$\frac{a}{b} = \frac{n}{k}. \quad \dots(48)$$

For $n = k$, we get $a = b$ according to (48). This corresponds to the particular case of Bohr's circular orbits.



Niels Bohr
(1885-1962)

By definition, in the Bohr-Sommerfeld model, the principal quantum number $n = n_r + k$. Using the expression of $R = R_\mu$ given by (38), the quantized energy (46) of the hydrogen-like systems is then written in the form:

$$E_k = -Z^2 \frac{k^2 \mu e^2}{2\hbar^2 (n_r + k)^2} \quad \dots (49)$$

To illustrate the nature of the orbits within the Bohr-Sommerfeld model, let us consider the particular case $n = 3$ for the hydrogen atom.

Knowing that the azimuthal quantum number $k = n - n_r$ ($n < n_r$ since $k = n_\varphi > 0$), we then determine all the possible values of n_r and k for $n = 3$:

- n_r 0 1 2.
- k 3 2 1.

We then obtain according to the relations (47) and (48):

- a circular orbit corresponding to $k = n = 3$; $a = b = 9a_0$;
- two elliptical orbits corresponding to $k = 2$ ($n_r = 1$); $a = 9a_0$, $b = 6a_0$ (flattest ellipse) and to $k = 1$ ($n_r = 2$); $a = 9a_0$, $b = 3a_0$.

The three orbits with the same semi-major axis ($a = 9a_0$) are illustrated in Figure 6 [2].

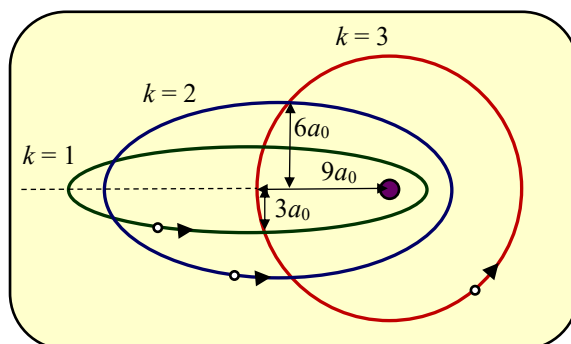


Figure 6. Electronic orbits within the framework of the Bohr-Sommerfeld model.

It now remains to take into account the orbital quantum number ℓ . For this, let us note that for a given value of n , there exists only one circular orbit corresponding to the maximum value $n = k$. Now, we already know that for a given n , ℓ takes the maximum value $\ell = n - 1 \Rightarrow n = \ell + 1$. Let's set $k = \ell + 1$, (48) is then written:

$$\frac{a}{b} = \frac{n}{\ell + 1}. \quad \dots (49)$$

For $\ell = 0$ corresponding to the ns orbitals, $a = b$. Subsequently, the circular orbits in the Bohr's model are only valid for ns orbitals (1s, 2s, 3s, and so on). For $\ell \neq 0$, $a \neq b$: all the electronic orbits in the $n\ell$ states (np , nd , nf , and so on) are elliptical within the framework of the Sommerfeld theory.

2.2.3. Expression of Sommerfeld's Relativistic Energy

Sommerfeld expressed the relativistic energy of the hydrogen-like systems taking into account the relativistic kinetic energy of the electron. The relativistic equation describing the motion of the electron in a given hydrogen-like systems is then written as [2, 14]:

$$E = E_c + V(r) = mc^2 \left\{ \frac{1}{\sqrt{1 - v^2/c^2}} - 1 \right\} - \frac{kZe^2}{r}. \quad \dots (50)$$

The solution of equation (50) is quite complex (see Ref. [15] for its demonstration). We will limit ourselves to specifying its solution and to see the physical consequences that can be drawn from it. Thus, the relativistic expression obtained by Sommerfeld is written:

$$E_{rel} = mc^2 \left\{ 1 + \frac{\alpha^2 Z^2}{(n-k+\sqrt{k^2-\alpha^2 Z^2})^2} \right\}^{-1/2} \quad \dots(51)$$

In this solution, α denotes the fine-structure constant.

With respect to energy mc^2 , the energy $E_{n,k} = E_{rel} - mc^2$ to second-order accuracy:

$$E_{n,k} = -\frac{Z^2 \alpha^2 mc^2}{2n^2} \left\{ 1 + \frac{\alpha^2 Z^2}{n} \left(\frac{1}{k} - \frac{3}{4n} \right) + (\dots) \right\} \quad \dots(52)$$

Within the framework of Bohr's theory, energy E_n is $2n^2$ time degenerate. The relativistic expression (52) shows that this degeneracy is completely lifted since the energy now depends on $k = \ell + 1$. This rise of degeneration corresponds to a separation of the n, k levels in several sub-levels of neighboring energies $E_{n,k}$.

Thus, Sommerfeld's theory allows highlighting the fine structure of energy levels. However, this important result is only valid in the case of ns states for which the spin-orbit interaction is absent (since $k = 1$ or $\ell = 0$). The correct explanation of the fine structure involves the spin of the electron hypothesized later by Goudsmit and Uhlenbeck in 1925 and integrated in the Dirac's model described in section 2.4. Moreover, within the framework of the Bohr-Sommerfeld model, the selection rule is written $\Delta k = \pm 1$. Which then comes down to the selection rule called Laporte's rule $\Delta \ell = \pm 1$ governing the dipolar transitions allowed between the fine-structure levels. Note that, Otto Laporte (1902-1971) was an American physicist of German origin. He contributed to the development of quantum mechanics, the theory of electromagnetic wave propagation, spectroscopy, and fluid dynamics. His name is lent to the Laporte's rule in spectroscopy.

Mains Contributions

Sommerfeld's most significant contributions to physics include:

- Elliptical electron orbits: In 1916, he improved the Bohr's model by proposing that electrons travel in elliptical rather than strictly circular paths to explain the "fine structure" of spectral lines.
- New quantum numbers: He introduced the azimuthal quantum number (defining the orbital's shape) and the magnetic quantum number (defining the orbital's orientation in a magnetic field).
- The fine-structure constant: He introduced this fundamental dimensionless constant, which characterizes the strength of the electromagnetic interaction between elementary particles.
- Quantum relativistic mechanics: He applied Albert Einstein's special theory of relativity to atomic physics, showing how electrons moving at relativistic speeds cause the splitting of spectral lines.

2.3. Semi-Relativistic Theory Of Sakho

2.3.1. Problem Position

Within the framework of the Bohr's theory, the quantized energy of hydrogen-like systems is given by relation (34) with the condition: $m/M = 0$:

$$E_n = -\frac{Z^2 \alpha^2 mc^2}{2n^2} \quad \dots (53)$$

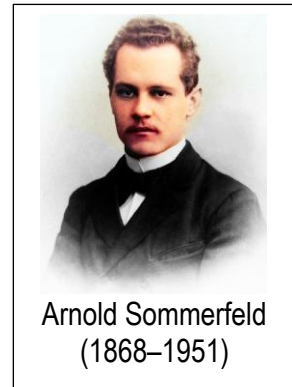
Furthermore, within the framework of the Bohr's model, the total energy of the hydrogen-like system is equal to the negative value of the electron's kinetic energy $E_n = -E_c$. So :

$$E_n = -\frac{Z^2 \alpha^2 mc^2}{2n^2} = -\frac{1}{2} m v_n^2 \quad \dots (54)$$

We deduce from (54) the quantized expression of the electron's speed:

$$v_n = \frac{Z\alpha c}{n} \quad \dots(55)$$

Expression (55) is valid in the infinitely heavy nucleus approximation (which assumes it is immobile). Moreover, in this expression, relativistic effects due to the variation of the electron's mass with velocity and spin are ignored. Yet, as early as 1905, Albert Einstein (1879-1955) showed through his theory of special relativity that the relativistic mass m of a fast particle varies with its velocity according to the law:



$$m(v) = \frac{m_0}{\sqrt{1-v^2/c^2}}. \quad \dots(56)$$

However, it was in 1913 (8 years after the development of special relativity) that Bohr developed his theory on the hydrogen atom. Consequently, he could take into account the dependence of the electron's mass on velocity in his theory. Sakho shown that it is possible to develop a semi-relativistic theory (taking into account only the variation of the electron's mass with velocity) to derive important physical consequences from it. This will allow one to theoretically interpret the effect of the dependence of the electron's mass on velocity on the energy levels of hydrogen-like systems and to express the average value of the fine-structure Hamiltonian for all non-degenerate states $n^2 L_j$ corresponding to the maximum values of the total quantum number j .

2.3.2. Variation of the Relativistic and Classical Momentum of the Electron

Within the framework of the theory of special relativity, the momentum p of a particle of rest mass m (setting $m = m_0$) is :

$$p^{rel} = \frac{mv}{\sqrt{1-v^2/c^2}}. \quad \dots(57)$$

Let's introduce the parameter $\beta = v/c$ to express relativistic momentum (p^{rel}) classical momentum (p^{cl}) of the electron. We obtain :

$$p^{rel} = \frac{mc\beta}{\sqrt{1-\beta^2}}; \quad p^{cl} = mc\beta. \quad \dots(58)$$

Figure 7 shows the shapes of the curves of variation of relativistic (p^{rel}/mc) and classical (p^{cl}/mc) momentum depending on the parameter $\beta = v/c$.

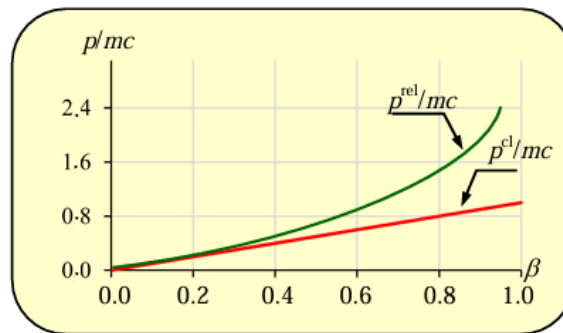


Figure 7. Variations of relativistic (p^{rel}/mc) and classical (p^{cl}/mc) momentum with $\beta = v/c$.

Sakho noticed that for $\beta < 0.4$, the relativistic and classical curves overlap.

2.3.3. Expression of the semi-relativistic energy of Sakho

To express the total semi-relativistic energy valid for $\beta < 0.4$, Sakho applied the Bohr's 1923 correspondence principle, according to which the results of quantum mechanics must tend toward those of classical mechanics in the limit of very high quantum numbers. In other words, when the discrete nature of measurable quantities is negligible, the results provided by quantum mechanics can be determined with very good approximation within the framework of classical mechanics. This correspondence principle also applies in relativistic mechanics. For example, when the ratio $v/c \ll 1$, the Lorentz factor $\gamma \approx 1$ and the laws of relativistic mechanics coincide with those of classical mechanics. The relativistic kinetic energy is given by the relation:

$$E_c = mc^2 \left\{ 1 - \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \right\}. \quad \dots(59)$$

That is to say:

$$E_n^{srel} = mc^2 \left\{ 1 - \frac{1}{\sqrt{1-\frac{v_n^2}{c^2}}} \right\}. \quad \dots(60)$$

Using (55), Sakho established the expression for the semi-relativistic energy of hydrogen-like systems as:

$$E_n^{srel} = mc^2 \left\{ 1 - \frac{1}{\sqrt{1 - \frac{Z^2 \alpha^2}{n^2}}} \right\}. \quad \dots(61)$$

Let us now look at the important physical consequences that can be drawn from expression (61) of the total energy of the hydrogen-like systems.

2.3.4. Significant Physical Consequences

• Effect of the variation of the electron mass with velocity on the energy levels

From an experimental point of view, it is observed that relativistic phenomena have the effect of lowering the energy levels of the hydrogen-like systems relative to the semi-classical Bohr energy levels. To verify this, Sakho plotted the semi-relativistic energy levels on the same energy diagram E_n^{srel} obtained using expression (61) and the semi-classical energy levels E_n^{scl} according to formula (53) considering the first three levels of the hydrogen atom. Calculations are based on $mc^2 = 0.51098$ MeV; $\alpha^2 = 5.3248 \times 10^{-5}$. The results obtained are shown in Figure 8.

It can be clearly seen in figure 8 that the variation of the electron's mass with velocity has the effect of lowering the energy levels of the hydrogen atom relative to Bohr's semi-classical levels, in accordance with experimental observations [16]. However, let us emphasize that the overall downward shift of these energy levels is due to the combined effects of the variation of the electron's mass with velocity and the Darwin contact term.

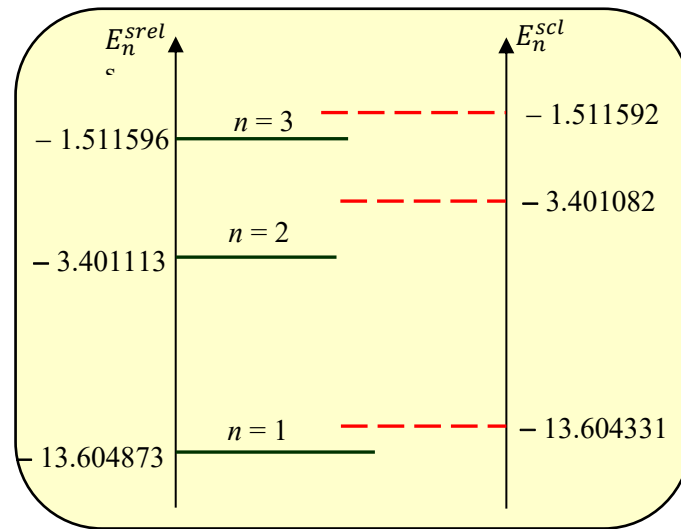


Figure 8. Effect of the variation of the electron mass with speed on the energy levels of the hydrogen atom.

Moreover, it will be seen in that taking the Darwin term into account gives a positive contribution for all the ns states, whereas the variation of the electron's mass with velocity contributes negative values (the sum of these two contributions, however, giving a negative value). This shows that the downward shift of the energy levels is mainly due to the effect of the variation of the electron's mass with velocity.

• Average value of the perturbation Hamiltonian due to the variation of the electron mass with velocity

From a theoretical point of view, the semi-relativistic expression (61) should be able to give the expressions of the energy shifts relative to the semi-classical Bohr levels. To verify this, Sakho considered to expand equation (61) in powers of $(Z\alpha/n)$ since whatever Z , $(Z\alpha/n)^2 < 1$. So he got :

$$E_n^{srel} = mc^2 \left\{ 1 - \left(1 - \frac{Z^2 \alpha^2}{n^2} \right)^{-1/2} \right\}$$

$$= mc^2 \left\{ 1 - \left(1 + \frac{Z^2 \alpha^2}{2n^2} + \frac{1}{2} \times \left(-\frac{1}{2} \right) \times \left(-\frac{1}{2} - 1 \right) \times \left(\frac{Z^2 \alpha^2}{n^2} \right)^2 + \dots \right) \right\}. \quad \dots(62)$$

By simplifying the above development, we then obtain:

$$E_n^{srel} = -\frac{Z^2 \alpha^2 mc^2}{2n^2} - \frac{3}{8} \frac{Z^4 \alpha^4 mc^2}{n^4}. \quad \dots(63)$$

This relationship clearly shows that by neglecting the second term on the right-hand side caused by the variation of the electron's mass with velocity, one recovers the semi-classical energy of hydrogen-like systems derived from the Bohr model.

Let's now move on expression the average value of W_{mv} . For this purpose we denote H_0 the unperturbed Hamiltonian (or non-relativistic Hamiltonian), the semi-relativistic Hamiltonian H^{srel} is then given by the defining relation:

$$H^{srel} = H_0 + W_{mv}. \quad \dots(64)$$

Knowing that the eigenvalue a of an operator A is equal to the average value of the operator (i.e. $a = \langle A \rangle$) in the physical state considered, then we obtain using (64) :

$$\langle H^{srel} \rangle = \langle H_0 \rangle + \langle W_{mv} \rangle \Rightarrow E_n^{srel} = E_n^0 + \langle W_{mv} \rangle_n. \quad \dots(65)$$

Comparing (63) and (65), one sees that:

$$E_n^0 = -\frac{Z^2 \alpha^2 mc^2}{2n^2}; \quad \langle W_{mv} \rangle_n = -\frac{3}{8} \frac{Z^4 \alpha^4 mc^2}{n^4}. \quad \dots(66)$$

Given that the fine structure of the levels results from their separation into several sub-levels, we need to find the average value of the Hamiltonian W_{mv} relative to each degree of freedom. To do this, Sakho used the equipartition theorem in classical statistical mechanics stating that in thermal equilibrium, the energy of a system is shared equally among all of its energetically accessible degrees of freedom. Thus, according to this theorem he applied in the case of the hydrogen-like system, Sakho stated that due to the variation of the electron's mass with velocity, the average energy to each degree of freedom is:

$$W_n^{mv} = \frac{1}{3} \langle W_{mv} \rangle_n. \quad \dots(67)$$

That means

$$W_n^{mv} = -\frac{1}{8} \frac{Z^4 \alpha^4 mc^2}{n^4}. \quad \dots(68)$$

The semi-relativistic expression (68) gives the energy shift of all levels of the hydrogen-like systems relative to the unperturbed Bohr's levels. In the particular case of the ground level and the first two excited levels, we obtain:

$$\begin{cases} W_1^{mv} = -\frac{1}{8} Z^4 \alpha^4 mc^2 \\ W_2^{mv} = -\frac{1}{128} Z^4 \alpha^4 mc^2 \\ W_3^{mv} = -\frac{1}{648} Z^4 \alpha^4 mc^2 \end{cases} \quad \dots(69)$$

The semi-relativistic results (69) can be recovered from Dirac's relativistic theory taking into account the combined effects of the variation of the electron's mass with velocity and the electron's spin. This is a striking proof of the validity of Sakho's semi-relativistic expression, thereby justifying its publication in 2012 [11].

Mains contributions

Ibrahima Sakho, born in 1967 in Dakar, Senegal, is a Senegalese physical chemist. The historical photograph opposite shows Ibrahima Sakho 26 years ago in his room 18F (building F, now demolished) when he was a 4th-year Physics and Chemistry Master's student at Cheikh Diop University in Dakar. It was in this room that he established the semi-empirical expression for the quantized energy of hydrogen-like systems on February 7, 1993, around 5:00 AM. His main contributions are the following:

1. The correction of the Bohr model in the semi-relativistic approach;
2. Development of the first semi-empirical method of atomic resonance (third-cycle thesis, 2007 [17]) and of the first semi-empirical method of photoionization (state doctorate thesis, 2013 [18, 19]). This semi-empirical method is referred to as Screening constant per Unit nuclear charge (SCUNC);
3. Development of the first modified theory of Slater atomic orbitals applied to the study of excited states of helium-like systems [20] and to the diagnosis of astrophysical plasmas and laboratory plasmas [21]. This method is called Modified Atomic Orbital Theory (MAOT).



Ibrahima Sakho born in 1967
Photo taken on May 6, 1993

In 1993, he expresses the first theoretical expression of the unit nuclear radius r_0 in Agreement with the Constant Density Model $R = r_0 A^{1/3}$ [22, 23]. In 2024, he presented his new Q - β -Decay Theory for Mirrors Nuclei $A = 2Z - 1$ and applied it to estimate accurately the speed of light in vacuum [24] and the rest mass energy $m_0 c^2$ of the electron and of the Q -Value of various mirrors nuclei ($A = 11-199$) [25].

2.4. Relativistic theory of Dirac

2.4.1. Relativistic wave equation

The Dirac's relativistic theory tries to unify quantum mechanics and the theory of special relativity. Let's start by the relativistic wave equation known as the Klein-Gordon equation [established independently in 1926 by the Swedish physicist Oskar Benjamin Klein (1894-1977) and the German Walter Gordon (1893-1936)]:

$$-\hbar^2 \frac{\partial^2 \Psi}{\partial t^2} = (-\hbar^2 \vec{\nabla}^2 c^2 + m^2 c^4) \Psi. \quad \dots(70)$$

Unfortunately, this equation poses a problem for resolution because it contains the square of the Hamiltonian operator (73). To resolve this problem, Dirac proposed to linearize the Hamiltonian H by taking into account the energy-momentum four-vector $(\vec{p}, iE/c)$ of the particle in accordance with the principles of special relativity. Consequently, H must be linear with respect to the components of the energy-momentum four-vector, that is:

$$p_k = i\hbar \frac{\partial}{\partial x_k}, p_4 = -i\hbar \frac{\partial}{\partial x_4} = iE/c. \quad \dots(77)$$

In these relationships, $k = 1, 2$ and 3 ($x_1 = x, x_2 = y, x_3 = z$) and $x_4 = ict$, in accordance with the coordinates of the position four-vector. Taking these coordinates into account, Dirac suggested writing the Hamiltonian H in the form of a linear sum of operators constituted by the components of the momentum-energy four-vector, namely:

$$H = \alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z + \alpha_4 p_4. \quad \dots(78)$$

In the relationship (78), the α_i ($i = 1 - 4$) are operators with certain values. Using (78), the relativistic wave equation of Dirac related to a free particle can then be written in the form:

$$i\hbar \frac{\partial \Psi}{\partial t} = -ic \sum_{k=1}^3 \alpha^k \partial_k \Psi + \beta m c^2 \Psi. \quad \dots(79)$$

In equation (79), α^k and β are matrices defined by the relations [2, 22, 23]:

$$\alpha^k = \begin{pmatrix} 0 & \sigma^k \\ \sigma^k & 0 \end{pmatrix} \quad ; \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad \dots(80)$$

where σ^k are the Pauli matrices and I the identity matrix 2×2 .

In a scalar potential $V(r)$, the relativistic Dirac wave equation taking into account the electric potential can then be written in the form:

$$i\hbar \frac{\partial \psi}{\partial t} = \left(H - \frac{Ze^2}{r} \right) \psi. \quad \dots(81)$$

In equation (81), the relativistic Hamiltonian is given by the expression:

$$H = -ic \sum_{k=1}^3 \alpha^k \partial_k + \beta mc^2. \quad \dots(82)$$

The relativistic wave equation (82) makes it possible to interpret many physical phenomena such as the electron spin, the fine structure of the energy levels of hydrogen-like systems, etc. The solution of equation (82) is of such a complexity that we cannot include it in this present supplement. We will therefore limit ourselves to studying the fine-structure Hamiltonian terms as they appear in the development of Hamiltonian (82) in the weakly relativistic domain.

Remark

When the charge particle q is subjected to an electromagnetic field described by a scalar potential V and a vector potential $\vec{A}$. The relativistic Klein-Gordon wave equation (76) is then written:

$$\left(i\hbar \frac{\partial}{\partial t} - qV \right)^2 \psi = \left[(-i\hbar \vec{\nabla} - q\vec{A})c^2 + m^2 c^4 \right] \psi. \quad \dots(83)$$

For a free particle, $V = 0$ and $\vec{A} = \vec{0}$. Equation (83) gives (76).

2.4.2. Relativistic weakly Hamiltonian

For weakly relativistic hydrogen-like systems, the Hamiltonian can be written in linear form:

$$H = mc^2 + H_0 + W. \quad \dots(84)$$

In equation (84), mc^2 is the rest energy of the electron, H_0 is the unperturbed Hamiltonian of the hydrogen-like system in the potential energy field of the nucleus $V(r) = -Ze^2/r$ and W represents all the relativistic effects neglected within the framework of Bohr's theory. The term W is called the fine-structure Hamiltonian. Within the framework of Dirac theory, the fine-structure Hamiltonian appears in the power series expansion of v/c of the relativistic Hamiltonian H :

$$H = mc^2 + \frac{\vec{p}^2}{2m} + V(\vec{R}) - \frac{\vec{p}^4}{8m^3c^2} + \frac{1}{2m^2c^2} \frac{1}{R} \frac{dV(\vec{R})}{dR} \vec{L} \cdot \vec{S} + \frac{\hbar^2}{8m^2c^2} \Delta V(\vec{R}) + (\dots). \quad \dots(85)$$

Comparing (84) and (85), we find the expression of the unperturbed Hamiltonian:

$$H_0 = \frac{\vec{p}^2}{2m} + V(\vec{R}). \quad \dots(86)$$

The fine-structure Hamiltonian then takes the form:

$$W_{sf} = -\frac{\vec{p}^4}{8m^3c^2} + \frac{1}{2m^2c^2} \frac{1}{R} \frac{dV(\vec{R})}{dR} \vec{L} \cdot \vec{S} + \frac{\hbar^2}{8m^2c^2} \Delta V(\vec{R}) + (\dots). \quad \dots(87)$$

The physical origin of each of the fine structure terms in (87) are the following:

- the term related to the variation of the electron's mass with velocity:

$$W_{mv} = -\frac{\vec{p}^4}{8m^3c^2}. \quad \dots(88)$$

- the term related to spin-orbit interaction (or LS coupling):

$$W_{SO} = \frac{1}{2m^2c^2} \frac{1}{R} \frac{dV(\vec{R})}{dR} \vec{L} \cdot \vec{S}. \quad \dots(89)$$

- Darwin term (or contact term) taking into account the non-point like nature of the nucleus charge:

$$W_D = \frac{\hbar^2}{8m^2c^2} \Delta V(\vec{R}). \quad \dots(90)$$

Considering the different fine structure terms, the Hamiltonian fine structure (87) can be written in the form:

$$W_{sf} = W_{mv} + W_{SO} + W_D + (\dots). \quad \dots(91)$$

The effects of these different terms are as follows:

- W_{mv} and W_D allow interpreting the overall downward shift of the energy levels of hydrogen-like systems relative to the semi-classical energy levels of Bohr;
- W_{SO} allows lifting the degeneracy of energy levels characterized by the same value of the orbital quantum number ℓ but with a different value from the total quantum number $j = \ell \pm s$, with s the spin of the electron.

The exact solution of the relativistic Dirac wave equation (81) leads to the following solution [2, 26, 27]:

$$E_{nj} = mc^2 \left[1 + \frac{Z\alpha}{n - \left(j + \frac{1}{2}\right) + \sqrt{\left(j + \frac{1}{2}\right)^2 - (Z\alpha)^2}} \right]^2 \Bigg]^{-1/2}. \quad \dots(92)$$

Expanding solution (92) in powers of $Z\alpha$, we obtain:

$$E_{nj} = mc^2 \left\{ 1 - \frac{1}{2} \frac{(Z\alpha)^2}{n^2} \left[1 + \frac{1}{2} \frac{(Z\alpha)^2}{n} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) \right] + (\dots) \right\}. \quad \dots(93)$$

The solution (93) includes an amount mc^2 due to the proper energy associated with any relativistic particle with non-zero rest mass. Furthermore, the relativistic correction introduces a term proportional to $(Z\alpha)^4$ relative to the Bohr energy $-(Z\alpha)^2/2n^2$.

2.4.3. Comparison with the Semi-Relativistic Energy of the Hydrogen-Like Systems

Relatively to rest energy mc^2 of the electron, the total energy of hydrogen-like systems in the weakly relativistic domain is given by the following truncated expression:

$$E_{nj} = -\frac{Z^2\alpha^2mc^2}{2n^2} - \frac{Z^4\alpha^4mc^2}{2n^3} \left(\frac{1}{j + 1/2} - \frac{3}{4n} \right). \quad \dots(94)$$

As indicated by the expansion (63), by neglecting the relativistic correction due to the variation of the electron's mass with velocity, the semi-relativistic energy (61) reduces to the semi-classical energy of hydrogen-like systems derived from Bohr's theory. It follows that the semi-relativistic expression (61) is also contained in the Dirac's relativistic formula (92). In other words, the semi-relativistic expansion (63) according to Sakho should appear in the truncated relativistic expression (94) according to Dirac. To verify this assertion, let's rewrite expansion (94) as follows:

$$E_{nj} = -\frac{Z^2\alpha^2mc^2}{2n^2} + \frac{3}{8} \frac{Z^4\alpha^4mc^2}{n^4} - \frac{Z^4\alpha^4mc^2}{2n^3(j + 1/2)}. \quad \dots(95)$$

Let's summarize the previous results by setting $E_n^0 = E_n^{scl}$ to designate the Bohr energy of hydrogen-like systems. We obtain:

$$\left\{ \begin{array}{ll} E_n^{scl} = -\frac{Z^2 \alpha^2 mc^2}{2n^2} & : \text{semi-classical energy of Bohr (1913)} \\ E_n^{srel} = -\frac{Z^2 \alpha^2 mc^2}{2n^2} - \frac{3}{8} \frac{Z^4 \alpha^4 mc^2}{n^4} + (...) & : \text{semi-relativistic energy of Sakho (1993)} \\ E_{nj} = -\frac{Z^2 \alpha^2 mc^2}{2n^2} + \frac{3}{8} \frac{Z^4 \alpha^4 mc^2}{n^4} - \frac{Z^4 \alpha^4 mc^2}{2n^3(j+1/2)} + (...) & : \text{relativistic energy of Dirac (1929)} \end{array} \right. \quad \dots(96)$$

The compared results (96) clearly show that the Dirac's relativistic formula (92) indeed contains the semi-relativistic expression (61) which only takes into account the variation of the electron's mass with speed. By neglecting the third term on the right-hand side of the relativistic energy E_{nj} , we do indeed find the semi-relativistic expression.

2.4.4. Semi-Relativistic and Relativistic Average Values of the Fine Structure Hamiltonian

Relatively to rest energy mc^2 of the electron, the Hamiltonian hydrogen-like systems in the weakly relativistic domain can be written in the form:

$$H = H_0 + W_{sf}. \quad \dots (97)$$

In equation (97), W_{sf} denotes the fine-structure Hamiltonian. The expectation values from this equation is :

$$\langle H \rangle = \langle H_0 \rangle + \langle W_{sf} \rangle.$$

Which then gives:

$$E_{nj} = E_n^0 + W_{nj}^{sf}. \quad \dots(98)$$

Comparison of (98) to (98) yields :

$$W_{nj}^{sf} = -\frac{Z^4 \alpha^4 mc^2}{2n^3} \left(\frac{1}{j+1/2} - \frac{3}{4n} \right). \quad \dots(99)$$

At the ground level $n = 1$ and at the excited levels $n = 2$ and $n = 3$ correspond the fine structure levels $1^2s_{1/2}$, $2^2s_{1/2}$, $2^2p_{1/2}$, $2^2p_{3/2}$, $3^2s_{1/2}$, $3^2p_{1/2}$, $3^2p_{3/2}$, $3^2d_{3/2}$ et $3^2d_{5/2}$. Using (99), we get.

$$\begin{aligned} & \bullet \text{ For } 1^2s_{1/2}: & W_{1,1/2}^{sf} &= -\frac{1}{8} Z^4 \alpha^4 mc^2 \\ & \bullet \text{ For } 2^2s_{1/2} \text{ and } 2^2p_{1/2}: & W_{2,1/2}^{sf} &= -\frac{5}{128} Z^4 \alpha^4 mc^2 \\ & \bullet \text{ For } 2^2p_{3/2}: & W_{2,3/2}^{sf} &= -\frac{1}{128} Z^4 \alpha^4 mc^2 \\ & \bullet \text{ For } 3^2s_{1/2} \text{ and } 3^2p_{1/2}: & W_{3,1/2}^{sf} &= -\frac{1}{72} Z^4 \alpha^4 mc^2 \\ & \bullet \text{ For } 3^2p_{3/2} \text{ and } 3^2d_{3/2}: & W_{3,3/2}^{sf} &= -\frac{1}{216} Z^4 \alpha^4 mc^2 \\ & \bullet \text{ For } 3^2d_{5/2}: & W_{3,5/2}^{sf} &= -\frac{1}{648} Z^4 \alpha^4 mc^2 \end{aligned} \quad \dots(100)$$

A reading of the above results shows a degeneration of energy levels having the same value of the total quantum number j but with a different value of the orbital quantum number ℓ . Comparing the relativistic average values (100) with the semi-relativistic average values (69), we observed that:

$$\begin{cases} W_1^{mv} = W_{1,1/2}^{sf} = -\frac{1}{8}Z^4\alpha^4mc^2 \\ W_2^{mv} = W_{2,3/2}^{sf} = -\frac{1}{128}Z^4\alpha^4mc^2 \\ W_3^{mv} = W_{3,5/2}^{sf} = -\frac{1}{648}Z^4\alpha^4mc^2 \end{cases} \quad \dots(101)$$

The results (101) show that the average values of the semi-relativistic Hamiltonian (68) coincide with the average values of the relativistic Dirac Hamiltonian (99) related to the non-degenerate fine-structure sublevels $1^2s_{1/2}$, $2^2p_{3/2}$ et $3^2d_{5/2}$. Which is striking evidence of the validity of the semi-relativistic formula (61)? Furthermore, the previous coincidence makes it possible to establish the general expression of the average value of the fine-structure Hamiltonian for all non-degenerate states corresponding to the maximum value $j_{\max}$ of the total quantum number j . The semi-relativistic expression (68) is then rewritten in the form :

$$W_{nj_{\max}}^{sf} = -\frac{1}{8}Z^4\alpha^4mc^2 \frac{1}{n^4} \quad \dots(102)$$

Now, one can determine in two different ways the average value of the fine-structure Hamiltonian of a non-degenerate level of hydrogen-like systems. Let's take the case of the $4^2f_{7/2}$ state (j is maximal for this level).

Firstly: from the relativistic theory of Dirac using (99):

$$W_{nj}^{sf} = -\frac{Z^4\alpha^4mc^2}{2 \times 4^3} \left(\frac{1}{7/2 + 1/2} - \frac{3}{4 \times 4} \right) = -\frac{1}{2048}Z^4\alpha^4mc^2 \quad \dots(103)$$

Secondly : more softly from the semi-relativistic theory of Sakho using (102)

$$W_{nj_{\max}}^{sf} = -\frac{1}{8}Z^4\alpha^4mc^2 \frac{1}{4^4} \frac{1}{2048} \quad \dots(104)$$

Let's illustrate with diagrams the effect of the fine-structure Hamiltonian on the ground state $n = 1$ and on the first excited level $n = 2$ of the hydrogen-like systems. Under the effect of the disturbance W_{sf} , the fundamental level is shifted downward of $(1/8)Z^4\alpha^4mc^2$ relative to the unperturbed Bohr level (fig.9).

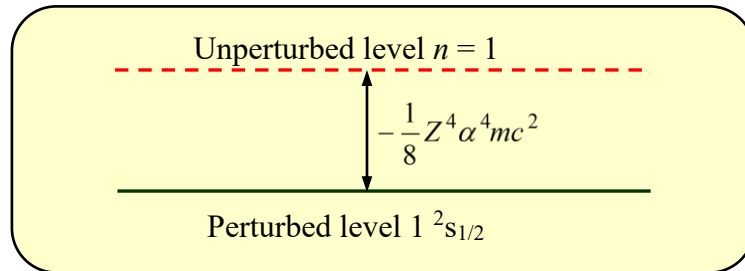


Figure 9. Effect of the fine-structure Hamiltonian on the ground state $1^2s_{1/2}$ of the hydrogen-like systems.

Similarly, under the effect of the fine-structure Hamiltonian, the two degenerate fine-structure sub-levels ($2^2s_{1/2}$, $2^2p_{1/2}$) and the $2^2p_{3/2}$ level are shifted down relative to the non-relativistic levels by $(5/8)Z^4\alpha^4mc^2$ and $(1/128)Z^4\alpha^4mc^2$ respectively (fig.9). It should be noted that W_{sf} does not reveal any fine structure on the ground level. Its effect is limited to a block shift of the level $1^2s_{1/2}$. Similarly, under the effect of the fine-structure Hamiltonian, the two degenerate fine-structure sublevels ($2^2s_{1/2}$, $2^2p_{1/2}$) and the $2^2p_{3/2}$ level are shifted downward relative to the non-relativistic levels by $(5/8)Z^4\alpha^4mc^2$ and $(1/128)Z^4\alpha^4mc^2$ respectively (fig. 10).

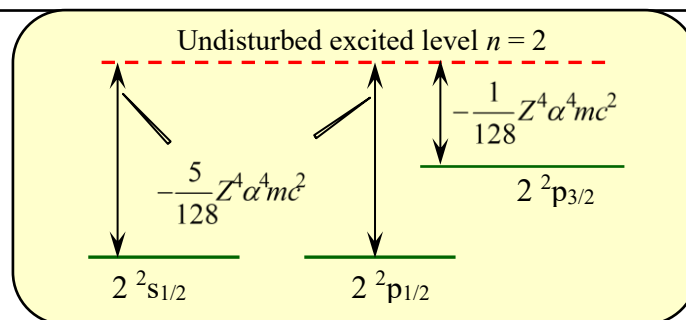


Figure 10. Effect of the fine-structure Hamiltonian on the first excited state $n = 2$ of the hydrogen-like systems. The splitting of the $2^2p_{1/2}$ and $2^2s_{1/2}$ states is not resolved with the framework of the Dirac's model.

Paul Adrien Maurice Dirac (1902-1984) was a British physicist. In 1926, Dirac published his version of quantum mechanics, unifying Heisenberg's matrix approach and Schrödinger's wave approach. His famous equation, now known as the Dirac equation (1928), predicts the existence of antimatter even before its experimental discovery by American physicist Carl Anderson (1905-1991) in 1932. The formulation he proposes introduces the concepts of relativistic wave function, creation/annihilation operators and bra-ket notations in the mathematical formalism of quantum mechanics.

3. CONCLUSION

This paper is an important overview of the means relativistic theories devoted to the corrections of the semi-classical Bohr's theory on the hydrogen like systems. The study start with the presentation of the Bohr's theory (1913) and the Bohr-Sommerfeld model (1916). After, the formalisms of the semi-relativistic theory of Sakho (1993) taking into account the relativistic mass correction by ignoring the electron's spin and the relativistic theory of Dirac (1928) are presented. It is shown that, the average value of the fine structure Hamiltonian predicted from the Dirac's relativistic theory for all the non-degenerated quantum states n^2L_j ($j = l \pm s$) of the hydrogen like systems can be obtained more softly from the semi-relativistic theory. This study elaborates a framework based on history of science that can help students to understand the means relativistic corrections of the Bohr's theory on the hydrogen like systems.

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