

The Hydrogen Atom – Extended Model

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Abstract This paper tries to prove that the existence and properties of the electron's spin can be established not only as a consequence of relativistic quantum mechanics, but also as a consequence of non-relativistic quantum mechanics of the Hydrogen atom or Hydrogenic atoms. It is, in fact, an extended model of the Hydrogen atom or Hydrogenic atoms. This new model starts from the assumption that to the foundation of atomic structure there is not only a potential of electrical nature, but also a potential of magnetic nature, which, together with the Coulomb potential, determine the movement of electrons around the atomic nucleus. As a consequence of this new model is obtained a non-relativistic theory of Hydrogen atom which takes into account the spin of the electron and leads us to a non-relativistic theory of the atom in agreement with the Stern-Gerlach experiment results. As well the model can be used in order to explain the spectrum of Alkali-atoms.

Keywords Spin, Magnetic field, Virtual, Nonrelativist, New model, Extended

1. Contents

Let us consider an electron that moves with velocity (v) on a circular orbit in the meridian plane of a nucleus. Such an electron produces a "current loop" in this plane. From the fundamental laws of electromagnetism we know that any current loop produces a magnetic field perpendicular oriented to the plane of the orbit. The expression of the magnetic field at the center of such a "current loop" can be described, according to the laws of electromagnetism, by the formula:

$$B = \frac{\mu_0}{2R} I \quad (1)$$

where (μ_0) is the vacuum magnetic permeability, (R) is the radius of the current loop, and (I) is the circulating current. Further, instead of using Cartesian coordinates $Oxyz$, it is convenient to introduce spherical coordinates $Or\vartheta\varphi$:

$$\begin{cases} x = r \sin\vartheta \cos\varphi \\ y = r \sin\vartheta \sin\varphi \\ z = r \cos\vartheta \end{cases} \Leftrightarrow \begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \vartheta = \arctan(z/\sqrt{x^2 + y^2}) \\ \varphi = \arctan(y/x) \end{cases} \quad (2)$$

Therefore, we can assume that the component of the magnetic induction in the z – direction is

$$B_z = \frac{\mu_0}{2r \sin\vartheta} I \quad (1')$$

because $R = r \sin\vartheta$ is the radius of the current loop in the meridian plane. But, from the electron's point of view, the nucleus revolves around him. Thus, the nucleus produces

also a "current loop". Therefore we can assume that the expression of the magnetic induction (B_z) of the magnetic field produced by nucleus in the point where is placed the electron, has the form

$$B_z = -\frac{\mu_0}{2r \sin\vartheta} I \quad (3)$$

(the minus sign appears because the two systems, electron and atomic nucleus, have the opposite velocities, (v) and ($-v$)). Now, as expression of circulating current (I) we can introduce the formula

$$I = \frac{Ze}{T} = \frac{Ze\omega}{2\pi} \quad (4)$$

where e is the elementary charge, Z is the atomic number, and $T = 2\pi/\omega$ is the orbital period of the atomic nucleus. For the angular velocity of the nucleus (ω) we allow the formula

$$\omega = \frac{v_f}{R} \quad (5)$$

where $v_f = c^2/v$ is the phase velocity of the de Broglie wave associated with the atomic nucleus. Thus, the expression of the circulating current (I) of the atomic nucleus becomes

$$I = \frac{Ze v_f}{2\pi R} \quad (6)$$

Substituting this expression in the expression of magnetic induction B_z Eq. (3), we get

$$B_z = \frac{\eta}{R^2} = \frac{\eta}{x^2 + y^2} = \frac{\eta}{r^2 \sin^2\vartheta} \quad (7)$$

where the constant η is given by

$$\eta = -\mu_0 \frac{Ze v_f}{4\pi} \quad (8)$$

Further, we introduce the formula $\mu_0 = 1/\epsilon_0 c^2$, where c is the speed of light and ϵ_0 is the vacuum permittivity, so that the constant η of Eq. (8) can be rewritten as

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$$\eta = -\frac{Z\hbar v_f}{e c} \alpha_e = -\frac{Z\hbar c}{e v} \alpha_e \quad (9)$$

where $\alpha_e = q_e^2/\hbar c$ is the fine structure constant, $\hbar = h/(2\pi)$ is the reduced Planck constant, and q_e^2 is the well-known expression $q_e^2 = e^2/4\pi\epsilon_0$. Thus, we admit that from the electron's point of view, the nucleus produces a magnetic field, whose expression can be written in vectorial form as

$$\vec{B} = B_z \vec{k} = \frac{\eta}{r^2 \sin^2 \vartheta} \vec{k} \quad (10)$$

where \vec{k} is the unit vector along Oz axis, and B_z is the z -component of the magnetic induction \vec{B} . Therefore, in order to correctly describe the motion of the electron, we must appeal to the Hamilton function of a particle with electric charge $q = -e$, located in an electromagnetic field represented in terms of the scalar and vector potentials V and \vec{A} . So, we introduce the Hamiltonian operator of the form

$$\hat{H} = \frac{1}{2m_0} (\hat{p} - q\vec{A})^2 + qV \quad (11)$$

where

$$V = -\frac{Zq}{4\pi\epsilon_0 r} \quad (12)$$

is the expression of the scalar potential V and m_0 is the rest mass of the electron. We do not know the expression of the vector potential \vec{A} . But, we know that for an electron located into a constant magnetic field, we can write this expression as

$$\vec{A} = \frac{1}{2} (\vec{B} \times \vec{r}) \quad (13)$$

We keep this expression for the case when the magnetic induction (\vec{B}) is a function of the position (r, ϑ, φ) of the electron. Therefore, substituting Eq. (10) into Eq. (13), the vector potential \vec{A} becomes

$$\vec{A} = A_x \vec{i} + A_y \vec{j} \quad (14)$$

where A_x and A_y are x and y -components of the potential vector \vec{A}

$$A_x = -\frac{1}{2} \frac{\eta y}{x^2 + y^2} \quad (15)$$

$$A_y = \frac{1}{2} \frac{\eta x}{x^2 + y^2} \quad (16)$$

in Cartesian coordinates (x, y, z) , and $A_z = 0$. Now, if we apply the transformations (2), we get

$$A_x = -\frac{1}{2} \frac{\eta \sin \varphi}{r \sin \vartheta} \quad (17)$$

$$A_y = \frac{1}{2} \frac{\eta \cos \varphi}{r \sin \vartheta} \quad (18)$$

in spherical polar coordinates (r, ϑ, φ) . Thus, the Hamiltonian operator \hat{H} of the electron can be decomposed as the sum

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (19)$$

where the expressions of the operators \hat{H}_0 and \hat{H}' , according to Eq. (11), are given by the formulas

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_0} - \frac{Zq_e^2}{r} \quad (20)$$

$$\hat{H}' = -\frac{q}{m_0} \vec{A} \hat{p} + \frac{q^2}{2m_0} \vec{A}^2 \quad (21)$$

Now, with the aid of components A_x and A_y and of the transformations (2), we can find the expressions

$$\vec{A} \hat{p} = -i\hbar \frac{\eta}{2} \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial}{\partial \varphi} \quad (22)$$

$$\vec{A}^2 = \frac{1}{4} \frac{\eta^2}{r^2 \sin^2 \vartheta} \quad (23)$$

so that \hat{H}' can be written as

$$\hat{H}' = \frac{i\alpha}{r^2 \sin^2 \vartheta} \frac{\partial}{\partial \varphi} + \frac{\beta}{r^2 \sin^2 \vartheta} \quad (24)$$

where the constants α and β are given by the relations :

$$\alpha = -\eta \mu_B = \frac{Z\hbar^2 c}{2m_0 v} \alpha_e \quad (25)$$

$$\beta = \frac{Z^2 e^2 \eta^2}{8m_0} = \frac{1}{4} \frac{Z^2 \hbar^2 c^2}{2m_0 v^2} \alpha_e^2 \quad (26)$$

in which μ_B is the Bohr magneton $\mu_B = e\hbar/2m_0$. Let us now consider the Schrodinger equation for an electron in the electromagnetic field of a nucleus of charge $+Ze$

$$\hat{H}\Psi(r, \vartheta, \varphi) = E \Psi(r, \vartheta, \varphi) \quad (27)$$

We assume a variables separable solution to this equation of the form $\Psi(r, \vartheta, \varphi) = R(r) Y(\vartheta, \varphi)$. Substituting this solution in Eq. (27), after the separation of variables, we get the following two independent equations:

$$\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} + \frac{2m_0}{\hbar^2} \left[E + \frac{Zq_e^2}{r} \right] R(r) - \frac{\lambda}{r^2} R(r) = 0 \quad (28)$$

for radial wave function, and respectively

$$\Delta_{\vartheta, \varphi} Y(\vartheta, \varphi) + \left(\lambda - \frac{\gamma^2}{\sin^2 \vartheta} \right) Y(\vartheta, \varphi) \frac{i\sigma}{\sin^2 \vartheta} \frac{\partial Y(\vartheta, \varphi)}{\partial \varphi} = 0 \quad (29)$$

for the angular wave function, and the constants are given by the formulas

$$\sigma = \frac{2m_0}{\hbar^2} \alpha = Z \frac{c}{v} \alpha_e \quad (30)$$

$$\gamma^2 = \frac{2m_0}{\hbar^2} \beta = \frac{\sigma^2}{4} \quad (31)$$

$$\lambda = \frac{2m_0 K^2}{\hbar^2} \quad (32)$$

The constant K^2 is the separation constant, and $L^2 = 2m_0 K^2$ signifies the angular momentum squared. We assume again a variables separable solution to the second equation Eq. (29) of the form $Y(\vartheta, \varphi) = \Theta(\vartheta) \Phi(\varphi)$. Thus this equation can be separated in others two independent equations

$$\frac{\sin \vartheta}{\Theta(\vartheta)} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \Theta(\vartheta)}{\partial \vartheta} \right) + \lambda \sin^2 \vartheta = M^2 \quad (33)$$

and respectively

$$\frac{d^2 \Phi(\varphi)}{d\varphi^2} - i\sigma \frac{d\Phi(\varphi)}{d\varphi} + (M^2 - \gamma^2) \Phi(\varphi) = 0 \quad (34)$$

where the constant M^2 is the separation constant. After the change of variable $\varphi = \cos \vartheta$, the first equation Eq. (33) can

be rewritten as the well-known equation

$$(1-s^2)\frac{d^2\theta(s)}{ds^2} - 2s\frac{d\theta(s)}{ds} + \left(\lambda - \frac{M^2}{1-s^2}\right)\theta(s) = 0 \quad (35)$$

For the second equation Eq. (34), we assume a solution of the form $\Phi(\varphi) = Ce^{i\varphi}$, where C is a real constant. From the normalization condition we find the value of constant C as $C = 1/\sqrt{2\pi}$. Inserting the solution of $\Phi(\varphi)$ into Eq. (34), we obtain now the following characteristic equation

$$t^2 - \sigma t - (M^2 - \gamma^2) = 0 \quad (36)$$

This is a quadratic equation for which, according to Eq. (31), we find the roots

$$t_{1,2} = \frac{\sigma}{2} \pm M \quad (37)$$

Now, we must consider the azimuth boundary condition $\Phi(\varphi) = \Phi(\varphi + 2\pi)$ which imposes the conditions

$$t_{1,2} = \frac{\sigma}{2} \pm M = \pm m \quad (38)$$

where m is a positive integer (including zero). Thus, we can write the constant M as $M = m_l \pm \sigma/2$, where we have used the notation $m_l = \pm m$. Further, we introduce for the constant M another notation $M = m_j$, so that we can write

$$m_j = m_l \pm \frac{\sigma}{2} \quad (39)$$

where m_l is the well-known orbital magnetic quantum number. Therefore, the solution $\Phi(\varphi)$ becomes

$$\Phi_{m_l}(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im_l\varphi} \quad (40)$$

Turning now to Eq. (35), we assume here a solution of the form

$$\theta(s) = (1-s^2)^{p/2} u(s) \quad (41)$$

which replaced in this equation leads us to the following differential equation for unknown function $u(s)$

$$(1-s^2)u''(s) - 2(p+1)su'(s) + \left[\lambda - p(p+1) + \frac{p^2-m_j^2}{1-s^2}\right]u(s) = 0 \quad (42)$$

In order to exclude the singularities of the points $s = \pm 1$, we must impose the condition $p^2 = m_j^2$ which generates the values of the exponent p as

$$p = \pm m_j \quad (43)$$

and the equation Eq. (42) gets the following well-known form

$$(1-s^2)u''(s) - 2(p+1)su'(s) + [\lambda - p(p+1)]u(s) = 0 \quad (44)$$

A solution may be found if we admit for σ the value $\sigma = 1$. With this value for σ , the solution $u(s)$ of Eq. (44) can be written as

$$u(s) = u_j^p(s) = \frac{d^{j+p}}{ds^{j+p}} [(1-s^2)^j] \quad (45)$$

if we admit that the constant λ has the expression

$$\lambda = j(j+1) \quad (46)$$

where

$$j = q - p \quad (47)$$

$$q = 0, 1, 2, 3, \dots \quad (48)$$

(the proof of formulas (46), (47) is provided by the Annex 1)
Another solution for Eq. (44) may be also

$$u(s) = (1-s^2)^{-p} \frac{d^{j-p}}{ds^{j-p}} [(1-s^2)^j] \quad (49)$$

for the same $\lambda = j(j+1)$ and $j = q - p$ ($q = 0, 1, 2, 3, \dots$)

Indeed, if we substitute $\sigma = 1$ in Eq. (30) and Eq. (39), we find that the velocity of the electron (v) gets the expression

$$v = Zc\alpha_e \quad (50)$$

and the quantum number m_j becomes

$$m_j = m_l + m_s \quad (51)$$

where m_s is the spin magnetic quantum number $m_s = \pm 1/2$

From Eq. (43) and Eq. (47), we can obtain now the formula

$$j = l \pm \frac{1}{2} \quad (52)$$

where l is the orbital quantum number, given by the formula

$$l = q + m_l \quad (53)$$

Also, from Eqs. (43) and (47), we can find the inequalities

$$-j \leq m_j \leq j \quad (54)$$

where j and m_j take only half-integers values (It should be mentioned here that in the state $l = 0$ the quantum number j can have a single value, $j = \frac{1}{2}$, so we can write $j \geq \frac{1}{2}$). Substituting now the solution $u(s)$ of Eq. (45) into Eq. (41), for m_j , we can write the solution $\theta(s)$ of Eq. (35) in the general form

$$\theta(s) = \theta_j^{m_j}(s) = C_j^{m_j} P_j^{m_j}(s) \quad (55)$$

where the $P_j^{m_j}(s)$ function is the solution Legendre's equation Eq. (35) for the half-integers quantum numbers j and m_j

$$P_j^{m_j}(s) = (1-s^2)^{m_j/2} \frac{d^{j+m_j}}{ds^{j+m_j}} [(1-s^2)^j] \quad (56)$$

Because this solution must be finite on the interval $[-1, 1]$ we must permit for m_j only the values $m_j \leq -1/2$. The constants $C_j^{m_j}$ are the multiplication factors determined by the normalization condition which gives

$$C_j^{m_j} = \sqrt{\frac{2^{2j+1}[(j+\frac{1}{2})!]^2}{2\pi(2j+1)!K_j^{m_j}}} \quad (57)$$

(the proof is provided by the Annex 2)

The expression of the $K_j^{m_j} = K(j, m_j)$ coefficients is given by the formula

$$K_j^{m_j} = K(j, m_j) = (j)_{j+m_j} [(j+m_j)!] + \frac{1}{2} S_j^{m_j} \quad (58)$$

the coefficients $S_j^{m_j} = S(j, m_j)$ have the expression

$$S_j^{m_j} = \sum_{i=1}^N \binom{i}{j+m_j}^2 (i!) [(j+m_j-i)!] [(j)_{j+m_j-i}] [(j)_i] \quad (59)$$

and the symbols $(j)_k$ are given by the expressions

$$(j)_k = j(j-1)(j-2) \dots (j-k+1) \text{ for } k \geq 1 \quad (60)$$

$$(j)_0 = 1 \text{ for } k = 0 \quad (61)$$

The N upper limit of the sum from Eq. (59) is $N = j + m_j - 1$ and the symbols $\binom{i}{j+m_j}$ are combinations of (i) from a set of $(j + m_j)$ (the binomial coefficients).

$$\binom{i}{j+m_j} = \frac{(j+m_j)!}{i!(j+m_j-i)!} \quad (62)$$

Now, it is convenient to define a radial coordinate with no units as $\rho = r/r_0$ where r_0 is the unit length or radius of the first Bohr orbit $r_0 = \hbar^2/m_0 q_e^2$. Thus, we obtain the radial equation Eq. (28) for the Hydrogenic atom as

$$\frac{d^2 R(\rho)}{d\rho^2} + \frac{2}{\rho} \frac{dR(\rho)}{d\rho} + \left(-2\varepsilon + \frac{2Z}{\rho} - \frac{j(j+1)}{\rho^2} \right) R(\rho) = 0 \quad (63)$$

where ε is a dimensionless constant $\varepsilon = -E/E_0$ and $E_0 = q_e^2/r_0$ is known as the energy unit. We assumed now a solution of the form $R(\rho) = R_0 R_\infty f(\rho)$ to this equation, where we have $R_0(\rho) \sim \rho^j$ and $R_\infty(\rho) \sim e^{-\sqrt{2\varepsilon}\rho}$ as asymptotic solutions of radial equation. Further, for generality, we can write

$$j = l \pm \frac{\sigma}{2} \quad (64)$$

Substituting the solution $R(\rho)$ into radial equation Eq. (63), we find the equation for the unknown radial function $f(\rho)$

$$\rho \frac{d^2 f(\rho)}{d\rho^2} + 2(j+1-b\rho) \frac{df(\rho)}{d\rho} + 2[Z-b(j+1)]f(\rho) = 0 \quad (65)$$

where we have introduced the notation $b = \sqrt{2\varepsilon}$. We can simplify this equation if we introduce a new variable with no units $X = 2b\rho = a_0 r$ where $a_0 = 2b/r_0$ so that we can write our differential equation as

$$Xf''(X) + (2j+2-X)f'(X) + \left(\frac{Z}{b} - j - 1 \right) f(X) = 0 \quad (66)$$

Now we can make the notations

$$i = 2j+1 = 2l+1 \pm \sigma \quad (67)$$

$$n_r = k - i = \frac{Z}{b} - j - 1 = \frac{Z}{b} - l \mp \frac{\sigma}{2} - 1 \quad (68)$$

$$k = \frac{Z}{b} + j = n_r + 2j + 1 \quad (69)$$

where the indexes (i) , (n_r) and (k) must be integers. So we can bring the equation to the following final form

$$Xf''(X) + (i+1-X)f'(X) + n_r f(X) = 0 \quad (70)$$

The solution of this equation is a polynomial of degree n_r $f(X) = \sum_{m=0}^{n_r} a_m X^m$ which leads us to following recursion relation between coefficients

$$a_{m+1} = \frac{m+j+1-Z/b}{(m+1)(2j+2+m)} a_m \quad (71)$$

Because the maximum value of m is the degree of the polynomial, we find the condition

$$n_r + j + 1 - \frac{Z}{b} = 0 \quad (72)$$

Therefore, the polynomial $f(X)$ is the same well-known generalized (associated) Laguerre polynomial $L_k^i(X)$. So, the radial wave function $R(r)$ may be written as follows

$$R_{n_j}(r) = R_{n_j}(X) = N_{n_j} X^j e^{-X/2} L_k^i(X) \quad (73)$$

where N_{n_j} are the multiplication factors, whose expression can be determined by the normalization condition of the wave function $\psi_{n_j m_j}(r, \vartheta, \varphi) = R_{n_j}(r) \theta_j^{m_j}(\vartheta) \Phi(\varphi)$ which leads us to the following equation

$$\frac{1}{a_0^3} N_{n_j}^2 \int_0^\infty e^{-X} X^{i+1} [L_k^i(X)]^2 dX = 1 \quad (74)$$

Using here the orthogonality condition of Laguerre polynomials written as

$$\int_0^\infty e^{-X} X^{i+1} [L_k^i(X)]^2 dX = \frac{(2k-i+1)(k!)^3}{(k-i)!} \quad (75)$$

the normalization condition Eq. (74) takes the form

$$\frac{1}{a_0^3} N_{n_j}^2 \frac{(2n \pm \sigma)(n+l \pm \sigma)!^3}{(n-l-1)!} = 1 \quad (76)$$

from which we deduce

$$N_{n_j} = a_0^{3/2} \sqrt{\frac{(n-l-1)!}{(2n \pm \sigma)(n+l \pm \sigma)!^3}} \quad (77)$$

Substituting now Eq. (64) into Eqs. (72) and (70), taking into consideration the expression of principal quantum number $n = n_r + l + 1$, we get the formulas

$$\frac{Z}{b} = n \pm \frac{\sigma}{2} = \frac{Z}{\sqrt{2\varepsilon}} \quad (78)$$

$$k = n + l \pm \sigma \quad (79)$$

Therefore, we find that the total energy eigenvalues for the Hydrogenic atom are given by the expression

$$E_n = -\frac{Z^2 e^4}{8\varepsilon_0^2 \hbar^2} \frac{m_0}{(n \pm \frac{\sigma}{2})^2} \quad (80)$$

2. Conclusions

A first conclusion that can be drawn from this extended model of the hydrogenic atom is that the changes produced by the own magnetic field \vec{B} in the evolution of this type of atom are taken into account through the dimensionless variable σ . From the above definitions of the indices (i) and (k) , in which this variable plays an important role, we deduce that it must be an integer. Also, we can observe that there is a relationship between the variable σ and velocity of the electron v , according to the formula Eq. (30). From this formula we can deduce that the number σ must be positive. Also, from the condition $m_j \leq -1/2$, we get $m_l \leq -\frac{1}{2}(1 \pm \sigma)$. As well, from Eq. (53), we can find the inequality $m_l \leq l$. Further, from these inequalities we get the condition

$$\sigma = \pm(2l+1) \quad (1)$$

Therefore, we can consider that the σ variable is an positive integer $\sigma \geq 1$. So, we can observe that for σ odd, although the electron spin stands out, the total energy formula does not correspond to the experimental results. This weakness of the model is certainly due to the fact that he does not take into account the radiative reaction force (the self force) which acts on the electron. Howbeit, if we admit that $\sigma = 2l + 1$ and we rewrite the radial equation Eq. (28) as follows

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m_0}{\hbar^2} \left[E - U(r) - \frac{\hbar^2}{2m_0} \frac{l(l+1)}{r^2} \right] R(r) = 0 \quad (2)$$

we can observe that it is possible to introduce here another expression for the potential energy $U(r)$ of the atom, as

$$U(r) = -\frac{Zq_e^2}{r} - c_1 \frac{q_e^2}{r^2} \quad (3)$$

where c_1 is a positive constant ($c_1 > 0$). Indeed, taking into consideration the expressions of the quantum numbers, λ and j from Eqs. (46) and (64), we obtain the equation

$$\lambda = j(j+1) = l(l+1) - \frac{\sigma^2}{4} \quad (4)$$

where we have chosen $j = l - \sigma/2$. Therefore, we can identify the second term of this equation as

$$\frac{\sigma^2}{4} = c_1 q_e^2 \frac{2m_0}{\hbar^2} \quad (5)$$

From this equation we can introduce the physics quantity

$$\Delta = \frac{1}{2} \frac{c_2}{c_1} \frac{\sigma}{2} = \frac{1}{2} \frac{c_2}{c_1} \sqrt{c_1 q_e^2 \frac{2m_0}{\hbar^2}} \quad (6)$$

which is named the quantum defect, and for which the experimental formula can be given by the following expression

$$\Delta = c_2 q_e^2 \frac{2m_0}{\hbar^2} \frac{1}{2l+1} \quad (7)$$

where c_2 is a positive constant, too. These formulas are the experimental formulas of the alkali atoms. For these atoms the energy eigenvalues are in accordance with the expression Eq. (80), for $Z = Z_{eff}$. Also, it can be shown that if we take $\sigma = 2$, and we introduce the formulas $j = l' = l - 1$, $m_j = m_l' = m_l - 1$, $n' = n - 1$, can be obtained a theoretical situation in agreement with the results of the Stern-Gerlach experiment. The expression of the electron energy eigenvalues, for $\sigma = 2$, can be written as

$$E_{n'} = -\frac{m_0 Z^2 e^4}{8\epsilon_0^2 \hbar^2} \frac{1}{(n')^2} \quad (8)$$

where $n' = 1, 2, 3, \dots$ becomes principal quantum number.

ANNEX 1

Let us consider the equation for $u(x)$ function [Eq. (65) – contents], as Eq. (1)

$$(1 - x^2)u''(x) - 2(p+1)xu'(x) + [\lambda - p(p+1)]u(x) = 0$$

where $x = \cos\theta$. We can look for the solution as a product between the function $v(x) = 1 - x^2$, raised to a power (t), and a power series in x

$$u(x) = (1 - x^2)^t \sum_{k=0}^{\infty} a_k x^k \quad (2)$$

Substituting this solution into the initial equation Eq. (1), we get

$$(1 - x^2)^t \sum_{k=0}^{\infty} \left\{ (k+1)(k+2)a_{k+2} + \left[L - p(p+1) - 2k(p+1) - 4kt - k(k-1) + \frac{4x^2 t(p+1) + 2x^2 t(2t-1) - 2t}{1-x^2} \right] a_k \right\} x^k = 0 \quad (3)$$

This equation has the singular points $x = \pm 1$. In order to exclude them, we rewrite the numerator of the fraction as

$$4x^2 t(p+1) + 2x^2 t(2t-1) - 2t = -2t\{1 - [2(p+t) + 1]x^2\} \quad (4)$$

Now we can obtain a simplification of the fraction if we impose the condition $p+t=0$. Therefore, we get for the power (t) the values

$$t = -p = \mp m_j \quad (5)$$

and the initial equation Eq. (1) becomes

$$\sum_{k=0}^{\infty} \{ (k+1)(k+2)a_{k+2} + [L - p(p+1) - 2k(p+1) + 4kp - k(k-1) + 2p]a_k \} x^k = 0 \quad (6)$$

Now, after a rearrangement of terms, we rewrite this equation as

$$\sum_{k=0}^{\infty} \{ (k+1)(k+2)a_{k+2} + [L - (p-k)(p-k-1)]a_k \} x^k = 0 \quad (7)$$

which leads us to the following recursion relation between the coefficients a_k

$$(k+1)(k+2)a_{k+2} = -[L - (p-k)(p-k-1)]a_k \quad (8)$$

We impose now the condition as the series be reduced to a polynomial of maximum degree $k_{max} = q$ ($q = 0, 1, 2, 3, \dots$).

Therefore, the recurrence relation *Eq. (8)* leads us to the formula

$$L = (p - q)(p - q - 1) = (q - p)(q - p + 1)$$

which can be written as

$$L = j(j + 1) \quad (9)$$

where

$$j = q - p \quad (10)$$

QED.

ANNEX 2

Starting from the solution of the Legendre equation for half-integers numbers j, m_j ($m_j \leq -1/2$)

$$P_j^{m_j}(x) = [v(x)]^{m_j/2} \frac{d^{j+m_j}}{dx^{j+m_j}} [v^j(x)] \quad (1)$$

where the function $v(x)$ has the expression $v(x) = 1 - x^2$ and is defined over the range $-1 \leq x \leq 1$, we can show the orthogonality of $P_j^{m_j}(x)$ functions with the same superscript m_j , but different subscripts j and k

$$L_{kj}^{m_j} = \int_{-1}^1 P_k^{m_j}(x) P_j^{m_j}(x) dx = 0, \text{ if } k \neq j \quad (2)$$

Also, we can calculate the expression for the coefficients of normalization $C_j^{m_j}$, when the indices j and m_j are half-integers numbers. Substituting the solutions *Eq. (1)* in the integral *Eq. (3)*, we get

$$L_{kj}^{m_j} = \int_{-1}^1 \left\{ v^{m_j}(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] \right\} \left\{ \frac{d^{j+m_j}}{dx^{j+m_j}} [v^j(x)] \right\} dx \quad (3)$$

from which we can see that the indexes (k) and (j) occur symmetrically and, therefore, without loss of generality, it is enough to investigate the case $k \geq j$. We use now the formula of integration by parts

$$\int_{-1}^1 f(x) g'(x) dx = f(x) g(x) \Big|_{-1}^1 - \int_{-1}^1 g(x) f'(x) dx \quad (4)$$

where, we note by $f(x)$ the first bracket, and by $g'(x)$ the two

$$f(x) = v^{m_j}(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] \quad (5)$$

$$g(x) = \frac{d^{j+m_j-1}}{dx^{j+m_j-1}} [v^j(x)] \quad (6)$$

After the first integration, we obtain the following expression for $L_{kj}^{m_j}$

$$L_{kj}^{m_j} = - \int_{-1}^1 \left\{ \frac{d^{j+m_j-1}}{dx^{j+m_j-1}} [v^j(x)] \right\} \frac{d}{dx} \left\{ v^{m_j}(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] \right\} dx \quad (7)$$

We continue the integration by parts, making the notations

$$f_1(x) = \frac{d}{dx} \left\{ v^{m_j}(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] \right\} = f'(x) \quad (8)$$

$$g_1(x) = \frac{d^{j+m_j-2}}{dx^{j+m_j-2}} [v^j(x)] \quad (9)$$

Applying again the formula of integration by parts *Eq. (4)*, we obtain

$$L_{kj}^{m_j} = -f_1(x) g_1(x) \Big|_{-1}^1 + \int_{-1}^1 \frac{d^{j+m_j-2}}{dx^{j+m_j-2}} [v^j(x)] \frac{d^2}{dx^2} \left\{ v^{m_j}(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] \right\} dx \quad (10)$$

Taking the x derivative of $f(x)$ *Eq. (5)*, we obtain

$$f_1(x) = m_j v^{m_j-1}(x) v'(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] + v^{m_j}(x) \frac{d^{k+m_j+1}}{dx^{k+m_j+1}} [v^k(x)] \quad (11)$$

Now we can see that $f_1(-1) = f_1(1) = 0$ if $m_j > 1$, so the integrated term will be zero, because it contains the $v(x)$ factor to a minimum power, $p_{min} = m_j - 2 + 1$ (where number 2 indicates the number of integrations), and the same

$v(x)$ factor to a maximum power, $p_{max} = m_j$, and therefore, this factor will be zero at both endpoints ($x = \pm 1$). Continuing the integration by parts, we can see that the degree of the derivative of the $f(x)$ increases by 1 on each integration, while the degree of the derivative of the $g(x)$ is reduced by 1 on each integration. After a number of (i) integrations by parts, the $f_{i-1}(x)$ factor of the integrated term will be composed from a sum of terms which will include the $v(x)$ factor at the half-integers powers which extend from $p_{min} = m_j - i + 1$ to $p_{max} = m_j$. All these terms will be zero at both endpoints, if $m_j > i - 1$. So, after a number of (i) integrations by parts we can write the expression of $L_{kj}^{m_j}$ Eq. (7) as follows

$$L_{kj}^{m_j} = (-1)^{i-1} f_{i-1}(x) g_{i-1}(x) \Big|_{-1}^1 + (-1)^i \int_{-1}^1 \frac{d^{j+m_j-i}}{dx^{j+m_j-i}} [v^j(x)] \frac{d^i}{dx^i} \left\{ v^{m_j}(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] \right\} dx \quad (12)$$

where

$$f_{i-1}(x) = \frac{d^{i-1}}{dx^{i-1}} [f(x)] \quad (13)$$

$$g_{i-1}(x) = \frac{d^{j+m_j-i}}{dx^{j+m_j-i}} [v^j(x)] \quad (14)$$

As we have seen above, for $i < m_j + 1$, the $f_{i-1}(x)$ factor of integrated term will be zero. For $i > m_j + 1$, this factor will no longer be zero. However, this time will be zero the second factor of product, $g_{i-1}(x)$, because, after we calculate higher and higher derivatives, we will have a sum of terms containing the $v(x)$ function as factor, and the lowest power of $v(x)$ in any of these terms will be $p_{min} = j - (j + m_j - i) = i - m_j > 1$ so that every term will go to zero at the endpoints. Therefore, if we integrate by parts $i = j + m_j$ times, we get

$$L_{kj}^{m_j} = (-1)^{j+m_j} \int_{-1}^1 v^j(x) \frac{d^{j+m_j}}{dx^{j+m_j}} \left\{ v^{m_j}(x) \frac{d^{k+m_j}}{dx^{k+m_j}} [v^k(x)] \right\} dx \quad (15)$$

Now if we let $k = p$, since k and j appeared symmetrically in the initial integral, we may write

$$L_{jp}^{m_j} = (-1)^{p+m_j} \int_{-1}^1 v^p(x) \frac{d^{p+m_j}}{dx^{p+m_j}} \left\{ v^{m_j}(x) \frac{d^{j+m_j}}{dx^{j+m_j}} [v^j(x)] \right\} dx \quad (16)$$

Also, we may consider the case $p \geq j$, which covers all possible cases. Further we can write the $v^j(x)$ function as follows

$$v^j(x) = (1 - x^2)^j = (1 - x)^j (1 + x)^j \quad (17)$$

Using the higher derivative formula for the product (the Leibniz's rule), we take the $(j + m_j)^{th}$ derivative of this function of the form

$$\frac{d^{j+m_j}}{dx^{j+m_j}} [v^j(x)] = (1+x)^j \frac{d^{j+m_j}}{dx^{j+m_j}} (1-x)^j + (1-x)^j \frac{d^{j+m_j}}{dx^{j+m_j}} (1+x)^j + \sum_{k=1}^N \binom{k}{j+m_j} \frac{d^k}{dx^k} (x+1)^j \frac{d^{j+m_j-k}}{dx^{j+m_j-k}} (1-x)^j \quad (18)$$

where $N = j + m_j - 1$. Since each derivative of the function $(1+x)^j$ brings down the exponent and then reduces the exponent by 1, we may write

$$\frac{d^k}{dx^k} (1+x)^j = (j)_k (1+x)^{j-k} \quad (19)$$

or correspondingly for the function $(1-x)^j$, we may also write

$$\frac{d^k}{dx^k} (1-x)^j = (-1)^k (j)_k (1-x)^{j-k} \quad (20)$$

Now if we let $k = j + m_j$ into Eqs. (21) and (22), we obtain

$$\frac{d^{j+m_j}}{dx^{j+m_j}} (1+x)^j = (j)_{j+m_j} (1+x)^{-m_j} \quad (21)$$

$$\frac{d^{j+m_j}}{dx^{j+m_j}} (1-x)^j = (-1)^{j+m_j} (j)_{j+m_j} (1-x)^{-m_j} \quad (22)$$

or, using the same symbol, we may also write

$$\frac{d^{j+m_j-k}}{dx^{j+m_j-k}} (1-x)^j = (-1)^{j+m_j-k} (j)_{j+m_j-k} (1-x)^{k-m_j} \quad (23)$$

If we replace these formulas in Eq. (18) and then we multiply both sides of equation by the functions $v^{m_j}(x)$, we obtain

$$\begin{aligned}
& v^{m_j}(x) \frac{d^{j+m_j}}{dx^{j+m_j}} [v^j(x)] \\
& = (-1)^{j+m_j} \left[(1+x)^{j+m_j} (j)_{j+m_j} + (x-1)^{j+m_j} (j)_{j+m_j} + (1+x)^{j+m_j} \sum_{k=1}^N \binom{k}{j+m_j} (j)_k (j)_{j+m_j-k} \left(\frac{x-1}{x+1}\right)^k \right] \quad (24)
\end{aligned}$$

Now taking the $(p+m_j)^{th}$ derivative of this expression, we get

$$\begin{aligned}
& \frac{d^{p+m_j}}{dx^{p+m_j}} \left\{ v^{m_j}(x) \frac{d^{j+m_j}}{dx^{j+m_j}} [v^j(x)] \right\} = \\
& = (-1)^{j+m_j} \left\{ (j)_{j+m_j} \frac{d^{p+m_j}}{dx^{p+m_j}} [(x+1)^{j+m_j} + (x-1)^{j+m_j}] + \sum_{k=1}^N \binom{k}{j+m_j} (j)_k (j)_{j+m_j-k} \frac{d^{p+m_j}}{dx^{p+m_j}} [(x-1)^k (x+1)^{j+m_j-k}] \right\} \quad (25)
\end{aligned}$$

Since the indexes (p) , (j) and (m_j) are half-integers numbers, the numbers $(p+m_j)$, $(j+m_j)$ and $(j-p)$ will be integers. Therefore, we can introduce the following higher derivatives formulas

$$\frac{d^{p+m_j}}{dx^{p+m_j}} [(x+1)^{j+m_j}] = A_{j+m_j}^{p+m_j} (x+1)^{j-p} \quad (26)$$

$$\frac{d^{p+m_j}}{dx^{p+m_j}} [(x-1)^{j+m_j}] = A_{j+m_j}^{p+m_j} (x-1)^{j-p} \quad (27)$$

where the symbols $A_{j+m_j}^{p+m_j}$ are the permutations of $(p+m_j)$ from a set of $(j+m_j)$

$$A_{j+m_j}^{p+m_j} = \frac{(j+m_j)!}{(j-p)!} \quad (28)$$

where we must impose the inequality $1 \leq p+m_j \leq j+m_j$. Also, we can use now the inequality $p \geq j$. Adding the m_j in the both members of this inequality, we get $p+m_j \geq j+m_j$. From these inequalities we find the condition $p=j$. Applying again the Leibniz's rule, further we may write

$$\begin{aligned}
& \frac{d^{p+m_j}}{dx^{p+m_j}} [(x-1)^k (x+1)^{j+m_j-k}] = (x+1)^{j+m_j-k} \frac{d^{p+m_j}}{dx^{p+m_j}} [(x-1)^k] + \\
& + (x-1)^k \frac{d^{p+m_j}}{dx^{p+m_j}} [(x+1)^{j+m_j-k}] + \sum_{q=1}^{N'} \binom{q}{p+m_j} \frac{d^{p+m_j-q}}{dx^{p+m_j-q}} [(x-1)^k] \frac{d^q}{dx^q} [(x+1)^{j+m_j-k}] \quad (29)
\end{aligned}$$

where $N' = p+m_j-1$. Since $p=j$, the index k is an integer in the range $1 \leq k \leq j+m_j-1$. Therefore, the first two terms of this equation will be zero. So, we can write

$$\frac{d^{p+m_j}}{dx^{p+m_j}} [(x-1)^k (x+1)^{j+m_j-k}] = \sum_{q=1}^{N'} \binom{q}{p+m_j} \frac{d^{p+m_j-q}}{dx^{p+m_j-q}} [(x-1)^k] \frac{d^q}{dx^q} [(x+1)^{j+m_j-k}] \quad (30)$$

Now we use again the higher derivatives formulas as follows

$$\frac{d^{p+m_j-q}}{dx^{p+m_j-q}} [(x-1)^k] = A_k^{p+m_j-q} (x-1)^{k-(p+m_j-q)} \quad (31)$$

$$\frac{d^q}{dx^q} [(x+1)^{j+m_j-k}] = A_{j+m_j-k}^q (x+1)^{j+m_j-k-q} \quad (32)$$

where we must impose the inequalities

$$1 \leq p+m_j-q \leq k \quad (33)$$

$$1 \leq q \leq j+m_j-k \quad (34)$$

from which we deduce

$$p+m_j-k \leq q \leq j+m_j-k \quad (35)$$

So, we have for the two indexes, p and q , the conditions

$$\begin{cases} p = j \\ q = j+m_j-k \end{cases} \quad (36)$$

Inserting these conditions in Eqs. (31), (32) we get

$$\frac{d^{p+m_j-q}}{dx^{p+m_j-q}} [(x-1)^k] = A_k^k = k! \quad (37)$$

$$\frac{d^q}{dx^q} [(x+1)^{j+m_j-k}] = A_q^q = q! \quad (38)$$

Also, we get $N' = N = j + m_j - 1$. Therefore, the expression Eq. (30) takes the final form

$$\frac{d^{p+m_j}}{dx^{p+m_j}} [(x-1)^k (x+1)^{j+m_j-k}] = \sum_{q=1}^N \binom{q}{j+m_j} (k!) (q!) \quad (39)$$

This is different from zero only when $p = j$. For $p \neq j$ will be zero. Also, for $p = j$, Eqs. (26) and (27) becomes

$$\frac{d^{p+m_j}}{dx^{p+m_j}} [(x+1)^{j+m_j}] = A_{j+m_j}^{j+m_j} = (j+m_j)! \quad (40)$$

$$\frac{d^{p+m_j}}{dx^{p+m_j}} [(x-1)^{j+m_j}] = A_{j+m_j}^{j+m_j} = (j+m_j)! \quad (41)$$

Thus, for $p = j$, Eq. (25) can be written as

$$\frac{d^{p+m_j}}{dx^{p+m_j}} \left[v^{m_j} \frac{d^{j+m_j}}{dx^{j+m_j}} (v^j) \right] = (-1)^{j+m_j} \left\{ 2(j)_{j+m_j} [(j+m_j)!] + \sum_{k=1}^N \sum_{q=1}^N \binom{k}{j+m_j} \binom{q}{j+m_j} (j)_k (j)_{j+m_j-k} [(k)!] [(q)!] \right\} \quad (42)$$

where, if we replace $q = j + m_j - k$ and we take into consideration the relations

$$\binom{q}{j+m_j} = \binom{j+m_j-k}{j+m_j} = \binom{k}{j+m_j} \quad (43)$$

we can write this equation as

$$\frac{d^{p+m_j}}{dx^{p+m_j}} \left\{ v^{m_j}(x) \frac{d^{j+m_j}}{dx^{j+m_j}} [v^j(x)] \right\} = 2(-1)^{j+m_j} K_j^{m_j} \quad (44)$$

Therefore, the integral $L_{jp}^{m_j}$ Eq. (16) takes the following form

$$L_{jp}^{m_j} = (-1)^{p+m_j} (-1)^{j+m_j} 2K_j^{m_j} \delta_{jp} \int_{-1}^1 (1-x^2)^j dx \quad (45)$$

where, in agreement with the previous results, we have used here the Kronecker symbol δ_{jp} that shows the orthogonality of functions $P_j^{m_j}(x)$ with $j \neq p$. Thus, for $j = p$, the integral Eq. (45) becomes

$$L_{jj}^{m_j} = 2K_j^{m_j} \int_{-1}^1 (1-x^2)^j dx \quad (46)$$

The final integral can be evaluated by using the trigonometric substitution $x = \cos\vartheta$ and the trigonometric formula

$$\sin^k \vartheta = \frac{k-1}{k} \sin^{k-2} \vartheta - \frac{1}{k} \frac{d}{d\vartheta} (\sin^{k-1} \vartheta \cos \vartheta)$$

After an integration by parts, the integral can be written as

$$I_k = \int_0^\pi \sin^k \vartheta d\vartheta = \frac{k-1}{k} I_{k-2} \quad (47)$$

where $k = 2j + 1$. Therefore, we can establish the following formula

$$I_k = \frac{k-1}{k} \frac{k-3}{k-2} \frac{k-5}{k-4} \dots \frac{3}{4} I_2 \quad (48)$$

Since k is an even number, we can write $k = 2m$ ($m \geq 1$, integer) and the integral I_k Eq. (48) becomes

$$I_k = \pi \frac{(2m)!}{2^{2m} \cdot (m!)^2} \quad (49)$$

or, using the quantum number j , the integral gets the formula

$$I_k = I_{2j+1} = \pi \frac{(2j+1)!}{2^{2j+1} [(j+\frac{1}{2})!]^2} \quad (50)$$

So, plugging this back into Eq. (46), we get finally

$$L_{jj}^{m_j} = \int_{-1}^1 P_j^{m_j}(x) P_j^{m_j}(x) dx = 2\pi K_j^{m_j} \frac{(2j+1)!}{2^{2j+1} [(j+\frac{1}{2})!]^2} \quad (51)$$

Now if we write the normalization condition for the functions $\theta_j^{m_j}(x) = C_j^{m_j} P_j^{m_j}(x)$, we obtain

$$\int_{-1}^1 \theta_j^{m_j}(x) \theta_j^{m_j}(x) dx = (C_j^{m_j})^2 L_{jj}^{m_j} = 1 \quad (52)$$

from which we deduce the constants $C_j^{m_j}$ as follows

$$C_j^{m_j} = \sqrt{\frac{2^{2j+1} [(j+\frac{1}{2})!]^2}{2\pi K_j^{m_j} (2j+1)!}} \quad (53)$$

QED.

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