Dirac equation, spin and fine structure Hamiltonian

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The Dirac equation is the starting point for relativistic quantum mechanics which evolved into the modern Quantum Field Theory. The purpose of this paper is to introduce it from a historical point of view and focus on two conspicuous applications. The first one is the explanation of the spin of the electron on a theoretical basis. The second is the derivation of the fine structure Hamiltonian that gives the relativistic corrections on the hydrogen atom.

I. HISTORICAL INTRODUCTION

Along the following sections we are going to give quite a number of historical references and comments but we want to devote this one entirely to the groundbreaking paper [1] in which Dirac introduced his new equation. After 80 years, it is noticeable how close this paper is to the modern reader. Definitively it is not only a fundamental contribution, it is also a very advisable reading.

The paper [1] has six sections and a general introduction that we label as 0. We describe here the contents with some comments avoiding deliberately formulas and technical points.

§0. Dirac notices firstly the discrepancy between the experiments and the quantum theory predictions for atoms. After mentioning the contribution of Pauli and Darwin to solve this problem, he indirectly suggests that they are artificial theories (with the funny sentence "The question remains as to why Nature should have chosen this particular model for the electron"). Finally he announces in an impersonal way a Hamiltonian in agreement with relativity and the experiments.

§1. *Previous Relativity Treatments*. This is a kind of technical continuation of the introduction. The Klein-Gordon equation (named here as Gordon-Klein) is considered as a tentative relativistic Schrödinger equation with two difficulties: Its limitation to define probabilities of dynamical variables and the existence of negative energies. The last paragraph contains an assertion between modest and prophetic: "we shall be concerned only with the removal of the first of these two difficulties. The resulting theory is therefore still only an approximation".

§2. *The Hamiltonian for No Field*. The content of this fundamental section is a derivation of the Dirac equation as a factorization of the Klein-Gordon equation in a way that could be found in any modern book except for slight changes in the notation. Something that sounds strange from the modern point of view is that Dirac seems to be prone to consider the needed extra dimensions (and even the matrices) as reflecting new "variables".

§3. *Proof of Invariance under a Lorentz Transformation*. Although the equation has been derived starting from a relativistic expression, it is not clear what Lorentz covariance means for it. The point to have in mind (that still puzzles students) is that the four coordinates of Ψ (the spinor wave function) are not the four coordinates of Minkowski space-time. In this section one can follow the steps of the proof but the underlying idea remains a little obscure. Paying a high price, the modern language of representations makes this point clearer [2, 4.2].

§4. *The Hamiltonian for an Arbitrary Field*. The equation for an electron in an electromagnetic field is displayed at the beginning and the rest of the section contains manipulations with $\boldsymbol{\sigma}$ that nowadays could be consider prolix.

§5. *The Angular Momentum Integrals for Motion in a Central Field*. This is an impressive and important part of the paper. In one sentence, the spin of the electron is deduced. Namely, it is proved is that $\boldsymbol{L} + \frac{\hbar}{2}\boldsymbol{\sigma}$ is a constant of motion under Dirac equation in a central field (and $\boldsymbol{L}$ is not). This is an honest theoretical physics answer for the philosophical question about the Nature in the introduction.

§6. *The Energy Levels for Motion in a Central Field*. The motivation here is to deduce that the correction for the hydrogen atom matches the theory of Pauli and Darwin. Dirac is sketchy in this section and some interesting implications appear in the second part of the paper [3]. Shortly after, Darwin published his study of the fine structure of the hydrogen atom [4].

Along this work we will tackle topics related to the sections in the paper by Dirac with the only important omission of the Lorentz covariance, which is more technical in nature. In connection with the last section, we derive the fine structure Hamiltonian which is one of the aftermaths of it.

II. SEVERAL FORMULATIONS

Let us start with some motivation following Dirac's steps. The idea to create a relativistic Schrödinger equation is to quantize the relation $E^2 = p^2 c^2 + m^2 c^4$ promoting E and p to be the corresponding operators. In this way it comes out the *Klein-Gordon equation* for the free particle (by a slip of the pen there is a wrong sign in [1])

$$-\hbar^2 \partial_t^2 \Psi = -\hbar^2 c^2 \nabla^2 \Psi + m^2 c^4 \Psi. \qquad (1)$$

This is a second order equation in time. It means that the wave function at a fixed time does not determine its evolution in later times. A deeper problem is that it lead to negative probabilities (see e.g. [5, §1.2]).

The Dirac equation is usually introduced, following the original [1, §5], as a "factorization" of Eq. (1). Let us examine a toy analogy. Consider the classical harmonic oscillator ruled by $\ddot{x} + \omega^2 x = 0$ and say that for some reason one wants to turn it into a first order linear equation $\alpha\dot{x} + \beta x = 0$. The first reaction is to claim that this is blatantly impossible because we need the freedom to impose two initial conditions, one for position and another for velocity. The key point is that the dimension of the solution vector space can be increased keeping the order promoting x to be a vector and consequently the coefficients to matrices. In our example $\ddot{x} + \omega^2 x = 0$ is equivalent to the vector equation

$$\alpha\dot{X} + \beta X = O \quad \text{with} \quad \alpha = \mathbf{1}_{2\times 2}, \ \beta = \begin{pmatrix} 0 & -1 \\ \omega^2 & 0 \end{pmatrix}. \quad (2)$$

The matrix equation forces $X = (x, \dot{x})^t$ with x a solution of the scalar equation. This is the cheap and well-known mathematical trick of hiding higher order derivatives in coordinates. A calculation shows $(\alpha\frac{d}{dt} - \beta)(\alpha\frac{d}{dt} + \beta) = \frac{d^2}{dt^2} + \omega^2$ (Cayley-Hamilton theorem is working here) and we can say that we have factorized the original equation.

In the same way, we could write Eq. (1) as

$$\left(-i\hbar\partial_t + c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2\right)\left(i\hbar\partial_t + c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2\right)\Psi = 0 \ (3)$$

if we impose for $i, j \in \{1, 2, 3\}$, $i \neq j$,

$$\alpha_j^2 = \beta^2 = 1, \quad \alpha_i\alpha_j + \alpha_j\alpha_i = 0 \quad \text{and} \quad \alpha_j\beta + \beta\alpha_j = 0. \quad (4)$$

Of course this cannot fulfilled with numbers, we need to move to the noncommutative realm of matrices. The first two relations for α_j are part of those for the Pauli matrices but the third spoils any choice of a 2×2 matrix β with $\beta^2 = 1$. Taking $\beta = 1$ would work flipping the middle $+$ sign into $-$. In fact it can be proved [6, XX.7] that the smallest dimension to have a solution of Eq. (4) with Hermitian matrices is 4. Roughly speaking, flipping signs requires to increase the square roots of 1 doubling the dimension. A possible choice fulfilling Eq. (4) is

$$\alpha_j = \begin{pmatrix} O & \sigma_j \\ \sigma_j & O \end{pmatrix} \qquad \text{and} \qquad \beta = \begin{pmatrix} I & O \\ O & -I \end{pmatrix}, \quad (5)$$

written in blocks of 2×2 matrices. It is not the only choice but it can be proved that all possible choices are equivalent except for a change of basis [6, XX.III.10].

After the previous factorization, we infer the *Dirac equation* in its Hamiltonian form

$$i\hbar\partial_t\Psi = H\Psi \quad \text{with} \quad H = c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2. \quad (6)$$

This is an evolution equation and then time plays a distinguished role (by the way, the conservation of the probability $\int \Psi^\dagger\Psi$ follows easily from it). With an eye to deal with Lorentz covariance, it is convenient to define

$$\gamma^j = \beta\alpha_j \quad \text{and} \quad \gamma^0 = \beta. \quad (7)$$

With this notation the Dirac equation becomes

$$\left(i\hbar\gamma^\mu\partial_\mu - mc\right)\Psi = 0 \quad (8)$$

where, as usual in relativity, it is assumed $\mu \in \{0, 1, 2, 3, 4\}$ and the summation convention. This is called the *covariant form* of the Dirac equation. In QFT (Quantum Field Theory) very often $\gamma^\mu\partial_\mu$ is abbreviated as $\not{\partial}$ and the equation acquires the minimalist form in natural units $(i\not{\partial} - m)\Psi = 0$. The explicit form of the γ^μ corresponding to the choice Eq. (5) is the so-called *Dirac representation*

$$\gamma^0 = \begin{pmatrix} I & O \\ O & -I \end{pmatrix}, \quad \gamma^j = \begin{pmatrix} 0 & \sigma_j \\ -\sigma_j & 0 \end{pmatrix}. \quad (9)$$

In some contexts it is convenient to define γ^0 differently, namely

$$\gamma^0 = \begin{pmatrix} O & I \\ I & O \end{pmatrix}, \quad \gamma^j = \begin{pmatrix} 0 & \sigma_j \\ -\sigma_j & 0 \end{pmatrix}. \quad (10)$$

This is called the *Weyl representation*. It corresponds to a different choice of $\boldsymbol{\alpha}$ and β i.e., to switch the two couples of columns and to change the sign of the last couple of rows in Eq. (5).

The relations Eq. (4) translate into the suggestive compact formula

$$\gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2\eta^{\mu\nu}\mathbf{1}_{4\times 4} \quad (11)$$

where $\eta^{\mu\nu}$ are the components of the Minkowski tensor. It turns out that under Lorentz transformations $\boldsymbol{\gamma} = (\gamma^0, \gamma^1, \gamma^2, \gamma^3)$ transforms as a vector and the Lorentz covariance of the Dirac equation means that there is a corresponding representation of the Lorentz group acting on Ψ.

Shortly we will examine some of the noteworthy achievements of the Dirac equation. Before going on, when one sees these 4×4 matrices a natural question shows up pointing an inconvenience. The physical meaning of the extra dimensions is unclear. The wave function was originally, as the name suggests, a function representing a wave, afterward it became a vector (a 2-spinor to be precise) to encode the two possibilities for the spin of the electron but we now have two more coordinates. The full answer is not easy and it is related to Dirac's self-criticism in [1, §1]. The equation contains information about two particles, the electron and the positron and they cannot be separated because they are excitations of the same quantum field [7, 37.4]. Then Ψ actually represents a field and the Dirac equation is a starting point of quantum field theory.

Nevertheless there is a symmetry between both particles, better expressed with Eq. (10), that implies that the new two extra components do not add degrees of freedom. Namely, when Eq. (10) is substituted in the Dirac equation $mc\Psi = i\hbar\gamma^\mu\partial_\mu\Psi$ we conclude that the first two components are determined by the two last components and vice-versa. As said in [2, §4.3], the four components are only necessary "to make room for the Dirac matrices" fulfilling Eq. (4). It motivates that in the applications we discuss, at some point we select one half of the 4-spinor Ψ.

III.   THE SPIN OF THE ELECTRON

The spin and particularly the spin of the electron baffled the pioneers of quantum physics who saw that atomic spectroscopy in some aspects confirmed the theory and in some other did not. It is enlightening the last sentence in the seminal paper by Schrödinger [8] in which after noticing some contradictions with the experiments, he claims "The deficiency must be intimately connected with Uhlenbeck-Goudsmit's theory of the spinning electron. But in what way the electron spin has to be taken into account in the present theory is yet unknown". We address the reader to [9] to read from a master how the concept of spin evolved and how influential was.

A major advance was provided by Pauli (and also Darwin contributed) who according with the abstract of his famous paper [10] arrived at "a formulation of the quantum mechanics of the magnetic electron by the Schrödinger method of eigenfunctions". Pauli matrices appear there by the first time.

There is something slightly discomforting in the equation introduced by Pauli, in fact he was not satisfied with it. In some way, it is not fundamental, it is created having in mind that it has to reflect the expected magnetic moment. In this section we are going to see that the equation that Pauli got is a kind of nonrelativistic limit of the Dirac equation (created from first quantum relativistic principles) and the spin of the electron is embodied in the equation. Dirac considered it "an unexpected bonus".

To couple Eq. (6) to an electromagnetic field, the natural equation (minimal coupling) is

$$i\hbar\partial_t\Psi = \Big(c\boldsymbol{\alpha}\cdot\big(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\big) + \beta mc^2 + e\Phi\Big)\Psi \qquad (12)$$

where, as usual, $\boldsymbol{A}$ is the vector potential and Φ is the scalar potential.

Recalling the form of β in Eq. (5) we note that we are adding the rest mass in the two first coordinates and subtracting it in the two latter coordinates. As we will promptly see, this causes that in the nonrelativistic setting the upper half Ψ_l of the spinor Ψ is "large" and the lower half Ψ_s is "small". Writing Eq. (12) in terms of Ψ_l and Ψ_s, we get

$$\begin{cases} i\hbar\partial_t\Psi_l = c\boldsymbol{\sigma}\cdot\big(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\big)\Psi_s + mc^2\Psi_l + e\Phi\Psi_l, \\ i\hbar\partial_t\Psi_s = c\boldsymbol{\sigma}\cdot\big(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\big)\Psi_l - mc^2\Psi_s + e\Phi\Psi_s. \end{cases} \qquad (13)$$

If Ψ is an eigenstate with energy $\mathcal{E}$, in nonrelativistic situations, $\mathcal{E}$ should be close to the rest mass mc^2 and then the second equation can be approximated by $2mc\Psi_s = \boldsymbol{\sigma}\cdot(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A})\Psi_l$ leading to v/c as the ratio of the size of Ψ_s to the size of Ψ_l, so the "small" part Ψ_s is actually small in this situation. When we substitute the approximate second equation into the first, we obtain

$$i\hbar\partial_t\Psi_l = \frac{1}{2m}\big(\boldsymbol{\sigma}\cdot(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A})\big)^2\Psi_l + mc^2\Psi_l + e\Phi\Psi_l. \quad (14)$$

Recalling the well-known formula

$$(\boldsymbol{\sigma}\cdot\boldsymbol{u})(\boldsymbol{\sigma}\cdot\boldsymbol{v}) = \boldsymbol{u}\cdot\boldsymbol{v} + i\boldsymbol{\sigma}\cdot(\boldsymbol{u}\times\boldsymbol{v}), \qquad (15)$$

which is also valid for operators, we have

$$i\hbar\partial_t\Psi_l = \frac{1}{2m}(S + P + mc^2)\Psi_l \qquad (16)$$

where

$$S = \frac{1}{2m}\big(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\big)^2 + e\Phi \qquad (17)$$

gives the terms that would appear using the Schrödinger equation and

$$P = -i\frac{e}{c}\boldsymbol{\sigma}\cdot(\boldsymbol{p}\times\boldsymbol{A} + \boldsymbol{A}\times\boldsymbol{p}) \qquad (18)$$

is a new extra (Pauli) term. Using the vector calculus formula for $\nabla\times(\varphi\boldsymbol{v})$ we have

$$(\boldsymbol{p}\times\boldsymbol{A} + \boldsymbol{A}\times\boldsymbol{p})\Psi_l = -i\hbar(\nabla\times\boldsymbol{A})\Psi_l = -i\hbar\boldsymbol{B}\Psi_l. \quad (19)$$

Finally, renaming Ψ_l as $\Psi e^{-imc^2t/\hbar}$ which corresponds to omit the contribution to the energy corresponding to the rest mass, we arrive to the *Pauli equation*

$$i\hbar\partial_t\Psi = \Big(\frac{1}{2m}\big(\boldsymbol{p}-\frac{e}{c}\boldsymbol{A}\big)^2 + e\Phi - \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{B}\Big)\Psi. \quad (20)$$

The term involving $\boldsymbol{\sigma}\cdot\boldsymbol{B}$ would not appear with Schrödinger's scalar wave function approach and shows an intrinsic coupling to the magnetic field with a gyromagnetic ratio e/m which doubles the one of a classic electron in a circular orbit. In other words, an electron behaves as a magnet with a strength that doubles the corresponding one to a classical spinning electron. This quantum property is, of course, the *spin*.

From the historical point of view, Eq. (20) was introduced by Pauli in [10] looking for something behaving as an angular moment to match the experiments. They suggested a new degree of freedom and motivate the introduction of vector wave functions with two coordinates. Ironically Kronig should be considered as the pioneer who introduced the spin but Pauli opposed to his idea and he did not publish it [9, §2], [11]. In a curious twist, later Kronig criticized the new view of the spin.

We have got Eq. (20) as a consequence of Dirac equation that is, so to speak, fundamental but a certain uneasy feeling persists because perhaps something is lost in the approximation and in principle the spin could be a nonrelativistic shadow of a more complex concept. Now, following [1, §5], we show another form to arrive to the spin without using any approximation.

Let us consider the Dirac equation in the form Eq. (6) for the free electron (Dirac also allows a central potential but it does not make any difference). A calculation proves

$$[H, L_z] = i\hbar c(\alpha_1 p_2 - \alpha_2 p_1). \qquad (21)$$

A similar calculation applies to the rest of the coordinates showing $[H, L] = -i\hbar c\boldsymbol{\alpha} \times \boldsymbol{p}$. It is then apparent that angular momentum is not conserved. This suggests that there is an internal spin of the electron compensating the missing angular momentum (this was taken by Pauli as starting point). Dirac just writes in his paper the formula for the corresponding operator S and checks $[H, L + S] = 0$. Here we give some insight about how to deduce or guess such term. We look for S_z Hermitian such that $[H, L_z + S_z] = 0$. When we impose that the coefficients of p_j and the independent term vanish we get the equations

$$-i\hbar\alpha_2 = [S_z, \alpha_1], \qquad i\hbar\alpha_1 = [S_z, \alpha_2] \qquad (22)$$

and

$$[S_z, \alpha_3] = 0, \qquad [S_z, \beta] = 0 \qquad (23)$$

The latter commutation formula implies that S_z is block diagonal and the former establishes a relation between both blocks. In this way we can write $S_z = \frac{1}{2}\hbar \operatorname{diag}(A, \sigma_3 A \sigma_3)$ with A a 2×2 Hermitian matrix. On the other hand, the equations Eq. (22) imply

$$2i\sigma_2 = A\sigma_1 + i\sigma_2 A\sigma_3, \quad -2i\sigma_1 = A\sigma_2 - \sigma_1 A\sigma_3. \quad (24)$$

In a more symmetric form, post-multiplying by σ_3,

$$2i\sigma_1 = \sigma_2 A - A\sigma_2, \quad 2i\sigma_2 = A\sigma_1 - \sigma_1 A. \qquad (25)$$

We recognize immediately the commutation relations for Pauli matrices and the equations suggest $A = \sigma_3$ leading to $S_z = \frac{1}{2}\hbar \operatorname{diag}(\sigma_3, \sigma_3)$. In general the missing angular moment is $\frac{1}{2}\hbar \operatorname{diag}(\boldsymbol{\sigma}, \boldsymbol{\sigma})$. In other words, we are just duplicating the usual spin matrices to match the four coordinates of the 4-spinor.

A last comment is that although Eq. (25) suggests $A = \sigma_3$ it does not imply it, any diagonal matrix with $a_{11} - a_{22} = 2$ verifies it. One can avoid this ambiguity imposing that A^2 is a multiple of the identity. This proxy of $\sigma_j^2 = \operatorname{Id}$ comes from considering eigenstates of the angular moment, or some sort of symmetry. The resulting equality $S_x^2 + S_y^2 + S_z^2 = \frac{3}{4}\hbar^2$ proves that we are in the case of $\frac{1}{2}$-spin.

IV.   THE FINE STRUCTURE HAMILTONIAN

We now focus on the case of the hydrogen atom model via Eq. (13) with $\Phi = -e/r$ and $\boldsymbol{A} = \boldsymbol{0}$ (no external magnetic field). To emphasize that the same arguments work for any central potential we write $V = e\Phi$ and we only assume $V = V(r)$.

For an eigenstate of energy $\mathcal{E}$, Eq. (13) acquires the time independent form

$$\begin{cases} \mathcal{E}\psi_l = c\boldsymbol{\sigma} \cdot \boldsymbol{p}\psi_s + mc^2\psi_l + V\psi_l, \\ \mathcal{E}\psi_s = c\boldsymbol{\sigma} \cdot \boldsymbol{p}\psi_l - mc^2\psi_s + V\psi_s. \end{cases} \qquad (26)$$

Our target is to find a kind of relativistic correction of the Schrödinger equation. For comparison, it seems natural to separate the rest energy mc^2 and try to write Eq. (26) with some degree of approximation as

$$H\psi = E\psi \qquad \text{where} \quad E = \mathcal{E} - mc^2 \qquad (27)$$

where ψ is a 2-spinor related in some way to ψ_l and ψ_s.

Recall that in Bohr model, as seen by Sommerfeld, the fine structure constant is the ratio of the electron velocity to c. Then the ratio of the relativistic kinetic energy to $\frac{1}{2m}p^2$ is 1 plus something comparable to α^2. Hence to keep the relativistic corrections we focus on a higher order in α^2. Namely, we do not distinguish between a factor 1 and a factor $1 + O(\alpha^4)$.

After these preliminary considerations, we are going to get a valid Eq. (27) following two approaches. The first one is taken from [12]. It is simpler but produces a nonstandard form of the result. The second approach (in which we follow mainly [13]) is more technical but suggests a general method that we do not explore here.

§1.   *The fine structure Hamiltonian via a direct approach and perturbation theory.*

We proceed as before eliminating ψ_s but this time we do not use any nonrelativistic approximation. In this way we arrive to the exact equation

$$c^2\boldsymbol{\sigma} \cdot \boldsymbol{p}(2mc^2 + E - V)^{-1}\boldsymbol{\sigma} \cdot \boldsymbol{p}\psi_l + V\psi_l = E\psi_l. \quad (28)$$

If we parallel the procedure to derive Pauli equation we should consider $(2mc^2 + E - V)^{-1}$ as the constant $(2mc^2)^{-1}$ but then we would lose the relativistic correction. We instead note that $E - V$ is the kinetic energy, which is $O(mc^2\alpha^2)$ in the Sommerfeld model (see the comments above), and we infer

$$(2mc^2 + E - V)^{-1} = \frac{1}{2mc^2}\left(1 - \frac{E - V}{2mc^2}\right) + O\left(\frac{\alpha^4}{mc^2}\right). \quad (29)$$

Note that the simple identity $[\boldsymbol{p}, V] = -i\hbar\nabla V$ shows

$$\boldsymbol{\sigma} \cdot \boldsymbol{p}\left(1 - \frac{E - V}{2mc^2}\right) = \left(1 - \frac{E - V}{2mc^2}\right)\boldsymbol{\sigma} \cdot \boldsymbol{p} - \frac{i\hbar}{2mc^2}\boldsymbol{\sigma} \cdot \nabla V. \quad (30)$$

Let us approximate in the right hand side the kinetic energy $E - V$ by $\frac{1}{2m}\boldsymbol{p}^2$. Then we get substituting Eq. (29) and Eq. (30) in Eq. (28) our tentative form of the Hamiltonian

$$H = \frac{1}{2m}\left(1 - \frac{\boldsymbol{p}^2}{4m^2c^2}\right)\boldsymbol{p}^2 - \frac{i\hbar}{4m^2c^2}(\boldsymbol{\sigma} \cdot \nabla V)(\boldsymbol{\sigma} \cdot \boldsymbol{p}) + V. \quad (31)$$

Appealing to the same heuristic argument as before, in the last approximation we are losing a factor $1 + O(\alpha^4)$ and we are under the allowed error.

The only remaining point is to simplify H to get a manageable expression and to identify the physical meaning of each term. The simplification repeats part of the strategy used in the Pauli equation: The application of Eq. (15) allows to write dot and cross products in terms

of electromagnetic data that here are very simple because V is a central potential. Namely, V necessarily verifies $\nabla V = \frac{1}{r}\frac{dV}{dr}\boldsymbol{r}$ and Eq. (15) gives

$$(\boldsymbol{\sigma}\cdot\nabla V)(\boldsymbol{\sigma}\cdot\boldsymbol{p}) = \frac{dV}{dr}\frac{\boldsymbol{r}}{r}\cdot\boldsymbol{p} + i\boldsymbol{\sigma}\cdot\left(\frac{dV}{dr}\frac{\boldsymbol{r}}{r}\times\boldsymbol{p}\right) \quad (32)$$
$$= -i\hbar\frac{dV}{dr}\frac{\partial}{\partial r} + \frac{i}{r}\frac{dV}{dr}\boldsymbol{\sigma}\cdot\boldsymbol{L}$$

where we have used $\boldsymbol{r}\cdot\nabla = r\frac{\partial}{\partial r}$ and the definition of angular momentum. If we substitute this in Eq. (31) and put $\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$, we finally obtain the *fine structure Hamiltonian*

$$H = H_0 - \frac{\boldsymbol{p}^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2r}\frac{dV}{dr}\boldsymbol{S}\cdot\boldsymbol{L} \quad (33)$$

where

$$H_0 = \frac{\boldsymbol{p}^2}{2m} + V \quad (34)$$

is the part coming from the Schrödinger equation and the rest of the terms are the corrections. The first one is the natural relativistic correction of the energy linked to the approximation of the relativistic energy

$$\sqrt{p^2c^2 + m^2c^4} \approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}. \quad (35)$$

The last term in Eq. (33) takes into account the coupling between the spin and the orbital angular momentum, it is the *spin-orbit term* and shows once again that the spin of the electron is embodied in the Dirac equation. Finally, the middle term is a little more mysterious. It is named the *Darwin term* and it can be interpreted as an effective smearing out of the potential due to the lack of localization of the electron (see [14] for more comments on this).

Actually Eq. (33) is the Hamiltonian as it appears in [12] but the form of the Darwin term seems to enter in contradiction with the rest of the texts we have checked ([5], [13], [15], [6], [14]). In them $-\frac{\hbar^2}{4m^2c^2}\frac{dV}{dr}\frac{\partial}{\partial r}$ is replaced by $\frac{\hbar^2}{8m^2c^2}\nabla^2 V$. The hint to solve this paradox came to us from a sentence in the old classic on atomic spectroscopy [16]. Note that these terms are of the lowest order. According to time independent perturbation theory they contribute to the energy as their expectations

$$-\frac{\hbar^2}{4m^2c^2}\langle\psi|\frac{dV}{dr}|\frac{\partial\psi}{\partial r}\rangle \quad\text{and}\quad \frac{\hbar^2}{8m^2c^2}\langle\psi|\nabla^2 V|\psi\rangle. \quad (36)$$

We are going to see that they coincide and then both terms give similar spectra to the limit of application of perturbation theory. We have for $\psi(\boldsymbol{r}) = R(r)Y(\theta,\varphi)$

$$2\langle\psi|\frac{dV}{dr}|\frac{\partial\psi}{\partial r}\rangle = \int_{S^2}\int_0^\infty \frac{dV}{dr}\frac{d(R^2)}{dr}|Y|^2 r^2\, dr d\Omega \quad (37)$$

and integrating by parts in the inner integral, this is

$$-\int_{S^2}\int_0^\infty \frac{d}{dr}\left(r^2\frac{dV}{dr}\right)R^2|Y|^2\, dr d\Omega = \langle\psi|\nabla^2 V|\psi\rangle, \quad (38)$$

where we have employed $r^2\nabla^2 V = \frac{d}{dr}\left(r^2\frac{dV}{dr}\right)$ because V is radial.

§2.   *The fine structure Hamiltonian via a Foldy-Wouthuysen transformation.*

Now we are going to show another approach that leads to the fine structure Hamiltonian in its standard form. To deduce the Pauli equation we showed that the equation Eq. (13) becomes decoupled in the nonrelativistic limit, getting Eq. (14). When we kept the relativistic terms, Eq. (28) was not entirely satisfactory because the left hand side that we would like to be the Hamiltonian depends itself on the energy. A clever idea introduced in [17] to deal with Eq. (13) keeping higher order terms is to introduce an artificial unitary change of basis U such that the system turns to be approximately decoupled. Roughly speaking it is like looking for a near to optimal choice of the small and large spinors. Recall that in our case $\boldsymbol{A} = \boldsymbol{0}$, $V = e\Phi$ (a central potential) and renaming, as before, the energy $\mathcal{E}$ in Eq. (26) as $E + mc^2$, we look for U such that

$$U\begin{pmatrix} V & c\boldsymbol{\sigma}\cdot\boldsymbol{p} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{p} & V - 2mc^2 \end{pmatrix}U^\dagger \approx \begin{pmatrix} H & O \\ O & H' \end{pmatrix}. \quad (39)$$

In honor to the authors of [17], U is called the *Foldy-Wouthuysen transformation*. In principle the method can be pushed to get any degree of approximation [18] [5] but the calculations become very complex (in an early published version of [18] the method is said to be "horrendous"). Here we only consider the first step that corresponds to

$$U = \begin{pmatrix} K & \frac{\boldsymbol{\sigma}\cdot\boldsymbol{p}}{2mc} \\ \frac{\boldsymbol{\sigma}\cdot\boldsymbol{p}}{2mc} & -K \end{pmatrix} \quad\text{with}\quad K = \sqrt{1 - \frac{\boldsymbol{p}^2}{4m^2c^2}}. \quad (40)$$

Note that U is unitary and Hermitian, $U = U^\dagger = U^{-1}$.

Before doing any calculation, let us examine the admissible degree of approximation in Eq. (39). We have that H is an approximation of $\frac{1}{2m}\boldsymbol{p}^2 + V$ then H' must be comparable to mc^2. If f is the size of the actual off-diagonal blocks in Eq. (39), the second couple of coordinates, our new small spinor, is suppressed by a factor $O(f/mc^2)$ with respect to the first. Then the off-diagonal upper block affects to H as $O(f^2/mc^2)$ and with f like $O(E\alpha)$ we get for H the admissible error $O(E\alpha^4)$ we want (recall that $E \sim \frac{1}{2}m(c\alpha)^2$ with Sommerfeld's heuristic).

Let us decompose the middle matrix in Eq. (39) as

$$M_V + M_p = \begin{pmatrix} V & O \\ O & V \end{pmatrix} + \begin{pmatrix} O & c\boldsymbol{\sigma}\cdot\boldsymbol{p} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{p} & -2mc^2 \end{pmatrix}. \quad (41)$$

When computing $UM_V U^\dagger$, it is clear that in the off-diagonal blocks V is multiplied by a factor $\boldsymbol{\sigma}\cdot\boldsymbol{p}/mc$ and this is absorbed by the admissible error $O(E\alpha)$. On the other hand, the first diagonal block coming form M_V is

$$H_V = KVK + \frac{1}{4m^2c^2}\boldsymbol{\sigma}\cdot\boldsymbol{p}V\boldsymbol{\sigma}\cdot\boldsymbol{p}. \quad (42)$$

In the same way, the off-diagonal blocks of $UM_pU^\dagger$ are third powers of $\boldsymbol{p}$ divided by m^2c and this is $O(E\alpha)$. The first diagonal block coming form M_p is

$$H_p = \frac{1}{m}K\boldsymbol{p}^2 - \frac{1}{2m}\boldsymbol{p}^2 \qquad (43)$$

The Hamiltonian $H_p + H_V$ is consequently valid but it is too cumbersome to be useful. So we simplify it employing

$$K \approx 1 - \frac{\boldsymbol{p}^2}{8m^2c^2} \qquad (44)$$

with the admissible error $O(\alpha^4)$. Hence

$$H_p \approx \frac{\boldsymbol{p}^2}{2m} - \frac{\boldsymbol{p}^4}{8m^3c^2}, \qquad (45)$$

as expected from Eq. (35). For H_V we obtain, substituting Eq. (44),

$$H_V \approx V + \frac{1}{8m^2c^2}(2\boldsymbol{\sigma}\cdot\boldsymbol{p}V\boldsymbol{\sigma}\cdot\boldsymbol{p} - V\boldsymbol{p}^2 - \boldsymbol{p}^2V). \qquad (46)$$

Note that $\boldsymbol{p}^2V = -\hbar^2\nabla^2V + 2(\boldsymbol{p}V)\cdot\boldsymbol{p} + V\boldsymbol{p}^2$. A calculation involving Eq. (15) shows that $\boldsymbol{\sigma}\cdot\boldsymbol{p}V\boldsymbol{\sigma}\cdot\boldsymbol{p} - (\boldsymbol{p}V)\cdot\boldsymbol{p} - V\boldsymbol{p}^2$ is

$$\hbar\boldsymbol{\sigma}\cdot(\nabla V \times \boldsymbol{p}) = \frac{\hbar}{r}\frac{dV}{dr}\boldsymbol{\sigma}\cdot(\boldsymbol{r}\times\boldsymbol{p}) = \frac{2}{r}\frac{dV}{dr}\boldsymbol{S}\cdot\boldsymbol{L}. \qquad (47)$$

And we arrive to the fine structure Hamiltonian in its standard form

$$H = H_0 - \frac{\boldsymbol{p}^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}\nabla^2V + \frac{1}{2m^2c^2r}\frac{dV}{dr}\boldsymbol{S}\cdot\boldsymbol{L} \qquad (48)$$

with H_0 as in Eq. (34).

V. DISCUSSION

The Dirac equation is a central topic in quantum mechanics and it opens the gate to QFT. It has many significant features from the theoretical and applied point of view. Some of these features treated in this paper are:

1. It allows to "factorize" the relativistic Schrödinger equation (a.k.a. Klein-Gordon equation) avoiding the unwanted properties of it that motivated that Schrödinger himself abandoned the relativistic approach and focused on the nonrelativistic version bearing his name.

2. It gives a theoretical basis for the existence of the spin of the electron. This is a major achievement because in the early times of quantum mechanics the spin was a source of misunderstandings (e.g. Stern-Gerlach experiment, anomalous Zeeman effect) and it had been introduced "by hand" to avoid the disagreement with the experiments.

3. When applied to the hydrogen atom, it produces a Hamiltonian that gives fine corrections on the energy levels that can be computed via perturbation theory and checked experimentally.

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