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The Quantum Theory of the Electron.

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The new quantum mechanics, when applied to the problem of the structure of the atom with point-charge electrons, does not give results in agreement with experiment. The discrepancies consist of "duplexity" phenomena, the observed number of stationary states for an electron in an atom being twice the number given by the theory. To meet the difficulty, Goudsmit and Uhlenbeck have introduced the idea of an electron with a spin angular momentum of half a quantum and a magnetic moment of one Bohr magneton. This model for the electron has been fitted into the new mechanics by Pauli,* and Darwin,† working with an equivalent theory, has shown that it gives results in agreement with experiment for hydrogen-like spectra to the first order of accuracy.

The Klein-Gordon equation

§ 1. *Previous Relativity Treatments.*

The relativity Hamiltonian according to the classical theory for a point electron moving in an arbitrary electro-magnetic field with scalar potential A_0 and vector potential **A** is

$$F \equiv \left(\frac{W}{c} + \frac{e}{c}A_0\right)^2 + \left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + m^2c^2,$$

where **p** is the momentum vector. It has been suggested by Gordon* that the operator of the wave equation of the quantum theory should be obtained from this F by the same procedure as in non-relativity theory, namely, by putting

$$W = ih\frac{\partial}{\partial t},$$

$$p_r = -ih\frac{\partial}{\partial x_r}, \qquad r = 1, 2, 3,$$

in it. This gives the wave equation

$$F\psi \equiv \left[\left(ih\frac{\partial}{c\,\partial t} + \frac{e}{c}A_0\right)^2 + \Sigma_r\left(-ih\frac{\partial}{\partial x_r} + \frac{e}{c}A_r\right)^2 + m^2c^2\right]\psi = 0, \qquad (1)$$

the wave function ψ being a function of x_1, x_2, x_3, t.

What is the difficulty??

The general interpretation of non-relativity quantum mechanics is based on the transformation theory, and is made possible by the wave equation being of the form

$$(H - W)\psi = 0, \qquad (2)$$

i.e., being linear in W or $\partial/\partial t$, so that the wave function at any time determines the wave function at any later time. The wave equation of the relativity theory must also be linear in W if the general interpretation is to be possible.

The case of no field

§ 2. *The Hamiltonian for No Field.*

Our problem is to obtain a wave equation of the form (2) which shall be invariant under a Lorentz transformation and shall be equivalent to (1) in the limit of large quantum numbers. We shall consider first the case of no field, when equation (1) reduces to

$$(-p_0^2 + \mathbf{p}^2 + m^2c^2)\,\psi = 0 \tag{3}$$

if one puts

$$p_0 = \frac{W}{c} = ih\frac{\partial}{c\,\partial t}.$$

The symmetry between p_0 and p_1, p_2, p_3 required by relativity shows that, since the Hamiltonian we want is linear in p_0, it must also be linear in p_1, p_2 and p_3. Our wave equation is therefore of the form

$$(p_0 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \beta)\,\psi = 0, \tag{4}$$

where for the present all that is known about the dynamical variables or operators α_1, α_2, α_3, β is that they are independent of p_0, p_1, p_2, p_3, *i.e.*, that they commute with t, x_1, x_2, x_3. Since we are considering the case of a particle moving in empty space, so that all points in space are equivalent, we should expect the Hamiltonian not to involve t, x_1, x_2, x_3. This means that α_1, α_2, α_3, β are independent of t, x_1, x_2, x_3, *i.e.*, that they commute with p_0, p_1, p_2, p_3. We are therefore obliged to have other dynamical variables besides the co-ordinates and momenta of the electron, in order that α_1, α_2, α_3, β may be functions of them. The wave function ψ must then involve more variables than merely x_1, x_2, x_3, t.

Equation (4) leads to

$$0 = (-p_0 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \beta)(p_0 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \beta)\psi$$
$$= [-p_0^2 + \Sigma\, \alpha_1^2 p_1^2 + \Sigma\,(\alpha_1\alpha_2 + \alpha_2\alpha_1)\, p_1 p_2 + \beta^2 + \Sigma\,(\alpha_1\beta + \beta\alpha_1)\, p_1]\,\psi, \quad (5)$$

where the Σ refers to cyclic permutation of the suffixes 1, 2, 3. This agrees with (3) if

$$\left.\begin{array}{ll} \alpha_r^2 = 1, & \alpha_r\alpha_s + \alpha_s\alpha_r = 0 \quad (r \neq s) \\ \beta^2 = m^2c^2, & \alpha_r\beta + \beta\alpha_r = 0 \end{array}\right\} \quad r, s = 1, 2, 3.$$

If we put $\beta = \alpha_4 mc$, these conditions become

$$\alpha_\mu^2 = 1 \qquad \alpha_\mu\alpha_\nu + \alpha_\nu\alpha_\mu = 0 \; (\mu \neq \nu) \qquad \mu, \nu = 1, 2, 3, 4. \quad (6)$$

We must now find four matrices α_μ to satisfy the conditions (6). We make use of the matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

which Pauli introduced* to describe the three components of spin angular momentum. These matrices have just the properties

$$\sigma_r^2 = 1 \qquad \sigma_r\sigma_s + \sigma_s\sigma_r = 0, \qquad (r \neq s), \tag{7}$$

that we require for our α's. We cannot, however, just take the σ's to be three of our α's, because then it would not be possible to find the fourth. We must extend the σ's in a diagonal manner to bring in two more rows and columns, so that we can introduce three more matrices ρ_1, ρ_2, ρ_3 of the same form as σ_1, σ_2, σ_3, but referring to different rows and columns, thus :—

$$\sigma_1 = \begin{Bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{Bmatrix} \quad \sigma_2 = \begin{Bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{Bmatrix} \quad \sigma_3 = \begin{Bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{Bmatrix},$$

$$\rho_1 = \begin{Bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{Bmatrix} \quad \rho_2 = \begin{Bmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{Bmatrix} \quad \rho_3 = \begin{Bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{Bmatrix}.$$

The ρ's are obtained from the σ's by interchanging the second and third rows, and the second and third columns. We now have, in addition to equations (7)

and also

$$\left.\begin{aligned} \rho_r^2 = 1 \qquad \rho_r\rho_s + \rho_s\rho_r = 0 \qquad (r \neq s), \\ \rho_r\sigma_t = \sigma_t\rho_r. \end{aligned}\right\} \tag{7'}$$

If we now take

$$\alpha_1 = \rho_1\sigma_1, \quad \alpha_2 = \rho_1\sigma_2, \quad \alpha_3 = \rho_1\sigma_3, \quad \alpha_4 = \rho_3,$$

all the conditions (6) are satisfied, *e.g.*,

$$\alpha_1^2 = \rho_1\sigma_1\rho_1\sigma_1 = \rho_1^2\sigma_1^2 = 1$$

$$\alpha_1\alpha_2 = \rho_1\sigma_1\rho_1\sigma_2 = \rho_1^2\sigma_1\sigma_2 = -\rho_1^2\sigma_2\sigma_1 = -\alpha_2\alpha_1.$$

The following equations are to be noted for later reference

$$\left.\begin{array}{l}\rho_1\rho_2 = i\rho_3 = -\rho_2\rho_1 \\ \sigma_1\sigma_2 = i\sigma_3 = -\sigma_2\sigma_1\end{array}\right\}, \qquad (8)$$

together with the equations obtained by cyclic permutation of the suffixes.

The wave equation (4) now takes the form

$$[p_0 + \rho_1(\boldsymbol{\sigma}, \mathbf{p}) + \rho_3 mc]\,\psi = 0, \qquad (9)$$

where $\boldsymbol{\sigma}$ denotes the vector $(\sigma_1, \sigma_2, \sigma_3)$.

§ 3. *Proof of Invariance under a Lorentz Transformation.*

Multiply equation (9) by ρ_3 on the left-hand side. It becomes, with the help of (8),

$$[\rho_3 p_0 + i\rho_2(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3) + mc]\psi = 0.$$

Putting

$$p_0 = ip_4,$$

$$\rho_3 = \gamma_4, \qquad \rho_2\sigma_r = \gamma_r, \qquad r = 1, 2, 3, \tag{10}$$

we have

$$[i\Sigma\gamma_\mu p_\mu + mc]\psi = 0, \qquad \mu = 1, 2, 3, 4. \tag{11}$$

The p_μ transform under a Lorentz transformation according to the law

$$p_\mu' = \Sigma_\nu a_{\mu\nu} p_\nu,$$

where the coefficients $a_{\mu\nu}$ are c-numbers satisfying

$$\Sigma_\mu a_{\mu\nu} a_{\mu\tau} = \delta_{\nu\tau}, \qquad \Sigma_\tau a_{\mu\tau} a_{\nu\tau} = \delta_{\mu\nu}.$$

The wave equation therefore transforms into

$$[i\Sigma\gamma_\mu' p_\mu' + mc]\psi = 0, \tag{12}$$

where

$$\gamma_\mu' = \Sigma_\nu a_{\mu\nu}\gamma_\nu.$$

Now the γ_μ, like the α_μ, satisfy

$$\gamma_\mu^2 = 1, \qquad \gamma_\mu\gamma_\nu + \gamma_\nu\gamma_\mu = 0, \qquad (\mu \neq \nu).$$

The algebraic structure of Dirac‘s matrices:

These relations can be summed up in the single equation

$$\gamma_\mu \gamma_\nu + \gamma_\nu \gamma_\mu = 2\delta_{\mu\nu}.$$

Dirac‘s equation for an arbitrary field

§ 4. *The Hamiltonian for an Arbitrary Field.*

To obtain the Hamiltonian for an electron in an electromagnetic field with scalar potential A_0 and vector potential $\mathbf{A}$, we adopt the usual procedure of substituting $p_0 + e/c \cdot A_0$ for p_0 and $\mathbf{p} + e/c \cdot \mathbf{A}$ for $\mathbf{p}$ in the Hamiltonian for no field. From equation (9) we thus obtain

$$\left[p_0 + \frac{e}{c}A_0 + \rho_1\left(\boldsymbol{\sigma}, \mathbf{p} + \frac{e}{c}\mathbf{A}\right) + \rho_3 mc\right]\psi = 0. \quad (14)$$

Let us repeat Dirac's argument slightly modernized

1 The form of the Dirac equation

The relativistic Hamiltonian is given by (see, for example, Messiah 1969)

$$H = e\Phi + \left[(\mathbf{p} - e\mathbf{A})^2 + m^2\right]^{1/2}, \qquad (1)$$

where Φ is a scalar potential, $\mathbf{A}$ the vector potential, and m the mass of the system. Assuming, in accordance with the postulates of quantum mechanics, that the probability density ρ,

$$\rho = \psi\psi* \geqslant 0, \qquad (2)$$

is positive definite, it follows that the Hamilton operator has to be hermitean. For the sake of simplicity in the following no field is considered. The Hamiltonian therefore reduces to

$$H = \left(p^2 + m^2\right)^{1/2}. \qquad (3)$$

From eqn 3 one can see immediately that when applying the correspondence principle

$$E \to \mathrm{i}\frac{\partial}{\partial t}; \qquad \mathbf{p} \to -\mathrm{i}\boldsymbol{\nabla}, \qquad (4)$$

because of the square root, the condition of linearity for the Hamilton operator is not met in a straightforward manner.

1.1 Polynomial algebras

Consider a second-order polynomial $P_2(x)$:

$$P_2(x) = a_{21}\sum_{i\neq j} x_i x_j + a_{22}\sum_j x_j^2, \qquad (5)$$

$$j = 1, ..., m, \qquad (6)$$

where the a_{ij} are elements of a symmetric matrix, and the following linear form $L(x)$:

$$L(x) = \sum_{j=1}^{m} \alpha_j x_j. \qquad (7)$$

If the linear form $L(x)$ satisfies the condition

$$P(x) + L^2(x) = 0, \qquad (8)$$

then the set of elements $\{\alpha_j\}$ forms an algebra with the following properties

(Raghavacharyulu and Menon 1970):

$$i = j : [\alpha_i, \alpha_j]_+ = -2a_{22}I, \quad (9)$$

$$i \neq j : [\alpha_i, \alpha_j]_+ = -a_{21}I, \quad (10)$$

where $[,]_+$ denotes an anticommutator and I is the identity element in $\{\alpha_j\}$. There are two rather well known special cases: (1) the Grassmann algebra

$$a_{21} = a_{22} = 0; \quad [\alpha_i, \alpha_j]_+ = 0 \quad (11)$$

and (2) the Clifford algebra

$$a_{22} = -1, \quad a_{21} = 0; \quad [\alpha_i, \alpha_j]_+ = 2\delta_{ij}. \quad (12)$$

Obviously the Clifford algebra is exactly the case needed to 'linearize' the square root in eqn 3, where $m = 2, 3$ corresponds to the Pauli case and $m = 4$ to the Dirac case:

$$\left(\sum_{j=1}^{m} p_j^2\right)^{1/2} = \sum_{j=1}^{m} \sigma_j p_j; \quad (P_2(p))^{1/2} = L(p)\,. \quad (13)$$

In order to represent the coefficients σ_j for each case, i.e. $m = 2, 3, 4$, one forms the smallest set of coefficients which shows group closure.

1.2 The Pauli group

For $m = 2$, the smallest set of elements σ_i forming a group is of order 8:

$$G_{\mathrm{P}}^{(m=2)} = \{\sigma_1, \sigma_2, -\sigma_1, -\sigma_2, \sigma_1\sigma_2, -\sigma_1\sigma_2, I, -I\}\,. \quad (14)$$

This group has five classes:

$$\mathcal{C}_1 = \{I\}\,, \quad \mathcal{C}_2 = \{-I\}$$

$$\mathcal{C}_3 = \{\sigma_1, -\sigma_1\} \quad \mathcal{C}_4 = \{\sigma_2, -\sigma_2\} \quad (15)$$

$$\mathcal{C}_5 = \{\sigma_1\sigma_2, -\sigma_1\sigma_2\}\,, \quad (16)$$

and therefore five irreducible representations, the dimensions of which are related to the group order as follows:

$$\sum_{i=1}^{5} n_i^2 = 8. \quad (17)$$

This implies that four irreducible representations $(D_i, i = 1, 4)$ are one dimensional $\left(n_i^2 = 1\right)$. This in turn implies that they are commutative and therefore not Clifford algebraic. The fifth irreducible representation

(D_5) is two dimensional and - as can easily be checked - is given by the following set of matrices:

$$D_5(\pm I) = \pm \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, D_5(\pm\sigma_1) = \pm \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{18}$$

$$D_5(\pm\sigma_2) = \pm \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, D_5(\pm\sigma_1\sigma_2) = \pm \begin{pmatrix} \mathrm{i} & 0 \\ 0 & -\mathrm{i} \end{pmatrix}$$

with Clifford algebraic properties. For $m = 2$ the problem of the linearization of the square root is therefore completely solved by

$$\left(p_1^2 + p_2^2\right)^{1/2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = p_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + p_2 \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}. \tag{19}$$

The same representation as in eqn 18 can also be used for the $m = 3$ case:

$$D_5(\sigma_3) = -\mathrm{i}D_5(\sigma_1)\, D_5(\sigma_2) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{20}$$

The matrices $D_5(\sigma_i)$, $i = 1, 2, 3$, are usually denoted simply by σ_i and are the famous Pauli spin matrices. For $m = 2, 3$, the corresponding group is usually called the Pauli group.

1.3 The Dirac group

For $m = 4$ the following subset of the Clifford algebra forms a group

$$G_{\mathrm{D}}^{(m=4)} = \left\{ \begin{array}{c} \pm I, \pm\gamma_\mu, \pm\gamma_\mu\gamma_\nu\, (\mu > \nu), \\ \pm\gamma_\mu\gamma_\nu\gamma_\sigma\, (\mu > \nu > \sigma), \gamma_1\gamma_2\gamma_3\gamma_4 = \gamma_5 \end{array} \right\}. \tag{21}$$

The order of this group is 32 and it has 17 classes. This implies (see eqn 17) that 16 irreducible representations are one dimensional (commutative) and one irreducible representation is four dimensional. This last irreducible representation is Clifford algebraic, and one particular realization of the representatives of $\gamma_i, i = 1, 4$, gives the famous Dirac matrices

$$\alpha_i = D(\gamma_i) = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}; \qquad i = 1, 2, 3, \tag{22}$$

$$\beta = D(\gamma_4) = \begin{pmatrix} \mathbf{I}_2 & 0 \\ 0 & -\mathbf{I}_2 \end{pmatrix},$$

with $\mathbf{I}_n$ being an n-dimensional unit matrix.

Since the Pauli groups are subgroups of the Dirac group, one can show that the irreducible representations of the Dirac group can be found in terms of representations induced by irreducible representations of $G_{\mathrm{P}}^{(m=2)}$. On the other hand, one can also show that representations of the Dirac group do not contain the irreducible representation D_5 (eqn 18). Considering therefore only the structure of the Pauli and Dirac groups and their irreducible representations, one can immediately show that there is no way of describing the relativistic Hamiltonian in terms of a 2×2 matrix operator equation without violating fundamental algebraic properties.

Dirac‘s connex to the Schrödinger & Pauli equations or the origin of the

Mass-velocity & Darwin terms,

Spin-orbit interaction

§ 6. *The Energy Levels for Motion in a Central Field.*

We shall now obtain the wave equation as a differential equation in r, with the variables that specify the orientation of the whole system removed. We can do this by the use only of elementary non-commutative algebra in the following way.

After separation of variables Dirac arrives at the following „radial“ equation:

$$F\psi \equiv [p_0 + V + \rho_2 p_r - \rho_1 jh/r + \rho_3 mc]\psi = 0.$$

If we write this equation out in full, calling the components of ψ referring to the first and third rows (or columns) of the matrices ψ_α and ψ_β respectively, we get

$$(F\psi)_\alpha \equiv (p_0 + V)\psi_\alpha - h\frac{\partial}{\partial r}\psi_\beta - \frac{jh}{r}\psi_\beta + mc\psi_\alpha = 0,$$

$$(F\psi)_\beta \equiv (p_0 + V)\psi_\beta + h\frac{\partial}{\partial r}\psi_\alpha - \frac{jh}{r}\psi_\alpha - mc\psi_\beta = 0.$$

The second and fourth components give just a repetition of these two equation

We shall now eliminate ψ_α. If we write hB for $p_0 + V + mc$, the first equatio

becomes

$$\left(\frac{\partial}{\partial r} + \frac{j}{r}\right)\psi_\beta = B\psi_\alpha,$$

which gives on differentiating

$$\frac{\partial^2}{\partial r^2}\psi_\beta + \frac{j}{r}\frac{\partial}{\partial r}\psi_\beta - \frac{j}{r^2}\psi_\beta = B\frac{\partial}{\partial r}\psi_\alpha + \frac{\partial B}{\partial r}\psi_\alpha$$

$$= \frac{B}{h}\left[-(p_0 + V - mc)\psi_\beta + \frac{jh}{r}\psi_\alpha\right] + \frac{1}{h}\frac{\partial V}{\partial r}\psi_\alpha$$

$$= -\frac{(p_0 + V)^2 - m^2c^2}{h^2}\psi_\beta + \left(\frac{j}{r} + \frac{1}{Bh}\frac{\partial V}{\partial r}\right)\left(\frac{\partial}{\partial r} + \frac{j}{r}\right)\psi$$

This reduces to

$$\frac{\partial^2}{\partial r^2}\psi_\beta + \left[\frac{(p_0 + V)^2 - m^2c^2}{h^2} - \frac{j(j+1)}{r^2}\right]\psi_\beta - \frac{1}{Bh}\frac{\partial V}{\partial r}\left(\frac{\partial}{\partial r} + \frac{j}{r}\right)\psi_\beta = 0. \quad (25)$$

The values of the parameter p_0 for which this equation has a solution finite at $r = 0$ and $r = \infty$ are $1/c$ times the energy levels of the system. To compare this equation with those of previous theories, we put $\psi_\beta = r\chi$, so that

$$\frac{\partial^2}{\partial r^2}\chi + \frac{2}{r}\frac{\partial}{\partial r}\chi + \left[\frac{(p_0 + V)^2 - m^2c^2}{h^2} - \frac{j(j+1)}{r^2}\right]\chi - \frac{1}{Bh}\frac{\partial V}{\partial r}\left(\frac{\partial}{\partial r} + \frac{j+1}{r}\right)\chi = 0. \quad (26)$$

If one neglects the last term, which is small on account of B being large, this equation becomes the same as the ordinary Schroedinger equation for the system, with relativity correction included. Since j has, from its definition, both positive and negative integral characteristic values, our equation will give twice as many energy levels when the last term is not neglected.

We shall now compare the last term of (26), which is of the same order of magnitude as the relativity correction, with the spin correction given by Darwin and Pauli. To do this we must eliminate the $\partial\chi/\partial r$ term by a further transformation of the wave function. We put

$$\chi = \mathrm{B}^{-\frac{1}{2}}\chi_1,$$

which gives

$$\frac{\partial^2}{\partial r^2}\chi_1 + \frac{2}{r}\frac{\partial}{\partial r}\chi_1 + \left[\frac{(p_0+\mathrm{V})^2 - m^2c^2}{h^2} - \frac{j(j+1)}{r^2}\right]\chi_1$$
$$+\left[\frac{1}{\mathrm{B}h}\frac{j}{r}\frac{\partial \mathrm{V}}{\partial r} - \frac{1}{2}\frac{1}{\mathrm{B}h}\frac{\partial^2 \mathrm{V}}{\partial r^2} + \frac{3}{4}\frac{1}{\mathrm{B}^2h^2}\left(\frac{\partial \mathrm{V}}{\partial r}\right)^2\right]\chi_1 = 0. \quad (27)$$

2 U 2

The elimination method slightly modernized:

Elimination method & spin-orbit coupling

In atomic units ($\hbar = m = 1$)

$$\mathcal{H} = c\boldsymbol{\alpha}\cdot\mathbf{p} + (\beta - I_4)\,c^2 + V I_4 \quad ,$$

by making use of the bi-spinors property of the wavefunction $|\psi\rangle = |\phi,\chi\rangle$, the corresponding eigenvalue equation can be split into two equations

$$c\boldsymbol{\sigma}\cdot\mathbf{p}\,|\chi\rangle - V\,|\phi\rangle = \epsilon\,|\phi\rangle \quad ,$$

$$c\boldsymbol{\sigma}\cdot\mathbf{p}\,|\phi\rangle + \left(V - 2c^2\right)|\chi\rangle = \epsilon\,|\chi\rangle \quad .$$

Clearly, the spinor $|\chi\rangle$ can now be expressed in terms of $|\phi\rangle$:

$$|\chi\rangle = (1/2c)\,\mathcal{B}^{-1}\boldsymbol{\sigma}\cdot\mathbf{p}\,|\phi\rangle \quad ,$$

$$\mathcal{B} = 1 + \left(1/2c^2\right)(\epsilon - V) \quad ,$$

yielding only one equation for $|\phi\rangle$:

$$\mathcal{D}\,|\phi\rangle = \varepsilon\,|\phi\rangle \quad ,$$

$$\mathcal{D} = (1/2)\,\boldsymbol{\sigma}\cdot\mathbf{p}\mathcal{B}^{-1}\boldsymbol{\sigma}\cdot\mathbf{p} + V \quad .$$

For a central field the operator $\mathcal{D}$ has the same constants of motion as the Dirac Hamiltonian, namely $\mathcal{J}^2$, $\mathcal{J}_z$, and $\mathcal{K}$.The differential equation for the radial amplitudes of $|\phi\rangle$, $R_\kappa(r)/r$ for a spherical symmetric potential $V(r)$,

$$\left[\frac{1}{2}\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\right) + V(r) - \epsilon\right] R_\kappa(r)\,0$$
$$= \left\{\frac{1}{4c^2}B^{-2}(r)\frac{dV(r)}{dr}\frac{\kappa}{r}\right.$$
$$+\frac{1}{4c^2}\left[\left[\epsilon - V(r)\right]B^{-1}(r)\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2}\right)\right]$$
$$\left.+\frac{1}{4c^2}B^{-2}(r)\frac{dV(r)}{dr}\frac{d}{dr}\right\} R_\kappa(r) \quad ,$$

1. For $c = \infty$ this equation is reduced to the radial Schrödinger equation.
2. By approximating the elimination operator $\mathcal{B}$ by unity $(\mathcal{B} = 1)$ the Pauli-Schrödinger equation is obtained, where the terms on the right-hand side are respectively the *spin-orbit coupling*, the *mass velocity term*, and the *Darwin shift*.
3. For $\mathcal{B} \neq 1$ relativistic corrections in order higher than c^{-4}, enter the description of the electronic structure via the normalization.