Chapter 4.

Introduction to Relativistic Quantum Mechanics

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Motivating factors that led to relativistic quantum mechanics are discussed. The idea is to underscore the extent to which classical special relativity including electrodynamics played a role in the development of quantum mechanics in general, and relativistic quantum mechanics in particular … and how easy it was to misinterpret equations. Special relativity anticipates relativistic quantum field theory. Yet, quantum chemistry requires that the number of particles remains fixed, making subtle interpretation unavoidable.

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Seeing the Light
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1. Klein-Gordon Equation

The quest for a mathematical theory of quantum mechanics began with great ambition. At the very least it should be consistent with the theory of special relativity that had revolutionized classical physics. Some were even bold enough to seek consistency with general relativity – a goal that to this day remains elusive.

Most of this early work centered on the energy-momentum relationship

$$E^2 = m^2c^4 + p^2c^2 \ . \tag{1.1}$$

where $\vec{p} = \gamma m\vec{v}$ for massive particles. A photon, having $m = 0$, obeys $E = pc$. Thus, the magnitude of its momentum is $p = E/c$ $= h/\lambda$. The French physicist Louis de Broglie (photo) argued, on the basis of eqn (1.1), that a particle-wave in free space must also obey $p = h/\lambda$. Thus was born the de Broglie wavelength and wave mechanics.

Louis de Broglie was born in 1892 to an aristocratic family of means in the small seaport town of Dieppe, Siene-Maritime in Normandy: Louis-Victor-Pierre-Raymond, 7th duc de Broglie. As a young man, he was neither inclined toward overwork, nor in any particular hurry to complete a thesis. It is said that his advisor invited him to his country estate for a long weekend. However, immediately upon his arrival, de Broglie was restricted, under lock and key, to several rooms in the main building. His advisor would not let him out until he wrote something. What he produced over a period of several days netted him the 1929 Nobel Prize. It would not be politically correct, but I have at times thought of trying something like this.

These five relatively brief sections on relativistic quantum mechanics serve to introduce the subject. Jumping straight into the celebrated cornerstone of relativistic quantum mechanics and quantum field theory, the Dirac equation, is too abrupt for my taste. Rather, a somewhat historical route is followed in which attention is paid to early attempts at a theory of relativistic quantum mechanics.

Moving forward from de Broglie's seminal contribution takes us to the subject of the present chapter, the Klein-Gordon equation, which was the first relativistic (Lorentz covariant) quantum mechanical model. To the best of my knowledge, the Klein-Gordon equation is not used nowadays in either physics or quantum chemistry except for some work with pions.[1] It nonetheless serves as an excellent pedagogical tool for the introduction of concepts. Disparaged shortly after its introduction, it was resurrected and vindicated a decade later when Pauli and his postdoc Victor Weisskopf showed that it is really

[1] On the other hand, the "Klein paradox," as of this writing, is a hot topic in the area of graphene physics. However, the relevant equation of motion is the Dirac equation, not the Klein-Gordon equation, though the difference is not large insofar as the paradox.

an equation in relativistic quantum field theory. This is a case where an incautious assumption at the outset led to misinterpretation.

Four-Momentum

A free particle in the non-relativistic limit obeys: $E = p^2/2m$. The p in $p^2/2m$ is a 3D object, and we know how to deal with it in non-relativistic quantum mechanics. However, Lorentz covariance requires that momentum transform as a four-vector. Specifically, it is necessary to ensure that the quantum mechanical momentum operator $\hat{p}^0$ is in accord with its classical counterpart, E/c. For the time being, carats will be placed atop symbols to denote their operator status.

When $\hat{p}^1$ acts on the wave function ψ of a free particle moving in the x-direction with specified momentum, it must yield h/λ times ψ. Because ψ is proportional to e^{ikx} (where $k = 2\pi/\lambda$), consistency with the classical three-momentum is achieved using $\hat{p}^1 = i\hbar\partial^1$. Lowering the index with the metric tensor $\eta_{\mu\nu}$ yields the familiar covariant form: $-i\hbar\partial_1$. In other words, operating on ψ with $-i\hbar\partial_1$ yields $h/\lambda = \hbar k$ times ψ, and likewise for the other spatial components when $e^{i\vec{k}\cdot\vec{r}}$ is used. The component $\hat{p}^0$ is taken to be $i\hbar\partial^0$ where $x^0 = ct$, and lowering this gives $i\hbar\partial_0$. From the correspondence with the classical expression for the four-momentum, it follows that the eigenvalue of $\hat{p}^0$ (equivalently, of $\hat{p}_0$) must be E/c.[2] Thus, $i\hbar c\,\partial_0\psi = i\hbar\partial_t\psi = E\psi = (\hat{p}^2/2m)\psi$. This reasoning yields the Schrödinger equation:

$$i\hbar\partial_t\psi = E\psi = \hat{H}\psi \ . \tag{1.2}$$

The arguments leading to eqn (1.2) do not constitute a derivation. They support an inference, or educated guess, on the basis of the behavior of a free particle, with the issue of spin put to the side, but not forgotten. A single derivative with respect to time appears in the non-relativistic limit given by the Schrödinger equation. The fact that the equation contains a first derivative with respect to time and a second derivative with respect to space makes it impossible for it to satisfy Lorentz covariance. There are ways to introduce relativistic effects into Schrödinger quantum mechanics (effective core potentials, spin-orbit operators, and other terms), but the theory cannot be made relativistic.

The above approach assigns operator status to energy through correspondence between the components of the classical four-momentum (E/c, $\vec{p}$) and the components of a quantum mechanical operator. In so doing, it avoids having to deal with the square root that arises with eqn (1.1). Specifically, the fact that $E = \pm(m^2c^4 + p^2c^2)^{1/2}$ forces one to deal with what appears to be negative translational energy.

Alternatively, the Schrödinger equation can be obtained from eqn (1.1) by taking the square root of each side of eqn (1.1) and expanding the positive square root on the right hand side in the small-p limit. This gives $mc^2(1 + p^2/m^2c^2)^{1/2} \approx mc^2 + p^2/2m$. However, this maneuver requires that we retain just the positive square root. This makes a

[2] A free particle's phase can be expressed as the contraction of four-vectors: $k^\nu x_\nu = \omega t - \vec{k}\cdot\vec{r}$. It is invariant with respect to Lorentz transformation.

great deal of sense on physical grounds, as the negative square root implies that the particle's translational energy is negative, which of course is impossible. Unfortunately, mathematics does not permit us to toss out half the solutions just because we do not like them. The solutions constitute a complete set of functions for the differential equation at hand. If some are removed, it is then impossible to meet the requirements of Lorentz covariance. Consequently, though the correct result for the non-relativistic limit is obtained, Lorentz covariance is eliminated up front when only the positive square root is taken, that is, even prior to taking the small-*p* limit.

Schrödinger was one of the first scientists to work on this problem. However, he put aside relativistic quantum mechanics because of his inability to introduce spin, as well as to find a way around the square root that gave unphysical results. Instead, he had to settle for the Schrödinger equation. You must admit that this is not bad for a consolation prize. We see that special relativity was in the picture from the very beginning of quantum mechanics.

Maintaining Lorentz Covariance

The majority of scientists who were attempting to formulate a theory of relativistic quantum mechanics appreciated that fiddling around with square roots was a dead-end. It simply went nowhere. Some thought a better strategy would be to work with eqn (1.1) in its given form. This yields a Lorentz covariant equation straightaway. The prescription is uncomplicated: eqn (1.1) is divided by c^2, the term p^2 is replaced with $-\hbar^2\nabla^2$, and E is replaced with $i\hbar\partial_t$. The resulting entity then operates on a wave function:

$$\left(\partial_{ct}{}^2 - \nabla^2 + \left(\frac{mc}{\hbar}\right)^2\right)\phi = 0 \ . \tag{1.3}$$

This is readily expressed in covariant form. The term $\partial_{ct}{}^2$ is equal to $\partial^0\partial_0$ and ∇^2 is equal to $-\partial^i\partial_i$. Thus, eqn (1.3) becomes

$$\left(\partial^\nu\partial_\nu + \left(\frac{mc}{\hbar}\right)^2\right)\phi = 0 \ . \tag{1.4}$$

The Greek letter ϕ serves to distinguish solutions of the Klein-Gordon equation from those of the Schrödinger equation, which are usually denoted ψ. These solutions differ significantly.

Equation (1.4) is the Klein-Gordon equation. The constant $\hbar / mc$ is the Compton wavelength divided by 2π. The Compton wavelength is the wavelength that corresponds to $h\nu = mc^2$, which gives $\lambda = h / mc$. The constant $\hbar / mc$ is the Compton radius.

Equation (1.4) resembles classical wave equations, for example, as encountered in electromagnetic theory. It is easy to obtain eqn (1.4), and in the early 1920's it fascinated a number of prominent scientists: Erwin Schrödinger, Vladimir Fock, Louis de Broglie, Theodor Kaluza, Oscar Klein, Walter Gordon, and others. The latter two published their work (separately) in 1926-27, despite its perceived shortcomings, and consequently their names became associated with eqn (1.4).

Setting the mass term in eqn (1.4) to zero gives a homogeneous wave equation. For example, using one spatial coordinate yields waves: $e^{\pm ikx}e^{\pm i\omega t}$. These solutions resemble those of the Schrödinger equation despite the fact that there are twice as many of them. The mass term in eqn (1.4) results in an additional phase, which can be seen as follows. Defining $\mu \equiv mc/\hbar$, eqn (1.4) is written, for one spatial coordinate,

$$\left(\partial^0\partial_0 + \partial^1\partial_1\right)\phi = -\mu^2\phi\,, \tag{1.5a}$$

which yields

$$\phi \propto e^{\pm ikx \pm i\omega t}\,, \tag{1.5b}$$

where $\omega = (\mu^2c^2 + k^2c^2)^{1/2}$. There are two ± symbols in the exponent. The one in front of ikx goes away in 3D, where $\vec{k}\cdot\vec{r}$ is used. The $\pm i\omega t$ remains, however, and it is subtle and a source of confusion. Nonetheless, the solution $\phi \propto e^{\pm ikx \pm i\omega t}$ is easily verified by substitution into eqn (1.5a).

Expanding the square root $(\mu^2c^2 + k^2c^2)^{1/2}$ in the non-relativistic limit yields

$$\omega = \big(\underbrace{\mu^2c^2}_{\frac{m^2c^4}{\hbar^2}} + k^2c^2\big)^{1/2} \tag{1.6a}$$

$$= \frac{mc^2}{\hbar}\left(1 + \frac{\hbar^2k^2}{m^2c^2}\right)^{1/2} \tag{1.6b}$$

$$\approx \frac{1}{\hbar}\left(mc^2 + \frac{p^2}{2m}\right). \tag{1.6c}$$

The non-relativistic limit of the Klein-Gordon equation therefore yields

$$\phi = e^{-imc^2t/\hbar}\,\psi\,, \tag{1.7}$$

where ψ is the Schrödinger wave function.

Thus, we have arrived at yet another route to the Schrödinger equation. Specifically, put $\phi = e^{-imc^2t/\hbar}\,\psi$ into the Klein-Gordon equation and sort the resulting terms according to powers of c. This enables us to see which terms survive when the limit $c \to \infty$ is taken. There is a bit of algebra, but when this is carried out the Schrödinger equation: $i\hbar\partial_t\psi = H\psi$ is obtained. The algebra is worked out in the box below, compliments of the expert.

Algebra

the expert

Referring to eqn (1.7), the wave function $\phi = e^{-imc^2t/\hbar}\,\psi$ is used with the Klein-Gordon equation, terms are sorted according to powers of c, and the limit $c \to \infty$ is taken in order to arrive at the non-relativistic limit. Using the definition $\mu = mc/\hbar$, the Klein Gordon equation is given by

$$
\begin{aligned}
0 &= \left(\partial_{ct}{}^2 - \nabla^2 + \mu^2\right) e^{-i\mu ct}\,\psi \\
&= \partial_{ct}\left(-i\mu e^{-i\mu ct}\psi + e^{-i\mu ct}\partial_{ct}\psi\right) + e^{-i\mu ct}\left(-\nabla^2 + \mu^2\right)\psi \\
&= e^{-i\mu ct}\left(-\cancel{\mu^2} - i\mu\partial_{ct} - i\mu\partial_{ct} + \partial_{ct}{}^2\right)\psi + e^{-i\mu ct}\left(-\nabla^2 + \cancel{\mu^2}\right)\psi \\
&= \left(-i2\mu\partial_{ct} + \partial_{ct}{}^2 - \nabla^2\right)\psi
\end{aligned}
$$

Using $\mu = mc/\hbar$ yields

$$
-\frac{\hbar^2}{2m}\left(\nabla^2 - \partial_{ct}{}^2\right)\psi = i\hbar\partial_t\psi
$$

The term $\partial_{ct}{}^2\psi$ vanishes in the limit $c \to \infty$, leaving the Schrödinger equation.

Wave equations based on the d'Alembertian operator $\partial^\nu\partial_\nu$ describe classical fields such as those encountered in electromagnetism. In addition, we are familiar with balls and springs, whose equations of motion contain second order spatial derivatives and second order time derivatives. In solving such equations, it is necessary to satisfy two initial conditions, one for displacement and another for the time derivative of the displacement. Consequently, the eigenvalues come in pairs, for example, $\pm\,\omega_0$ for a simple harmonic oscillator without loss. The oscillation amplitude (for one spatial dimension) at a given point is given by $x = Ae^{i\omega_0 t} + Be^{-i\omega_0 t}$, with the understanding that in classical physics real parts are taken.

In quantum mechanics, a particle's position and conjugate momentum cannot be specified independently, as this would violate the commutation relation $[x, p] = i\hbar$. Thus, it is not obvious that a wave equation that is second order in space and time will be suitable quantum mechanically. It turns out that in relativistic quantum field theory position is demoted from the status it enjoys as an operator in non-relativistic quantum mechanics. Instead it is a parameter that tells us where in spacetime a field displacement takes place, with field displacement being the operator. Think of it this way: With space and time treated on equal footing, for position to have operator status would require that time also has operator status. This approach has been pursued, but it is not popular. Recall that the same thing was encountered with phonons, where displacement amplitude enjoys operator status, whereas the spatial location of the displacement does not.

Assuming a pair of energy eigenvalues $\pm E$ is obtained from the second-order differential equation, how can they be interpreted for a free particle? After all, a free particle cannot have energy $-E$. It is often stated that all energy scales are arbitrary, so nothing happens to the equations of motion if a large negative number is added to all of our energies. But this $-E$ is different. When momentum increases, it becomes more negative, which is unacceptable. In fact, relativity places a lower bound on energy. Let us now work through this and other perplexing issues.

2-Component Form

The Klein-Gordon equation can be expressed in a form that is Schrödinger-like, in the sense that a term $i\hbar\partial_t\phi$ is separated from everything else. This facilitates calculations, for example, when the electromagnetic fields are added. It is not possible to truly eliminate the other time derivative and retain relativistic covariance, because the spatial derivatives are second-order. Relativistic covariance requires that space and time derivatives are either each first-order (Dirac equation) or each second-order (Klein-Gordon equation). They cannot be of mixed order in the sense that one is first-order and the other is second-order. When the Klein-Gordon equation is organized in a manner such that the term $i\hbar\partial_t\phi$ appears alone on the left hand side of the equation, the other time derivative is subsumed into a 2-component representation, as explained below.

The price paid for lowering the apparent order of time differentiation is that more components are needed. Solutions go from being a single scalar function ϕ to being a pair of components. The same idea was encountered in classical electrodynamics. In going from a second-order differential operator acting on the four-vector gauge field: $\partial^\nu\partial_\nu A^\mu$, to a first-order differential operator acting on the electromagnetic field strength tensor: $\partial_\alpha F^{\mu\nu}$, the price paid was the larger number of components of $F^{\mu\nu}$. Note that the components of $F^{\mu\nu}$ contain first order differentiation of the gauge field, for example, $F^{12} = \partial^1 A^2 - \partial^2 A^1$. The second-order nature of Maxwell's equations has not been altered. The math has just been modified.

When $i\hbar\partial_t\Phi$ appears as the left hand side of a representation of the Klein-Gordon equation, the right hand side is, by definition, of the form $\hat{H}\Phi$. Here and hereafter, the 2-component vector is denoted Φ. The Hamiltonian thus defined is easily organized by using the Pauli matrices and the unit matrix, as these four matrices constitute a basis in the space of 2D complex matrices. The components are in general complex. When they are real this has important physical significance, but in general they are complex. In the section that follows this one, we shall see how the charged nature of the Klein-Gordon field manifests in the 2-component representation.

To see how the above facts come about, including the mathematics falling into place, requires some manipulation. Keep in mind the scientific atmosphere in which the work was carried out in the 1920's and 1930's. Pauli introduced the exclusion principle in 1924 and the spin matrices that bear his name in 1927. The use of spinors began to catch on. They were no longer a mathematical oddity invented by Élie Cartan. There was a huge amount of discussion, trial and error, dead ends, glorious mistakes, and so on. I say this to dispel any notion you might have that important scientific results fall into place, without tumult, accepted without controversy. And you are getting a distilled version. If the mathematical maneuvers seem less than obvious, bear with it and focus on the physics.

To begin, the following definitions are introduced

$$\varphi \equiv \tfrac{1}{2}\left(\phi + \frac{i\hbar}{mc^2}\partial_t\phi\right) \tag{1.8}$$

$$\chi \equiv \tfrac{1}{2}\left(\phi - \frac{i\hbar}{mc^2}\partial_t\phi\right). \tag{1.9}$$

We will see that the functions φ and χ are the components. The time derivative that is missing when we segregate $i\hbar\partial_t\Phi$ from the rest in order to obtain a Schrödinger-like equation has been subsumed into the components. This is analogous to the first order differential contained in the electromagnetic field strength tensor $F^{\mu\nu}$. Note that the alternate addition and subtraction of eqns (1.8) and (1.9) gives, respectively:

$$\phi = \varphi + \chi \tag{1.10a}$$

and

$$\partial_t\phi = \frac{mc^2}{i\hbar}(\varphi - \chi). \tag{1.10b}$$

The functions φ and χ satisfy the equations

$$\left(i\hbar\partial_t - mc^2\right)\varphi = -\frac{\hbar^2}{2m}\nabla^2\left(\varphi + \chi\right) \tag{1.11a}$$

$$\left(i\hbar\partial_t + mc^2\right)\chi = \frac{\hbar^2}{2m}\nabla^2\left(\varphi + \chi\right). \tag{1.11b}$$

This is easily verified. For example, substitution of φ and χ from eqns (1.8) and (1.9) recovers the Klein-Gordon equation. Likewise, adding eqns (1.11a) and (1.11b) leads to a trivial identity, whereas subtraction yields the Klein-Gordon equation. Next, eqns (1.11a) and (1.11b) are expressed in terms of the 2-component vector

$$\Phi = \begin{pmatrix}\varphi \\ \chi\end{pmatrix}. \tag{1.12}$$

As mentioned above, the Klein-Gordon equation is easily organized for use with Φ by using the unit matrix σ_0 and the Pauli matrices σ_i. The symbol σ is used with the understanding that the space in which these matrices operate bears no relation to either physical space or spin-½ space. Rather, the space in which they operate is that of the components φ and χ. This organization enables eqns (1.11a) and (1.11b) to be expressed as

$$i\hbar\partial_t\sigma_0\Phi = \left(mc^2\sigma_3 - \left(\frac{\hbar^2}{2m}\nabla^2\right)(\sigma_3 + i\sigma_2)\right)\Phi \ . \tag{1.13}$$

This has the appearance of a Schrödinger equation in the sense that a single time derivative appears on the left hand side. The large parentheses on the right hand side contains the effective Hamiltonian that results from isolation of the term $i\hbar\partial_t\Phi$:

$$\hat{H} = mc^2\sigma_3 - \left(\frac{\hbar^2}{2m}\nabla^2\right)(\sigma_3 + i\sigma_2) \ . \tag{1.14}$$

Thus, the Schrödinger-like equation $i\hbar\partial_t\Phi = \hat{H}\Phi$ has the explicit form

$$\begin{pmatrix} i\hbar\partial_t & 0 \\ 0 & i\hbar\partial_t \end{pmatrix}\begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \begin{pmatrix} mc^2 - \dfrac{\hbar^2}{2m}\nabla^2 & -\dfrac{\hbar^2}{2m}\nabla^2 \\ \dfrac{\hbar^2}{2m}\nabla^2 & -mc^2 + \dfrac{\hbar^2}{2m}\nabla^2 \end{pmatrix}\begin{pmatrix} \varphi \\ \chi \end{pmatrix} . \tag{1.15}$$

Keep in mind that φ and χ contain the time derivative according to eqns (1.8) and (1.9).

Currents and Densities

The positive and negative "energies" that result from taking the square root of the energy-momentum relationship: $E^2 = m^2c^4 + p^2c^2 \;\Rightarrow\; E = \pm(m^2c^4 + p^2c^2)^{1/2} \equiv \pm E_p$, have nothing to do with quantum mechanics *per se*. Though nature is quantum mechanical, the difference between $+E_p$ and $-E_p$ exceeds $2mc^2$. Thus, whatever the nature of the problem with interpretation of the plus and minus signs, it must be present in the classical limit. Later we will see that, of course, there never was a negative energy in the sense of a particle having negative kinetic energy. It turns out that electric charge is responsible for the ± that appears in front of E_p.

In Schrödinger quantum mechanics, the continuity equation: $\partial_t\rho = -\nabla\cdot\vec{J}$, where $\rho = \psi^*\psi$, leads straightaway to the expression for the probability-current density for a particle traveling in field-free space, $\vec{J}$:

$$\vec{J} = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right) . \tag{1.16}$$

In fact, it is registry with the continuity equation that constitutes the justification for interpreting $\psi^*\psi$ as a probability density, with $\vec{J}$ its corresponding probability-current density. In other words, in order to interpret $\psi^*\psi$ as a probability density, it is necessary that it satisfy: $\partial_t \rho = -\nabla \cdot \vec{J}$.

Along the same lines, for the Klein-Gordon function ϕ to be interpreted as probability amplitude, with $\phi^*\phi$ its corresponding probability density, the latter must satisfy a relativistic continuity equation. We shall follow this line of thought for the time being, knowing full well that it is destined to fail. This exercise will reveal the true nature of ϕ.

Application of Gauss's law to $\partial_t \rho = -\nabla \cdot \vec{J}$ shows that the integral of $\phi^*\phi$ over all space must be conserved according to the number of particles it describes, *i.e.*, ϕ is normalized. In addition, $\phi^*\phi$ must transform as the zeroth component of a four-vector density. In other words, $P = \phi^*\phi$ must transform according to $P \to \gamma P$.[3] This ensures that $\int d^3 r\, P$ is the same in all inertial frames because $x' = \gamma^{-1} x$ and $P' \to \gamma P$ go together, in which case $dx'dy'dz'P' = dxdydz\, P$.

Pursuant to the above, to obtain expressions for the Klein-Gordon flux and density, the same basic strategy that led to eqn (1.16) is followed. This time, however, we begin with the Klein-Gordon equation rather than with the Schrödinger equation. First, the complex conjugate of eqn (1.4) is taken:

$$\underbrace{\partial^\nu \partial_\nu \phi + \left(\frac{mc}{\hbar}\right)^2 \phi = 0}_{\text{eqn (1.4)}} \rightarrow \partial^\nu \partial_\nu \phi^* + \left(\frac{mc}{\hbar}\right)^2 \phi^* = 0 \,. \tag{1.17a}$$

Next, the expression on the right is multiplied from the left by ϕ to obtain

$$\phi \partial^\nu \partial_\nu \phi^* + \left(\frac{mc}{\hbar}\right)^2 \phi\phi^* = 0 \,. \tag{1.17b}$$

Finally, multiply eqn (1.4) from the left by ϕ^* and subtract it from the above equation. This yields

$$\phi \partial^\nu \partial_\nu \phi^* - \phi^* \partial^\nu \partial_\nu \phi = 0. \tag{1.18}$$

Writing out the time and space parts explicitly yields

$$0 = -\left(1/c^2\right)\underbrace{\left(\phi\, \partial_t \partial_t \phi^* - \phi^* \partial_t \partial_t\, \phi\right)}_{\partial_t \left(\phi\, \partial_t \phi^* - \phi^* \partial_t\, \phi\right)} + \underbrace{\left(\phi\, \nabla^2 \phi^* - \phi^* \nabla^2\, \phi\right)}_{\nabla \cdot \left(\phi\, \nabla \phi^* - \phi^* \nabla \phi\right)} . \tag{1.19}$$

The parenthetic term on the lower right has the same mathematical form as its Schrödinger counterpart in eqn (1.16). Therefore, on the basis of this match, eqn (1.19) is multiplied by $i\hbar / 2m$, and the term on the lower right is labeled $\nabla \cdot \vec{J}$. That is, it is assigned

[3] This is analogous to the conservation of electric charge in going between inertial frames that was encountered in Chapter 2, *Electrodynamics*.

the same label as was used for the Schrödinger probability-current density of eqn (1.16). Thus, eqn (1.19) becomes

$$0 = -\frac{i\hbar}{2mc^2}\partial_t\left(\phi\,\partial_t\phi^* - \phi^*\partial_t\,\phi\right) + \underbrace{\frac{i\hbar}{2m}\nabla\cdot\left(\phi\nabla\phi^* - \phi^*\nabla\phi\right)}_{\nabla\cdot\vec{J}}. \tag{1.20}$$

Charged Currents

Equations (1.19) and (1.20) can be multiplied by any constant. The choice $i\hbar/2m$ is attractive because it achieves registry between the Klein-Gordon and Schrödinger flux densities. However, this choice is flawed. We shall see that when eqn (1.19) is multiplied by $iq\hbar/2m$ rather than by $i\hbar/2m$ things fall into place. Instead of a probability-current density, we have a charge-current density. The minus and plus signs that were deemed problematic earlier correspond to a particle and its antiparticle, which has the same mass but opposite charge, for example, an electron and a positron.

The problem with eqn (1.20) as it stands is that the function ϕ must accommodate both $e^{i\omega t}$ and $e^{-i\omega t}$ solutions. When these are introduced alternately into the left parentheses, they yield quantities that differ in sign. This is how the unphysical result of negative probability density arose. We have no choice except abandonment of the interpretation of the first term on the right hand side of eqn (1.20) as ∂_t operating on a probability density. On the other hand, with charge q multiplying eqn (1.20), the second term is interpreted as the divergence of the charge-current density.

Returning to the first term in eqn (1.20), we multiply it by electric charge q and make the substitutions introduced earlier as eqn (1.10), and reproduced below as eqn (1.21):

$$\phi = \varphi + \chi \qquad\qquad \partial_t\phi = \frac{mc^2}{i\hbar}(\varphi - \chi)\,. \tag{1.21}$$

Using these with the first term in eqn (1.20) yields:[4]

$$\underbrace{-q\frac{i\hbar}{2mc^2}\partial_t\left(\phi\,\partial_t\phi^* - \phi^*\partial_t\,\phi\right)}_{\partial_t\rho} = \partial_t\, q\left(|\varphi|^2 - |\chi|^2\right). \tag{1.22}$$

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[4] Using eqn (1.21), the first term on the right hand side of eqn (1.22) becomes:

$$\left(\frac{-i\hbar q}{2mc^2}\right)\partial_t\left((\varphi+\chi)\left(\frac{imc^2}{\hbar}\right)(\varphi^*-\chi^*) - (\varphi^*+\chi^*)\left(\frac{-imc^2}{\hbar}\right)(\varphi-\chi)\right)$$

$$= \frac{q}{2}\partial_t\left((\varphi+\chi)(\varphi^*-\chi^*) + (\varphi^*+\chi^*)(\varphi-\chi)\right) = \partial_t\, q\left(\varphi\varphi^* - \chi\chi^*\right).$$

It follows that the substitution: $\phi \to \phi^*$ results in $q \to -q$. Specifically, the substitution $\phi \to \phi^*$ on the left hand side causes ρ to change sign. This comes as no surprise, as ρ is a charge density. If ϕ is the solution for a charged particle, ϕ^* is the solution for a particle of the same mass and opposite charge. Though particle and antiparticle are evident in the single component function ϕ and its complex conjugate, respectively, the components φ and χ do not represent the particle and its antiparticle in as transparent a way. Note however, that the charge density can vanish, meaning that the components somehow represent particles and their antiparticles.

Antiparticle

To see how the antiparticle emerges in the mathematical treatment that uses the 2-component representation, let us return to the free particle Hamiltonian given by eqn (1.14). With the electromagnetic potential now included, courtesy of minimal coupling, this Hamiltonian becomes

$$\hat{H} = mc^2\sigma_3 + \frac{1}{2m}\left(-i\hbar\nabla - \frac{q}{c}\vec{A}\right)^2 (\sigma_3 + i\sigma_2) + qV \ , \tag{1.23}$$

where $\vec{A}$ is the magnetic vector potential and V is the electric scalar potential. It is understood that qV is multiplied by the unit matrix, σ_0, and likewise that $\hat{H}$ operates in the 2D space of the spinor components φ and χ. Now take the complex conjugate of the equation: $i\hbar\partial_t\Phi = \hat{H}\Phi = E\Phi$, and multiply all of this from the left by σ_1 to obtain

$$-i\hbar\partial_t\sigma_1\Phi^* = \sigma_1\hat{H}^*\sigma_1\sigma_1\Phi^* = E\sigma_1\Phi^* , \tag{1.24}$$

where $\sigma_1\sigma_1 = 1$ has been inserted. As mentioned earlier, despite the use of suggestive symbols like $\hat{H}$ and E, try to avoid thinking of these as representing the energy of the particle in the sense of the energy that follows from a quantum mechanical eigenvalue equation. For example, we have seen that E can assume both positive and negative values: $E = \pm(m^2c^4 + p^2c^2)^{1/2} = \pm E_p$. Consequently, E should not be interpreted as simply the energy of the particle, as there is no way to reconcile the negative energy $-E_p$.

In comparing eqns (1.23) and (1.24), the following mathematical points are noted: (1) $\sigma_1\sigma_3\sigma_1 = -\sigma_3$; (2) $-i\sigma_1\sigma_2{}^*\sigma_1 = i\sigma_2{}^* = -i\sigma_2$; and (3) in taking the complex conjugate of $(-i\hbar\nabla - (q/c)\vec{A})^2$, the cross term changes sign. Thus, substituting q' for the q in eqn (1.23) and using the above identities, eqn (1.24) becomes

$$-i\hbar\partial_t\sigma_1\Phi^* = \left(mc^2\underbrace{\sigma_1\sigma_3\sigma_1}_{-\sigma_3} + \frac{1}{2m}\left(i\hbar\nabla - \frac{q'}{c}\vec{A}\right)^2 \underbrace{\left(\sigma_1\left(\sigma_3 - i\sigma_2{}^*\right)\sigma_1\right)}_{-(\sigma_3 + i\sigma_2)} + q'V \right)\sigma_1\Phi^* \tag{1.25}$$

$$= \left(-mc^2\sigma_3 - \frac{1}{2m}\left(-i\hbar\nabla + \frac{q'}{c}\vec{A} \right)^2 (\sigma_3 + i\sigma_2) + q'V \right)\sigma_1\Phi^* . \qquad (1.26)$$

When the substitution $q' = -q$ is made and everything is multiplied by -1, this becomes

$$i\hbar\partial_t\sigma_1\Phi^* = \left(mc^2\sigma_3 + \frac{1}{2m}\left(-i\hbar\nabla - \frac{q}{c}\vec{A} \right)^2 (\sigma_3 + i\sigma_2) + qV \right)\sigma_1\Phi^* . \qquad (1.27)$$

From these maneuvers we see that $\sigma_1\Phi^*$ is a solution of the Schrödinger-like equation. However, this has been achieved by replacing the original q with $q' = -q$. To give a specific example, suppose the particle is an electron. Then the q in eqn (1.23) is $-e$, where e is the magnitude of the electron charge, 1.6×10^{-19} Coulombs. The q appearing in eqn (1.27) is then $+e$. In other words, if the spinor for the particle with mass m and charge q is Φ, the spinor for the counterpart particle that has mass m and charge $-q$ is $\sigma_1\Phi^*$. The antiparticle spinor is $\sigma_1\Phi^*$. In this example, the particle is the electron and the antiparticle is the positron.

Earlier we saw that the particle's charge density is $q\left(|\varphi|^2 - |\chi|^2\right) = q\Phi^\dagger\sigma_3\Phi$. The charge density for the corresponding antiparticle is

$$q\left(\sigma_1\Phi^*\right)^\dagger \sigma_3\left(\sigma_1\Phi^*\right) = q\Phi^{*\dagger}\sigma_1\sigma_3\sigma_1\Phi^* \qquad (1.28)$$

$$= q\Phi^{*\dagger}(-\sigma_3)\Phi^* \qquad (1.29)$$

$$= -q\left(|\varphi|^2 - |\chi|^2\right). \qquad (1.30)$$

Replacing φ with χ^* and χ with φ^* in the 2-component representation (*i.e.*, $\Phi \to \sigma_1\Phi^*$) is the equivalent to replacing ϕ with ϕ^* in the single function (ϕ) representation. We saw that $\phi \to \phi^*$ results in the charge density changing sign, identifying ϕ^* as the antiparticle function. This is the same as the above.

Klein-Gordon Field

We have seen that the inability of the Klein-Gordon equation to be interpreted as a quantum mechanical equation of motion can be appreciated from different perspectives. For example, it cannot satisfy the relativistic counterpart to the well-known continuity equation of non-relativistic quantum mechanics: $\partial_t\rho = -\nabla\cdot\vec{J}$, where probability density is $\rho = \psi^*\psi$ and probability-current density is $\vec{J} = (i\hbar/2m)(\psi\nabla\psi^* - \psi^*\nabla\psi)$. Rather, it satisfies a conservation principle for charge density and charge-current density. This is a useful exercise. The appropriate format for discussing the physics of the Klein-Gordon and Dirac equations is field theory.

We encountered this in our dealings with phonons and photons.

Example 1.1. Free Particle

An illustrative case is a particle that is free except for confinement to a large box. The box can be taken as a cube (volume L^3) without loss of generality. Because of the particle's confinement, its spatial momentum components are quantized. The general solution for an eigenstate has the form

$$\phi_n = A_n e^{-ik_{n,\nu}x^\nu} \ . \tag{1}$$

where A_n is the normalization constant, and boundary conditions are taken to be periodic to simplify the math. The label n refers collectively to the indices for the quantized momentum components: n_1, n_2, n_3. Recall that a given value of $\vec{p}_n$ corresponds to two solutions: $E_n = \pm(p_n{}^2 c^2 + m^2 c^4)^{1/2}$. Again, these are not quantum mechanical energy eigenvalues, but solutions to a second-order differential equation. When $k_{n,\nu}x^\nu$ is written in terms of its zeroth and spatial components, eqn (1) becomes

$$\phi_{n(\pm)} = A_{n(\pm)} \exp\left(i\vec{k}_n \cdot \vec{r} \mp i\omega_n t\right). \tag{2}$$

The subscript $n(\pm)$ means that n_1, n_2, n_3 are specified and one or the other value of $\pm(p_n{}^2 c^2 + m^2 c^4)^{1/2}$ can be taken (either + or –). The charge densities for this plane wave (corresponding to + and –) are obtained by inserting the $\phi_{n(\pm)}$ given by eqn (2) into the expression for ρ given by eqn (1.22), which is repeated here

$$\underbrace{-q\frac{i\hbar}{2mc^2}\partial_t\left(\phi\,\partial_t\phi^* - \phi^*\partial_t\,\phi\right)}_{\partial_t\rho} = \partial_t\, q\left(|\,\varphi\,|^2 - |\,\chi\,|^2\right). \tag{1.22}$$

The left hand side (without the ∂_t that precedes the parentheses) is the charge density

$$\rho \ = -\frac{i\hbar q}{2mc^2}\left(2A_{n(\pm)}A^*{}_{n(\pm)}(\pm i\omega_n)\right) \ = \pm q\frac{E_n}{mc^2}\left|A_{n(\pm)}\right|^2. \tag{3}$$

This charge density is integrated over the volume of the box. It is distributed uniformly throughout the box: a consequence of the periodic boundary condition. Thus, it is simply multiplied by the volume L^3, yielding the enclosed charge of $\pm q$. The normalization constant is (with the phase of the square root set to zero)

$$A_{n(\pm)} = A_n = \sqrt{\frac{1}{L^3}\frac{mc^2}{E_n}}. \tag{4}$$

The general solutions for the plus and minus choices of the charge are expressed as sums over the eigenstates by using expansion coefficients $C_{n(\pm)}$

$$\phi_{+} = \sum_{n} C_{n(+)} A_n \exp\left(i\vec{k}\cdot\vec{r} - i\omega_n t\right) \tag{5}$$

$$\phi_{-} = \sum_{n} C_{n(-)} A_n \exp\left(i\vec{k}\cdot\vec{r} + i\omega_n t\right) . \tag{6}$$

Let us now see how this works with the 2-component representation. What we have is a 2D eigenvalue problem: $\hat{H}\Phi = E\Phi$, in which the function Φ can be expressed as a 2-component vector times a plane wave.

$$\Phi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \begin{pmatrix} \varphi_0 \\ \chi_0 \end{pmatrix} \exp\left(i\vec{k}\cdot\vec{r} - i\omega t\right) . \tag{7}$$

It is understood that the components φ_0 and χ_0 have no space or time dependence, as this appears only in the exponential. Using this with eqn (1.15) yields two eigenvalues and eigenvectors. The equation $\hat{H}\Phi = E\Phi$:

$$E\begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \begin{pmatrix} mc^2 + \dfrac{\hat{p}^2}{2m} & \dfrac{\hat{p}^2}{2m} \\ -\dfrac{\hat{p}^2}{2m} & -mc^2 - \dfrac{\hat{p}^2}{2m} \end{pmatrix} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} \tag{8}$$

gives

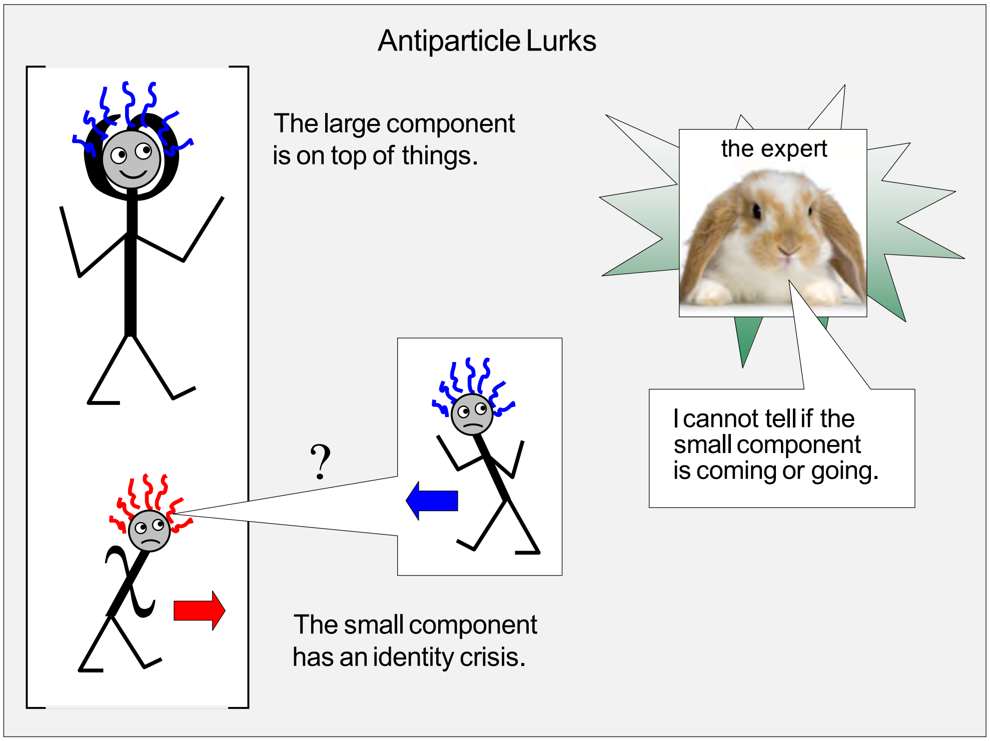
$$\det\begin{pmatrix} mc^2 + \dfrac{\hbar^2 k^2}{2m} - E & \dfrac{\hbar^2 k^2}{2m} \\ -\dfrac{\hbar^2 k^2}{2m} & -mc^2 - \dfrac{\hbar^2 k^2}{2m} - E \end{pmatrix} = 0 \;\; \Rightarrow \;\; E^2 = m^2 c^4 + \hat{p}^2 c^2 . \tag{9}$$

Putting the plus and minus values alternately into the characteristic equation yields the eigenvectors. Including the normalization constants, and after a fairly large amount of algebraic manipulation, these are

$$\begin{pmatrix} \varphi^{(+)} \\ \chi^{(+)} \end{pmatrix} = A_{(+)} \begin{pmatrix} mc^2 + E_p \\ mc^2 - E_p \end{pmatrix} \exp\left(i\vec{k}\cdot\vec{r} - i\omega_p t\right) \tag{10}$$

$$\begin{pmatrix} \varphi^{(-)} \\ \chi^{(-)} \end{pmatrix} = A_{(-)} \begin{pmatrix} mc^2 - E_p \\ mc^2 + E_p \end{pmatrix} \exp\left(i\vec{k}\cdot\vec{r} + i\omega_p t\right) . \tag{11}$$

One sees right away that there are large and small components. For the $+E_p$ solutions, the upper component dominates to a quite large degree, except at very high energies.



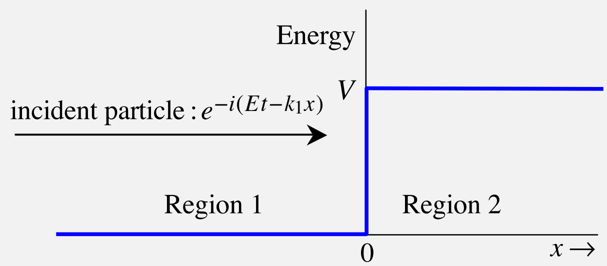
For energies that might be encountered in molecules that contain heavy atoms (*e.g.*, ~ 100 keV for distances of ~ a Compton radius), the large component dominates by at least an order of magnitude. The main issue with the small component is interpretation. You can find many instances in which it is stated that if the large component is a particle, the small component is its antiparticle. Let us settle this once and for all. A state ket or wave function or whatever you want to call it does not mix charges. The state is not mainly an electron with a small positron part. If this were the case, the electron would have a finite probability of annihilating another electron.

Charge is an outstanding quantum number. It plays a role in symmetries such as charge conjugation, but no one has ever turned an electron into a positron. What the small spinor component describes is what field theory transfers to the quantum mechanical equations of a system whose number of particles is fixed. Rather than introducing a positron, an electron can appear to be traveling in the opposite direction.

Example 1.2. Klein Paradox

In this example we shall discuss the reflection, transmission, and several intriguing features of an electrically charged particle that is incident at a step potential, and whose dynamics obey the Klein-Gordon equation. The case of an incident wave packet will be discussed later, but for now the energy of the incident wave is assumed to have a single, though variable, positive value. We will see that relativistic quantum mechanics is not able to provide an adequate description of what happens. Relativistic quantum field theory is needed, as this enables the creation and annihilation of particle-antiparticle pairs when an incident wave is disturbed violently at a sharp boundary such as a step potential. Figure 1 indicates the general idea.

Figure 1. An incident charged particle obeys the Klein-Gordon equation. In a quantum mechanical treatment of the scattering, for sufficiently large V the reflected flux exceeds the incident flux, and a propagating wave moves to the right in Region 2. Such results are explained using relativistic quantum field theory.



Scattering from a step potential is one of the most elementary examples in the non-relativistic Schrödinger theory. I am not going to discuss the Schrödinger case, as you have undoubtedly encountered it many times. Suffice it to say that for the Schrödinger case, when the energy exceeds V there is both reflection and transmission, whereas when E is less than V there is total reflection, with exponential decay of the wave in the classically forbidden region. In the Klein-Gordon case, the situation is not so simple, and this is the focus of the present example. The Dirac equation yields a similar result that will be discussed, time permitting, in another example after we have begun working with the Dirac equation for spin-½ particles. It differs from the spin-zero Klein-Gordon case most importantly in that the Pauli exclusion principle needs to be taken into account when particle-antiparticle pairs are produced in the scattering.

In the presentation that follows, the Klein-Gordon equation is treated at the outset as an equation in relativistic quantum mechanics. Thus, the Klein-Gordon function ϕ is treated as a wave function, much like its counterpart in the Schrödinger theory. We know that this is not right, because we have seen that ϕ, when it is complex, describes a charged field, not a quantum mechanical wave function. In playing along with the quantum mechanics ansatz, we are adhering to the original interpretation – the one that resulted in the system being judged as paradoxical at the time of Oskar Klein's 1929 publication.[5] Inci-

[5] O. Klein, "Die Reflexion von Elektronen an einem Potentialsprung nach der relativistischen Dynamik von Dirac," *Zeitschrift für Physik* **53**, 157 (1929).

dentally, Klein used the Dirac equation rather than the simpler approach examined below by way of the Klein-Gordon equation.

Referring to Fig. 1, a particle that obeys the Klein-Gordon equation is incident from the left on a step potential energy that rises at $x = 0$. The constants $\hbar$ and c each are set equal to 1, except when otherwise noted, to simplify notation. The momenta in Regions 1 and 2 are taken as square roots using the Klein-Gordon dispersion relation (box below). Referring to Fig. 1, they satisfy

$$\text{Region 1:}\ \ k_1{}^2 = E^2 - m^2 \tag{1}$$

$$\text{Region 2:}\ \ k_2{}^2 = (E - V)^2 - m^2\ . \tag{2}$$

The expression for $k_2{}^2$ indicates that the incident wave undergoes both reflection and transmission for $|E - V| > m$. On the other hand, for $|E - V| < m$, k_2 is imaginary and consequently there is total reflection. It will prove useful in subsequent discussions to refer to probability density and flux. Thus, the expressions for these are taken from eqn (1.20), albeit with the inclusion (through minimal coupling) of the scalar potential:

> The electromagnetic field is introduced through minimal coupling, as indicated below for Region 2 in Fig. 1. Energy is taken as positive in Fig. 1. The vector potential term plays no role in the present case, and the electrostatic term qV_0 is equal to the potential energy V indicated in Fig. 1.
>
> minimal coupling
>
> quantum version
>
> $$E^2 = k^2 + m^2 \ \Longrightarrow\ \Big(\underbrace{(i\partial_t - \underbrace{qV_0}_{V})^2}_{\text{returns } E} - \underbrace{(-i\nabla - q\vec{A})^2}_{\text{returns } k_2{}^2} - m^2 \Big)\phi = 0$$
>
> This accounts for $k_2{}^2$ in eqn (2).

$$\rho \ = -\frac{i}{2m}\left(\phi\,\partial_t\phi^* - \phi^*\partial_t\,\phi\right) - \underbrace{\frac{V}{m}\phi^*\phi}_{\text{only in Region 2}} \tag{3}$$

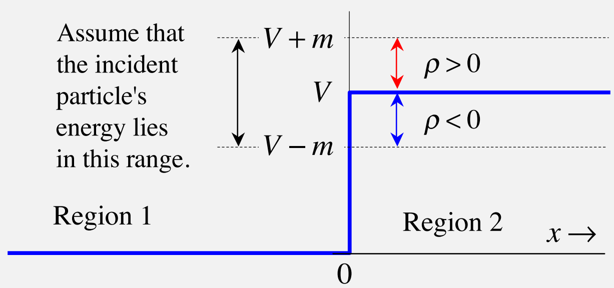
$$\vec{J} \ = \ \frac{i}{2m}\left(\phi\nabla\phi^* - \phi^*\nabla\phi\right). \tag{4}$$

Again, note that $\vec{A} = 0$, and V is nonzero only in Region 2.

Equation (2) indicates that for $E - V > m$, both reflection and transmission take place. In taking the square roots of $k_1{}^2$ and $k_2{}^2$ [eqns (1) and (2)], it is necessary to identify the correct signs. For the energy region $E - V > m$, the choices are straightforward: $k_1 = +(E^2 - m^2)^{1/2}$ and $k_2 = +[(E-V)^2 - m^2]^{1/2}$ are needed for a particle incident from the left, as they ensure that flux passes from left to right. This is much like the Schrödinger case. For example, substituting $E = m + p^2/2m$ (taking the non-relativistic limit) into the expression for k_1 given by eqn (2) yields $[(m + p^2/2m)^2 - m^2]^{1/2} \approx p = k_1$, and likewise for k_2.

Referring to Fig. 2 and eqn (2), in the energy interval: $V+m>E>V-m$, reflection is 100% because k_2 is imaginary. In choosing whether to use the plus or minus sign, we see that it is necessary to use $k_2 = +i[(E-V)^2-m^2]^{1/2}$, as this ensures that $e^{-i(Et-k_2x)}$ decays exponentially for $x>0$. There is, however, a great deal more to the story in this energy interval, as we shall now see.

Figure 2. The wave is attenuated in Region 2 in the energy range indicated by the black double arrow. In the quantum mechanical description, the probability density in Region 2 is positive in the range $V+m>E>V$ (red double arrow), and negative in the range $V>E>V-m$ (blue double arrow). This shows that, in fact, ρ cannot be interpreted as probability density.



When $\phi = e^{-i(Et-k_2x)}$ is introduced into eqn (3), the probability density for Region 2, ρ_2, is obtained:

$$\rho_2 = \frac{E-V}{2m}\phi^*\phi\,. \tag{5}$$

Referring to eqn (4), note that the probability current density $\vec{J}$ vanishes in Region 2 because k_2 is imaginary. Keep in mind that we are following the historical route in which the Klein-Gordon equation was originally treated as an equation in relativistic quantum mechanics.

Exercise: Obtain eqn (5) starting from eqn (3).

Now for an interesting part: When E lies in the range $V+m>E>V$, the probability density in Region 2 is positive, whereas when E lies in the range: $V>E>V-m$, the probability density in Region 2 is negative, which is nuts. On the basis of what you already know about the Klein-Gordon equation, you undoubtedly sense that an antiparticle is somehow involved. This is true, but we shall wait until later to discuss what is really going on. One thing is certain, however: The appearance of negative probability density caused quite a stir in 1929.

Moving on to the next energy regime, when the potential energy step V is sufficiently large, the situation becomes even more intriguing. Energy values smaller than $V-m$ can accommodate real k_2. Specifically, $|E-V|>m$ is satisfied when

$$E<V-m\,. \tag{6}$$

This is fascinating. According to the mathematics, a transmitted wave actually *propagates* at energies below the height of the step potential V. This bewildered people for years, and it is capable of doing so even today. Though we are using the Klein-Gordon equation, essentially the same result is obtained with the Dirac equation.

When the potential energy step is sufficiently large there is apparently a transmitted wave (Fig. 3). Working through the mathematics involves nothing more complicated than matching wave functions and their derivatives at the boundary. This yields the following expressions for the transmitted and reflected fluxes:

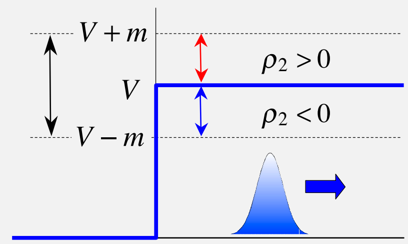


Figure 3. For $E < V - m$, a wave propagates to the right in Region 2.

$$\frac{J_{trans}}{J_{inc}} = \frac{4k_1 k_2}{(k_1 + k_2)^2} \tag{7}$$

$$\frac{J_{refl}}{J_{inc}} = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 . \tag{8}$$

Despite the strange effects that we seem to be encountering, the probability flux densities still obey: $J_{refl} + J_{trans} = J_{inc}$.

A choice of sign needs to be made for k_2 in the regime $E < V - m$, namely, whether it is $+ [(E-V)^2 - m^2]^{1/2}$ or $- [(E-V)^2 - m^2]^{1/2}$. The correct choice is not immediately obvious, in contrast to the other energy regimes. However, the group velocity of the wave in Region 2 will tell us how a wave packet travels, so let us use this to establish the sign of k_2 when $E < V - m$. Differentiating eqn (2) yields

$$\frac{\partial E}{\partial k_2} = v_g = \frac{k_2}{E - V} . \tag{9}$$

For $V > E + m$ (the energy region of interest), the denominator is negative. Thus, a packet propagating to the right (positive group velocity) must have a negative value of k_2 . In other words, we must choose $k_2 = - [(E-V)^2 - m^2]^{1/2}$. Of course, eqn (9) also works with negative group velocity and positive k_2 . However, this creates an even more horrendous problem. Causality is violated because a packet must approach from the right before the incident particle has reached the step.

It seems that nothing is sacred. Not only is there transmitted flux, but also its momentum points in a direction that is opposite the direction of the group velocity. Moreover, the reflected flux exceeds the incident flux, for example, as seen in eqn (8) with k_2 negative. It is even possible for the magnitudes of the transmitted and reflected fluxes to exceed considerably that of the incident flux (Fig. 4). These results are seriously in need of interpretation. They demonstrate unequivocally that a single particle quantum mechanical description is inadequate.

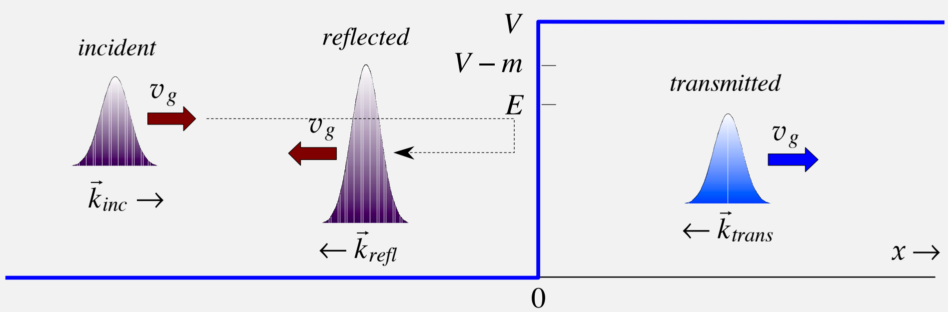


Figure 4. An incident Klein-Gordon wave packet scatters from a high step potential. In the case shown here, the area of the reflected packet is twice that of the incident packet. There is a transmitted packet whose area is the same as that of the incident packet. This seemingly strange behavior is a consequence of imposing a quantum mechanical description on a system in which particle-antiparticle pairs are produced. It is assumed that the energy spread of the packets is small enough to justify treating the packets as having well-defined energy.

Explanation

The Klein-Gordon and Dirac equations are firmly rooted in relativistic quantum field theory – the progenitor of relativistic quantum mechanics. Consequently, explanations of the Klein paradox from a relativistic quantum mechanics perspective, notably with a fixed number of particles, can be confusing insofar as interpretation: negative kinetic energy, a wave packet whose momentum points in a direction opposite that of its group velocity, a reflected flux that exceeds the incident flux, and a transmitted wave inside the step barrier when $E < V - m$. We have seen that complex solutions of the Klein-Gordon equation describe fields whose squared moduli $\phi\phi^*$ need to be multiplied by charge to make them charge densities, not quantum mechanical wave functions whose squared moduli are probability densities. This is central to understanding what is going on.

Phonon Model Revisited

It is noteworthy that we have arrived at so complete a description of the physics, given that no explicit steps were taken along the way, at least consciously, to quantize the Klein-Gordon field. After all, it is the quantization of the Klein-Gordon field that enables bosons to be created, and this is apparently what is going on with the Klein-Gordon paradox. It turns out that this physics was there all along. We simply did not recognize that our so-called wave function ϕ was really a non-Hermitian field operator. To appreciate how this works, let us go all the way back to Part IV, where quantization of a toy model that was referred to as a "dual-use model," yielded phonons. In revisiting the development presented there, it will become clear how the field-theoretic description falls into place. You should review this material before proceeding. Skip Chapters 2-8 of Part IV, which deal with applications, and read Chapters 1, 9, and 10.

Part IV began with a seemingly harmless model consisting of identical mass points bound harmonically to one another with a single spring-constant parameter. These mass points are also each bound to a fixed lattice with a different spring-constant parameter. Transformation to k-space yielded a Hamiltonian comprising a sum of uncoupled harmonic oscillators. Quantization was introduced with $[x_n, p_{n'}] = i\hbar\delta_{n,n'}$ yielding a k-space representation in the standard form of creation and annihilation operators acting in a number-valued Fock space. Quantization using commutators yielded massless bosons called phonons.

In Chapter 9 of Part IV, the discrete mass points were extended to a continuous mass density. We saw that the displacement $\hat{q}$ is an operator, whereas the location on the space where the displacement takes place (x in one dimension), is a parameter. In short, we have $\hat{q}(x)$, $\hat{p}(x)$, and $[\hat{q}(x), \hat{p}(x')] = i\hbar\delta(x - x')$. The operators $\hat{q}(x)$ and $\hat{p}(x)$ are expressed as summations over k of creation and annihilation operators. Following this, time behavior was added resulting in $\hat{a}_k(t) = \hat{a}_k e^{-i\omega t}$, the 1D space was extended to 3D, and the 3D space was extended to infinity. The resulting field displacement operator (eqn (44) in Part IV, Chapter 9) is

$$\hat{\phi}(\vec{r},t) = \int d^3k \frac{1}{(2\pi)^{3/2}\sqrt{2\omega_k}} \left(e^{i(\vec{k}\cdot\vec{r} - \omega_k t)} \hat{a}(\vec{k}) + e^{-i(\vec{k}\cdot\vec{r} - \omega_k t)} \hat{a}(\vec{k})^\dagger \right) .$$

This Hermitian form applies to real fields.

In Part IV, Chapter 10, our so-called "dual-use" phonon model was converted to something whose physics is qualitatively different than that of phonons through a change of the model's parameter values. It turns out that the mathematical form of the operator equation and its solutions are impervious to the sizes of the parameters. Thus, what began as a phonon model became the Klein-Gordon equation by changing parameter values and renaming the functions that are operated on.

To accommodate particles and their antiparticles it is necessary to have complex classical fields that become non-Hermitian quantum fields. The reason is that the field must have two components, one to account for a system's particle nature and the other to account for its antiparticle nature. In other words, the creation and annihilation terms must be independent of one another. Thus, $\hat{b}(\vec{k})^\dagger$ is substituted for $\hat{a}(\vec{k})^\dagger$:

$$\hat{\phi}(\vec{r},t) = \int d^3k \frac{1}{(2\pi)^{3/2}\sqrt{2\omega_k}} \left(e^{i(\vec{k}\cdot\vec{r} - \omega_k t)} \hat{a}(\vec{k}) + e^{-i(\vec{k}\cdot\vec{r} - \omega_k t)} \hat{b}(\vec{k})^\dagger \right) .$$

This operator annihilates particles with wave vector $\vec{k}$ and creates antiparticles with wave vector $\vec{k}$. Its Hermitian adjoint does the reverse: creates particles with wave vector $\vec{k}$ and annihilates antiparticles with wave vector $\vec{k}$. This adjoint operator is

$$\hat{\phi}(\vec{r},t) = \int d^3k \frac{1}{(2\pi)^{3/2}\sqrt{2\omega_k}} \left(e^{i(\vec{k}\cdot\vec{r} - \omega_k t)} \hat{b}(\vec{k}) + e^{-i(\vec{k}\cdot\vec{r} - \omega_k t)} \hat{a}(\vec{k})^\dagger \right) .$$

Back to the Step Potential

The impulsive disturbance presented by the step potential enables pair production to take place at positive incident energies smaller than $V - m$. Were a fully quantized electrodynamics system under consideration, the interaction of an electrically charged incident particle with a charged target would be mediated by the exchange of longitudinal and timelike photons. When the distance between the particles is small, the exchange of photons is intense. A high-energy photon can decompose into a pair of particles, and the pair can survive if the system energy exceeds the threshold for pair production. Otherwise, the pair annihilates. In the present toy model, the electromagnetic field is not quantized. Instead, we deal with a hypothetical electrostatic potential that results in potential energy of $+V$ for one member of the pair and $-V$ for the other member of the pair, assuming of course that each member of the pair is inside the potential.

When $V - m$ exceeds E, it is sensible, on the basis of quantum mechanics, to expect the wave to decay exponentially inside the step potential in a very short distance. This is not what happens with the mathematics, however, as is evident from the expression $k_2 = [(V-E)^2 - m^2]^{1/2}$, which is real for $V - E > m$. In other words, quite the opposite of pronounced exponential damping takes place: A wave actually propagates in Region 2.

Leaving this striking feature aside for the time being, one can expect (again on the basis of quantum mechanics) a decay distance d inside the potential that satisfies the relation: $\delta E \delta t \sim \hbar$. For $\delta E \sim mc^2$ and $\delta t \sim d/c$, the characteristic distance d is of order $\hbar / mc$. Were the particle an electron, $\hbar / mc$ would be the Compton radius (0.00386 Å). However, the only particles that are known to obey the Klein-Gordon equation are the charged and neutral pions: π^+, π^-, and π^0. Taking the incident particle to be a charged pion (say π^+), its mass is 270 times that of an electron, so d is proportionately smaller: 1.43×10^{-5} Å, which is roughly the diameter of a nucleon.

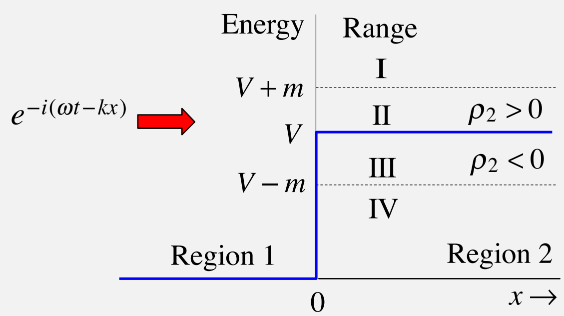
The disturbance presented by the potential is of such a nature that it compresses the wave to a distance inside the potential that is much less than the Compton radius. This strong disturbance creates a particle-antiparticle pair. Note that no additional energy is required. The energy needed to produce a π^+ particle inside the potential V has the same magnitude as the energy gained by producing a π^- antiparticle in the same potential.

Let us now examine the system step-by-step: lowering the energy through the different regions starting with $E > V + m$.

Relativistic Quantum Field Theory: Pair Production

Figure 5 illustrates the case of a positively charged particle incident from the left on the (blue) step potential whose strength is V. The particle's energy, E, can be varied. Keep in mind that E includes the mass energy, m. When E exceeds $V + m$ (Range I in Fig. 5) the particle moves as expected – in much the same way as it would in non-relativistic quantum mechanics – with reflection and transmission taking place at the $x = 0$ boundary. The wave vectors for Regions 1 and 2 are, respectively, $k_1 = [E^2 - m^2]^{1/2}$ and $k_2 = [(E-V)^2 - m^2]^{1/2}$. In Range I, the incident particle does not experience the strong disturbance (impulsive force) needed to create a particle-antiparticle pair that survives for more than a fleeting moment. Rather, it negotiates the step boundary without trauma.

Figure 5. Four distinct energy ranges are identified (labeled I – IV). A particle incident from the left scatters differently in the different ranges. In II and III, virtual particle-antiparticle pairs are produced, none of which survive. In range IV the pairs survive, with the particle adding to the reflected current and the antiparticle moving to the right.



Next, consider Range II: $V + m > E > V$. The wave vector in Region 2 is imaginary throughout this energy range: $k_2 = i[m^2-(E-V)^2]^{1/2}$. In taking the square root, $+i$ is chosen (rather than $-i$) to ensure that the wave decays exponentially for $x > 0$. When E is only slightly smaller than $V + m$, the strength of the damping inside the classically forbidden region is modest. In this case, the incident wave can penetrate a significant distance into Region 2. Again, this is akin to non-relativistic quantum mechanics.

In lowering E through Range II, from just below $V + m$ down to $E = V$, we see that damping becomes progressively more severe, and extremely so, with k_2 having the value im at $E = V$. Notice that for $E = V$, introducing explicit c and $\hbar$ gives $\hbar k_2 = imc$. Thus, $|k_2| = mc/\hbar$, and we see that the penetration distance $k_2{}^{-1}$ is much smaller than the Compton radius. As mentioned earlier, the mass of a charged pion is 270 times that of an electron, making $k_2{}^{-1}$ 270 times smaller than the Compton radius. The Compton radius is 0.00386 Å, so $\hbar/mc$ for the pion is 1.43×10^{-5} Å. The charge density in Region 2 is positive throughout Range II. Despite the fact that an interesting energy regime is encountered as E gets close to V, nothing too shocking has been unearthed, at least at first glance. We sense, however, that fascinating stuff looms. For example, the charge density ρ_2 changes sign in going between Ranges II and III, as seen from eqn (5) (albeit with q added to make ρ_2 a charge density): $\rho_2 = q(E-V)\phi\phi^*/m$.

Recall from earlier in this chapter that the Klein-Gordon field could be represented using a 2-component form. There, we found that the net charge of the field was proportional to the difference between the upper and lower densities, as seen in eqn (1.22): $\rho = q(|\varphi|^2-|\chi|^2)$. The sign of the charge density depends on the magnitudes of the upper and lower components. In the present example, this is manifest mathematically as $E - V$ changing sign as it passes through zero. Though the overall charge of the system is preserved, the charge density in Region 2 drops from $q\phi\phi^*$ at $E = V + m$ to zero at $E = V$.

The system enters Range III when the incident energy drops below V. As mentioned above, the charge density in Region 2, ρ_2, goes through zero and changes sign at $E = V$, remaining negative throughout Range III. The wave vector k_2 continues to be imaginary, with a plus sign ensuring exponential decay for $x > 0$: $k_2 = +i[m^2-(E-V)^2]^{1/2}$. The 2-component representation is helpful insofar as interpreting what is going on.

Transient particle-antiparticle pairs are created and annihilated throughout Ranges II and III. They are said to be "virtual," as they do not survive. In Range II, at energies very slightly lower than $V + m$, the incident wave penetrates a significant distance into the potential, and pair production is minimal because the disturbance experienced by the wave is slight. Thus, ρ_2 is positive. As E is lowered in Range II, the penetration distance becomes progressively smaller, the impulsive nature of the disturbance increases, and transient pair production increases. The charge density ρ_2 becomes smaller, because both the incident π^+ and the π^+ component of the virtual pair are pushed toward Region 1, whereas the π^- antiparticle is happy in Region 2. Pair production is electrically neutral, so ρ_2 diminishes as the energy is lowered toward $E = V$. Keep in mind that there is no net production of particles and antiparticles, as the virtual pairs do not survive. The incident particle is reflected back into Region 1.

As E approaches $V - m$ from above (Fig. 5, Range III) the disturbance experienced by the incident wave is indeed significant. The charge density ρ_2 approaches $-q\phi\phi^*$, with the π^- antiparticle surviving for a long time before annihilating with π^+.

At energies below $V - m$ (see Figs. 4 and 5), the pair survives, with its π^+ component adding to the reflected current, and its π^- antiparticle moving to the right. Just above the threshold for stable pair production, the π^+ component requires that an amount of energy be supplied that is equal to V. However, this is exactly the amount of energy that the π^- antiparticle contributes by virtue of it being in the attractive potential presented by V. Everything falls into place.

Comments on Relativistic Quantum Field Theory

In the present example, we found that care is required when interpretation is attempted in terms of quantum mechanics. Indeed, quantum mechanics is inadequate. The only theory of fundamental particles that is consistent with special relativity is relativistic quantum field theory (RQFT). For example, it provides the only means whereby particles can be created and annihilated. Said differently, relativity ensures that antiparticles exist. It is profound that the seemingly innocuous premise introduced at the start of Chapter 1: homogeneity and isotropy of empty space, leads to the existence of antimatter.

The mathematics of quantum field theory is non-trivial. It is built around the creation and annihilation of massive particles and the gauge bosons that mediate their interactions. These "objects" are quanta of their respective fields. Such features have no counterparts in quantum mechanics. In condensed matter and electronic structure theory, the implementation of second quantization strategies is widespread, with creation and annihilation operators acting in a number-valued Fock space to carry out bookkeeping. However, these low-energy applications differ qualitatively from the ones under consideration in RQFT. They are mathematical conveniences, whereas in RQFT the creation and annihilation of field quanta describe phenomena.

A take-home message is that we should be wary of mysterious things that appear in relativistic quantum mechanics. Figure 4 and the discussion that surrounds it is a good example. We find that, from the quantum mechanics perspective, the reflected flux exceeds the incident flux, and there is a transmitted flux whose wave vector points in a direction opposite that of its group velocity. These would be cause for despair had we not known beforehand that a particle-antiparticle pair is involved. Pair production and annihilation cannot be accommodated within quantum mechanics. However, some of the interesting stuff can be appreciated through consideration of the symmetries of time reversal (Appendix 4), parity, and charge conjugation.

The charge conjugation operator, *C*, reverses the sign of a particle's charge, turning the particle into its antiparticle. The parity operator, *P*, inverts coordinates: $\vec{r} \rightarrow -\vec{r}$. Time reversal is like motion reversal. That is, a particle with its momentum reversed that propagates forward in time gets to the same place as it would by propagating backward in time and then having its momentum reversed. Time-reversal symmetry is subtle. Sakurai [25] gives a thorough explanation (pages 266-282), pointing out that the form of the time reversal operator, *T*, depends on the system being considered. For example, a spin-zero particle behaves differently than a spin-½ particle under time reversal. Incidentally, the product *CPT* is a robust symmetry, relying only on Lorentz covariance, even when its ingredients are not separately good symmetries.

We have seen that negative energies that arise in relativistic quantum mechanics are associated with antiparticles. However, propagation forward in time with negative *E* is the same mathematically as propagation backward in time with positive *E*, *i.e.*, $e^{iEt} = e^{-iE(-t)}$. Referring to Fig. 4, the wave vector and group velocity point in opposite directions. However, the wave vector is for a charged current, whereas the group velocity is for the material object independent of its charge, so nothing is out of order. Insofar as the negative energy solutions looking the same as time reversal, Feynman and Stueckelberg have argued that an antiparticle is a particle traveling backwards in time. I have yet to warm up to this interpretation, but this most likely reflects my amateur status in this area.

2. Introducing Spin: Pauli's Approach

Let us now follow the reasoning of Wolfgang Pauli that culminated in his introduction of the matrix representation of spin that bears his name. The photo on the right shows Pauli in his youth. He had written important papers in the area of general relativity, including a widely cited encyclopedia article, by the time he was eighteen, and he received a doctorate in theoretical physics at the age of twenty-one. Despite its non-relativistic and seemingly *ad hoc* nature, Pauli's model influenced Dirac's development of a relativistic quantum mechanical theory for fermions, as well as van der Waerden's derivation of the same result shortly thereafter, as discussed in Section 4.

Pauli used 2D matrices, whereas the matrices introduced by Dirac are 4D. It is interesting that Dirac's 4D matrices can be expressed in terms of Pauli's three 2D matrices plus the unit matrix. In hindsight the 4D representation comes as no surprise. After all, Dirac's theory had to accommodate both spin (Pauli's model) and antiparticles (Klein-Gordon), though Dirac's thinking about antiparticles was fuzzy at the time of his seminal 1928 paper. It is often stated that, because of the need to accommodate spin and antiparticles, a representation of at least 4D is necessary. This is not correct. We have seen that a single-component complex function suffices in the Klein-Gordon theory. As pointed out by Sakurai [3], in the Dirac theory it is possible to get by with a 2D representation, but this creates difficulty when trying to carry out the parity operation. Consequently, we shall take four as the dimension of choice in the Dirac theory.

An interesting historical fact involves the algebraic structures enlisted by Pauli and Dirac with their matrices. The English mathematician William Kingdon Clifford developed these and related algebras half a century earlier, himself strongly influenced by the work of Hermann Grassmann. Nowadays this mathematics falls under the heading of Clifford algebra or geometric algebra. Clifford introduced the latter term. He was shy and would never have attached his name to one of his achievements. The Pauli and Dirac matrices are simply means of representing the Clifford or geometric algebras. To the best of anyone's knowledge, neither Pauli nor Dirac was aware of Clifford's work.

A quarter century earlier the Dutch physicist Pieter Zeeman (photo) had found that strong magnetic fields caused atomic spectral lines to split into components. In quantum mechanics, such splitting arises because the quantization of electron angular momentum results in levels whose energies are proportional to an azimuthal quantum number times the strength of the applied magnetic field. However, some of the level splitting that Zeeman observed did not appear to have the right number of components. Certain angular momentum projections had just two components. Should not the number be $2L + 1$, with L being zero or a positive integer?

Moreover, there was the 1922 experiment of Otto Stern and Walter Gerlach, where only two angular momentum components were observed? This was equally puzzling. Clearly, an explanation would require new physics. This new physics emerged in the 1920's.

After discussing Pauli's contribution and a brief excursion involving spin exchange symmetry, the Dirac equation will be obtained by following the approach introduced by the Dutch mathematician Bartel Leendert van der Waerden. As mentioned earlier, this derivation enlists Pauli's strategy. It is followed by Dirac's derivation. His reasoning was intuitive yet rigorous. The amount of math is modest – certainly not so much as to obfuscate the physics. We will see how the Dirac equation joins with Schrödinger, Klein-Gordon, Pauli, and Electrodynamics. Limiting cases such as the low-energy regime, zero mass, and plane wave solutions, as well as phenomena such as the amusing but useless Zwitterbewegung, will also be discussed. Again, these notes should be taken as a precursor to serious study of the subject. The texts by Aitchison and Hey [5-6], Sakurai [3], Schwabl [4] and Guidry [7] are excellent, and there are many others.

Using 2×2 Matrices

Pauli introduced a set of 2×2 matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{2.1}$$

to account for spin-½ particles, with $s_i = \hbar\sigma_i / 2$. At this point no attention is paid to covariant notation. For example, no distinction is made between σ_i and σ^i . The approach was non-relativistic. For example, with $\vec{s} = s_1\hat{x} + s_2\hat{y} + s_3\hat{z}$, where $\vec{s} = \hbar\vec{\sigma}/2$, a fourth component (needed for Lorentz covariance) is missing. It is understood that $\vec{s}$ and $\vec{\sigma}$ are 2×2 matrix operators.

Little was known at the time about spin except its existence and that it has certain properties. Being intrinsic,[6] it has no spatial wave function. The $\pm\hbar/2$ states span a 2D space, and they can be combined with spatial wave functions. The example considered here is a free electron moving in the $+z$-direction in field-free space. We know that there is no such thing as an electron in field-free space. Nonetheless, the field-free case serves as a useful pedagogical tool. In the non-relativistic limit, such a state can be described as the product of a plane wave times a 2-spinor, or a wave packet built out of plane waves times a 2-spinor. For $s_z = +\hbar/2$, the former is written (with normalization suppressed)

$$\psi = e^{ikz}\begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{2.2}$$

The operator $\vec{p}\cdot\vec{\sigma}$ accounts for spin as well as linear momentum, $\vec{p}$. For example,

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[6] As used here, intrinsic means fundamental to the particle. Spin is not internal to the particle.

$$\vec{p}\cdot\vec{\sigma}\,\psi = \left(\sigma_1 p_x + \sigma_2 p_y + \sigma_3 p_z\right)\psi \tag{2.3}$$

$$= (2/\hbar)\left(s_x p_x + s_y p_y + s_z p_z\right)\psi\,. \tag{2.4}$$

We are free to take $\vec{p} = p\hat{z}$ for the plane wave, with the z-axis taken as the spin quantization axis, with no loss of generality. In this case, $\vec{p}\cdot\vec{\sigma}\,\psi$ is equal to $\hbar k\psi$ for the (spin-up) ψ given by eqn (2.2). Alternatively, using

$$\psi' = e^{ikz}\begin{pmatrix}0\\1\end{pmatrix} \tag{2.5}$$

gives $\vec{p}\cdot\vec{\sigma}\,\psi' = -\hbar k\psi'$. Spin is isotropic in its rest frame, but it can be polarized relative to an external frame such that it has a projection in a given direction.

Pauli Equation

Pauli realized that it is of great importance that the $\vec{\sigma}$ matrices obey the relation

$$\boxed{(\vec{\sigma}\cdot\vec{p})^2 = p^2\,.} \tag{2.6}$$

This property makes possible the introduction of spin into a Hamiltonian. It introduces a 2D state space to handle the two spin components, and it does so without altering the non-spin physics. Specifically, it enables the system to be described using a two-component state vector that has special transformation properties, namely, the 2-spinor. To verify eqn (2.6), write the left hand side in Cartesian components and arrange terms into convenient groups:

$$\begin{aligned}(\vec{\sigma}\cdot\vec{p})^2 &= (\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3)(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3) = \sigma_1{}^2 p_1{}^2 + \sigma_2{}^2 p_2{}^2 + \sigma_3{}^2 p_3{}^2 + \\ &\quad + \sigma_1\sigma_2 p_1 p_2 + \sigma_1\sigma_3 p_1 p_3 + \sigma_2\sigma_1 p_2 p_1 + \sigma_2\sigma_3 p_2 p_3 + \sigma_3\sigma_1 p_3 p_1 + \sigma_3\sigma_2 p_3 p_2 \\ &= \boxed{p_1{}^2 + p_2{}^2 + p_3{}^2} + (\sigma_1\sigma_2 + \sigma_2\sigma_1)\,p_1 p_2 \\ &\quad + (\sigma_2\sigma_3 + \sigma_3\sigma_2)\,p_2 p_3 + (\sigma_3\sigma_1 + \sigma_1\sigma_3)\,p_3 p_1\,.\end{aligned} \tag{2.7}$$

Only the boxed term survives. In other words, it is necessary that $\{\sigma_i, \sigma_j\} = 0$, where the squiggly bracket denotes anticommutation. In obtaining eqn (2.7), use has been made of the following: (i) the σ_i matrices (because their matrix elements are simply numbers) commute with p_j for all values of i and j; (ii) $\sigma_i{}^2 = 1$ for all i; and (iii) $[p_i, p_j] = 0$ for all i and j. Referring to eqn (2.7), the fact that the σ_i anti-commute (note the red lines) gives eqn (2.6). Of course, here we afford ourselves the wisdom of hindsight. Pauli inferred the anti-commutation relations and the other properties of the matrix $\vec{\sigma}$ from the fact that eqn (2.6) must be satisfied.

Thus, $(\vec{\sigma}\cdot\vec{p})^2$ will be used in the Hamiltonian, with a two-component wave function describing the free particle. Let us now introduce an electromagnetic field through minimal coupling. Using eqn (2.6), the Hamiltonian for a particle of charge q in the presence of the vector potential $\vec{A}$ and scalar potential V is

$$\hat{H} \;=\; \frac{1}{2m}\left(\vec{\sigma}\cdot\left(\vec{p}-\frac{q}{c}\vec{A}\right)\right)^2 + qV\,. \tag{2.8}$$

It is understood that this Hamiltonian operates on a 2-spinor. The identity $(\vec{\sigma}\cdot\vec{A}_1)(\vec{\sigma}\cdot\vec{A}_2)$ $= \vec{A}_1\cdot\vec{A}_2 + i\vec{\sigma}\cdot(\vec{A}_1\times\vec{A}_2)$, where $\vec{A}_1$ and $\vec{A}_2$ are arbitrary vector operators, is now used. It can be found in the handout entitled Miscellaneous Math. This identity enables eqn (2.8) to be written

$$\hat{H} \;=\; \frac{1}{2m}\left\{\left(\vec{p}-\frac{q}{c}\vec{A}\right)^2 + i\vec{\sigma}\cdot\left(\left(\vec{p}-\frac{q}{c}\vec{A}\right)\times\left(\vec{p}-\frac{q}{c}\vec{A}\right)\right)\right\} + qV\,. \tag{2.9}$$

The terms $\vec{p}\times\vec{p}$ and $\vec{A}\times\vec{A}$ vanish, leaving

$$\hat{H} \;=\; \frac{1}{2m}\left\{\left(\vec{p}-\frac{q}{c}\vec{A}\right)^2 - i\frac{q}{c}\vec{\sigma}\cdot\left(\vec{p}\times\vec{A}+\vec{A}\times\vec{p}\right)\right\} + qV\,. \tag{2.10}$$

The second term in the large brackets is made more transparent by using $\vec{p} = -i\hbar\nabla$ and the identity: $\nabla\times(\vec{A}\psi) = -\vec{A}\times(\nabla\psi) + (\nabla\times\vec{A})\psi$, where the parentheses on the right hand side of the equal sign indicate that differentiation does not continue to the right. Thus, eqn (2.10) becomes

$$\hat{H} \;=\; \frac{1}{2m}\left\{\left(\vec{p}-\frac{q}{c}\vec{A}\right)^2 - \frac{q\hbar}{c}\vec{\sigma}\cdot\left(\nabla\times\vec{A}\right)\right\} + qV\,. \tag{2.11}$$

The interaction of spin with the external field is now explicit. The fact that $\nabla\times\vec{A} = \vec{B}$ enables eqn (2.11) to be written in a familiar form:

$$\boxed{\hat{H} \;=\; \frac{1}{2m}\left(\vec{p}-\frac{q}{c}\vec{A}\right)^2 - \frac{q}{mc}\vec{s}\cdot\vec{B} + qV\,,} \tag{2.12}$$

where $\vec{s} = \hbar\vec{\sigma}/2$.

The magnetic field $\vec{B}$ in eqn (2.12) entered as an external field through the introduction of the potential $\vec{A}$. The $\vec{s} \cdot \vec{B}$ term is responsible for the splitting observed by Pieter Zeeman. We shall deal with a relativistic effect that is referred to as spin-orbit interaction, which is proportional to $\vec{s} \cdot \vec{l}$, where $\vec{l}$ is the orbital angular momentum of an electron, when we get to the Dirac theory.

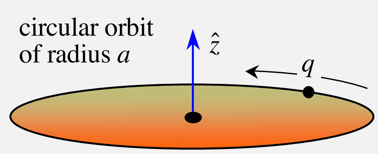
The Pauli and Dirac theories give correct results for the g-factor without the need to carry out a lengthy calculation using classical physics, such as the one done by Llewelyn Thomas (referred to as Thomas precession, which was discussed briefly in Chapter 1). For example, eqn (2.12) has the correct g-factor value of 2 for this level of theory. Corrections to the $g = 2$ value are only one part in 10^3. These are due to quantum electrodynamics (QED), as discussed below. The $g = 2$ result of course also follows from the Dirac theory.

Classical Model

If the interaction energy from classical electrodynamics, $-\vec{\mu}_s \cdot \vec{B}$, is simply added to the Hamiltonian, the spin magnetic moment $\vec{\mu}_s$ must be assigned the value $g(q/2m)\vec{s}$. As mentioned above, the dimensionless parameter g is called the g-factor. The magnetic moment of a circulating electron is $\vec{\mu}_l = (q/2m)\vec{l}$, as indicated in Fig. 2.1. In this case, there is no g-factor (more properly, its value is one). The g-factor for spin reflects the fact that the spin magnetic moment is not due to circulating charge, as opposed to the case shown in Fig. 2.1 where $\vec{\mu}_l = (q/2m)\vec{l}$.

Figure 2.1. A particle of charge q and mass m is in a circular orbit of radius a. Its magnetic moment is $\vec{\mu} = (q/2m)\vec{l}$.

$$\begin{aligned}\vec{\mu} &= (\text{current} \cdot \text{area})\hat{z} \\ &= (qv/2\pi a)(\pi a^2)\hat{z} \\ &= (qmva/2m)\hat{z} \\ &= (q/2m)\,\vec{l}\end{aligned}$$



As mentioned above, $g = 2$ is already present in eqn (2.12). It does not have to be imported, as happens when $g(q/2m)\vec{s} \cdot \vec{B}$ is introduced *ad hoc* into the Hamiltonian.[7]

It is often said that the Dirac equation is necessary in order to obtain the correct value of the g-factor. Indeed, the Dirac equation gives the correct answer, and the inclusion of quantum electrodynamics corrections to an extremely high degree of accuracy only increases the value of g to 2.0023193043622(15). It is significant that Pauli's approach achieves $g = 2$ for the non-relativistic limit. This is the same result obtained using the Dirac theory, as discussed in Section 5. The success of the Pauli theory in predicting $g =$

[7] Equation (2.12) was derived without the *ad hoc* introduction of a g-factor. Nonetheless, g is a useful quantity. For example, a proton has $g = 5.58$. This value is due to the fact that the proton is not an elementary particle. Whereas the electron does not experience the strong force, the proton constituents do. The proton consists of three quarks bound by gluons, and its internal structure accounts for the value $g = 5.586$. Likewise for the neutron, whose g value is -3.826.

2 is due to spin's 2D representation in a 3D world. The fact that this result is obtained in the non-relativistic theory indicates that, whereas spin-orbit interaction is relativistic, spin is not.

Though it treats correctly the interaction of fermion spin with an external field, Pauli's approach does not account for antiparticles. Alternatively, antiparticles emerge with the Klein-Gordon equation but spin is absent. The Dirac equation handles both antiparticles and spin.

It is said that the Klein-Gordon equation and the Schrödinger equation apply only to spinless particles, which automatically excludes all fundamental massive particles, as they are all fermions. Spin is introduced *ad hoc* into the Schrödinger equation. For example, we are familiar with how the statistical properties of electrons are imported into the Schrödinger equation, and spin-orbit interaction is simply added.

It is not correct to say that only spinless particles are treated in the Schrödinger theory. To have consistent physics, one must think of the Schrödinger equation for an electron as associated with a specific spin orientation that persists forever in the absence of a spin-changing process such as spin-orbit interaction. This point is discussed in detail by David Hestenes [23].

Chapter 3. Spin Exchange Symmetry

An important symmetry is now derived using the above material and some angular momentum algebra. It is stated as follows. When the projection quantum numbers (± ½) of two spins are exchanged: $m_1 \leftrightarrow m_2$, the spin function $\psi(m_1, m_2)$ either changes sign or not, depending on the value of the total spin.[8] Specifically, $\psi(m_1, m_2)$ can be $\psi(m_2, m_1)$ or $-\psi(m_2, m_1)$. For example, the singlet ($S = 0$) is anti-symmetric with respect to this exchange (Fig. 3.1), whereas the triplet ($S = 1$) is symmetric. It is assumed that we are dealing with spin-½ particles. This plays a role in the exclusion principle.

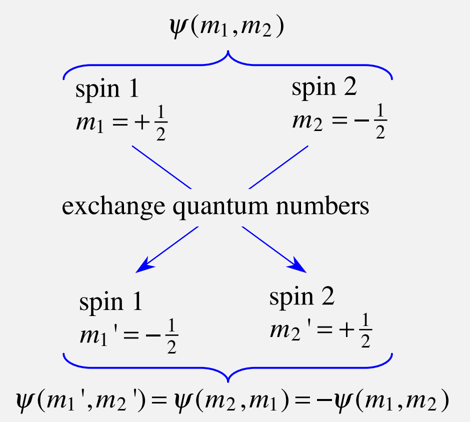


Figure 3.1. This illustrates the antisymmetry that accompanies exchange of spin quantum numbers for the case $S = 0$.

To see how this comes about, consider combinations of two spins $\vec{s}_1$ and $\vec{s}_2$, where $s_1 = s_2 = ½$, as in the case of two electrons. The spatial wave functions are suppressed, leaving just the spins, which can be represented using coupled or uncoupled bases. The operator for the square of the total angular momentum, $|\vec{s}_1 + \vec{s}_2|^2$,[9] will be applied to the column vector

$$\psi = \begin{pmatrix} \psi(++) \\ \psi(+-) \\ \psi(-+) \\ \psi(--) \end{pmatrix}. \tag{3.1}$$

The entries are spin functions $\psi(m_1, m_2)$: $\psi(+-) = \psi(m_1 = +1/2, m_2 = -1/2)$, and so on. It is not necessary to explain this choice of entries right now. Just take it as a given for the time being. Four independent $\psi(m_1, m_2)'s$ are required to span the spin space, and the entries in eqn (3.1) satisfy this.

By expressing ψ in the uncoupled basis used in eqn (3.1), and having $|\vec{s}_1 + \vec{s}_2|^2$ operate on ψ, the effect of exchanging spin quantum numbers is demonstrated. The idea behind this is to expose symmetries on the right hand side, and then use the left hand side to establish the properties of these symmetries.

[8] For spin-½ the projection quantum numbers are + ½ and − ½. Particle labels are given as numeric subscripts, *e.g.*, m_1 is the projection quantum number for particle 1. An equivalent description is to use the ket $|m_1, m_2\rangle$ to keep track of spin quantum numbers.

[9] What is meant by $|\vec{s}_1 + \vec{s}_2|^2$ is the operator $\hat{S}^2$ that corresponds to the squared magnitude of the angular momentum that derives from the vector addition of vector operators $\vec{s}_1$ and $\vec{s}_2$.

In terms of the coupled representation, $\psi(S,M_S)$, the entries in eqn (3.1), from top to bottom, are given by

$$\begin{aligned}
\psi(++) &= \psi(1,1) \\
\psi(+-) &= \frac{1}{\sqrt{2}}\big(\psi(1,0)+\psi(0,0)\big) \\
\psi(-+) &= \frac{1}{\sqrt{2}}\big(\psi(1,0)-\psi(0,0)\big) \\
\psi(--) &= \psi(1,-1)\,.
\end{aligned} \tag{3.2}$$

Because the middle entries in eqn (3.1) each contain $S = 1$ and $S = 0$, it will be possible to find conditions for which one or the other of these vanishes. These conditions constitute the exchange symmetries.

The law of cosines enables $|\vec{s}_1+\vec{s}_2|^2$ to be written

$$\begin{aligned}
|\vec{s}_1+\vec{s}_2|^2 &= |\vec{s}_1|^2+|\vec{s}_2|^2+2\vec{s}_1\cdot\vec{s}_2 \\
&= \tfrac{3}{2}+2\big(s_{1x}s_{2x}+s_{1y}s_{2y}+s_{1z}s_{2z}\big) \\
&= \tfrac{3}{2}+s_1{}^{+}s_2{}^{-}+s_1{}^{-}s_2{}^{+}+2s_{1z}s_{2z}\,.
\end{aligned} \tag{3.3}$$

where s^+ and s^- are raising and lowering operators, and $|\vec{s}_1|^2 = |\vec{s}_2|^2 = ¾$ has been used. Letting $|\vec{s}_1+\vec{s}_2|^2$ operate on the ψ given by eqn (3.1), and carrying out a bit of angular momentum algebra, yields

$$\begin{aligned}
|\vec{s}_1+\vec{s}_2|^2\,\psi &= \left(\tfrac{3}{2}+s_1{}^{+}s_2{}^{-}+s_1{}^{-}s_2{}^{+}+2s_{1z}s_{2z}\right)\begin{pmatrix}\psi(++)\\ \psi(+-)\\ \psi(-+)\\ \psi(--)\end{pmatrix} \\
&= \begin{pmatrix}2\psi(++)\\ \psi(+-)+\psi(-+)\\ \psi(-+)+\psi(+-)\\ 2\psi(--)\end{pmatrix}.
\end{aligned} \tag{3.4}$$

The right hand side of eqn (3.4) is obtained by operating on the right hand side of eqn (3.1) with eqn (3.3). When $\vec{s}_1+\vec{s}_2$ addition forms $S = 1$, we have $|\vec{s}_1+\vec{s}_2|^2\,\psi = S(S+1)\psi = 2\psi$. From eqn (3.4) it follows that $\psi(+-) + \psi(-+) = 2\psi(+-) = 2\psi(-+)$. In other words,

$$\psi(m_1, m_2) = \psi(m_2, m_1) \quad \text{for } S = 1. \tag{3.5}$$

Thus, the triplet function is symmetric with respect to exchange of spin projection quantum numbers. In bringing eqns (3.1) and (3.4) into registry for a given S, there is subtlety. As mentioned above, in terms of the coupled basis $\psi(S, M_S)$, the right hand side of eqn (3.1) is given by

$$\begin{pmatrix} \psi(++) \\ \psi(+-) \\ \psi(-+) \\ \psi(--) \end{pmatrix} = \begin{pmatrix} \psi(1,1) \\ \frac{1}{\sqrt{2}}\left(\psi(1,0)+\psi(0,0)\right) \\ \frac{1}{\sqrt{2}}\left(\psi(1,0)-\psi(0,0)\right) \\ \psi(1,-1) \end{pmatrix}. \tag{3.6}$$

When $S = 1$ is chosen, $\psi(0,0)$ in eqn (3.6) must vanish to make the column vector an eigenvector of $|\vec{s}_1 + \vec{s}_2|^2$ with eigenvalue $S(S+1) = 2$. Setting $\psi(0,0) = 0$ is the same as setting $\psi(+-) - \psi(-+) = 0$, as stated in eqn (3.5). Alternatively, when $\vec{s}_1 + \vec{s}_2$ forms the singlet ($S = 0$), each of the four entries of the column vector on the right hand side of eqn (3.4) must vanish. From the two middle entries we see right away that: $\psi(+-) + \psi(-+)$ $= 0$ can only be true if

$$\psi(m_1, m_2) = -\psi(m_2, m_1) \quad \text{for } S = 0. \tag{3.7}$$

This also ensures that $\psi(++) = \psi(--) = 0$ for $S = 0$. These top and bottom entries are $S = 1$, so we know from the outset that they must vanish for $S = 0$. The logic behind eqn (3.4) is now clearer. As stated earlier: "The strategy is to expose symmetries on the right hand side and use the left hand side to establish the properties of these symmetries."

The exchange symmetry in eqns (3.5) and (3.7) is due to spin's properties. We introduced by fiat the fact that exchange takes place, and a consequence emerged. It would have been equally acceptable to invoke an explicit exchange path and work out the symmetry. For example, this might involve rotations of spin reference frames. This is revealing insofar as the origin of sign changes in fermion and boson exchanges is concerned. It is discussed in the context of the spin-statistics connection.

4. Dirac Equation: van der Waerden's Approach

Let us now return to the development of a theory for the relativistic quantum mechanics of spin-½ massive fermions, focusing on the electron. To begin, the 2×2 matrix $\vec{\sigma} \cdot \vec{p}$ is introduced into the relativistic energy-momentum relation: $E^2 = p^2c^2 + m^2c^4$, in a way that is, for all practical purposes, the same as its introduction by Pauli into the non-relativistic expression for the energy of a free particle, $E = p^2 / 2m$. This was the idea of the Dutch mathematician Bartel Leendert van der Waerden (photo). The use of $\vec{p} \rightarrow \vec{\sigma} \cdot \vec{p}$ ensures spinor solutions, though the possible forms that these spinors might assume is not obvious *a priori*, as both antiparticles and spin must be taken into account. The relativistic $\vec{p}$ used here has canonical momentum whose space part is $-i\hbar\nabla$, the same as in non-relativistic quantum mechanics.

A 4-spinor can be anticipated on the basis of Pauli's 2-spinor for dealing with spin ½ and the Klein-Gordon 2-component vector. Indeed, it turns out that the number of components that accommodates these features with the least mathematical overhead is four. The fact that Klein-Gordon solutions can be expressed as single-component complex wave functions means that a 4-spinor is not essential. However, if fewer than four components are used, difficulty is encountered when it comes to carrying out the parity operation [5]. As a result, despite the fact that fewer than four components can be made to work, this requires more effort, not less. The position taken in the present section is that four is the desired number of components.

Using $\vec{p} \rightarrow \vec{\sigma} \cdot \vec{p}$, the right hand side of $(mc)^2 = (E/c)^2 - p^2$ is factored to yield

$$(mc)^2 = \left(\frac{E}{c} - \vec{\sigma} \cdot \vec{p}\right)\left(\frac{E}{c} + \vec{\sigma} \cdot \vec{p}\right). \tag{4.1}$$

To turn on relativistic quantum mechanics, the substitutions $E = i\hbar\partial_t$ and $\vec{p} = -i\hbar\nabla$ are now introduced. We shall neglect electromagnetic fields for the time being and introduce them later through minimal coupling. The ansatz composed of eqn (4.1) together with $E \rightarrow i\hbar\partial_t$ and $\vec{p} \rightarrow -i\hbar\nabla$ is all that is needed to obtain the Dirac equation. The rest is mathematical manipulation. The resulting expression operates on a two-component state vector that we shall label ϕ. This is not surprising because in the non-relativistic limit this theory must revert to the Pauli result. The above maneuvers yield the following interesting and suggestive equation:

$$(mc)^2\phi = \left(i\hbar\,\partial_{ct} + i\hbar\vec{\sigma} \cdot \nabla\right)\left(i\hbar\,\partial_{ct} - i\hbar\vec{\sigma} \cdot \nabla\right)\phi\,. \tag{4.2}$$

The order in which the parenthetic terms appear of course is immaterial.

To obtain a theory for the relativistic quantum mechanics of fermions, it is desirable that the time derivative appears in first order in the final equation. Failure to achieve this had plagued earlier attempts to formulate a theory of relativistic quantum mechanics. It is also essential to treat space and time even-handedly if the theory is to be covariant. The even-handed requirement led to the Klein-Gordon equation, which is second-order in both space and time derivatives. No one knew what to do with the square root: $E = \pm(p^2c^2 + m^2c^4)^{1/2}$, so a second-order partial differential equation was used.[10]

Despite the fact that a differential equation that is second order in both space and time derivatives meets the even-handed requirement, it has other difficulties as a quantum mechanical equation of motion, namely, those encountered in the Klein-Gordon equation. So why not seek an equation that is first order in both space and time derivatives? This was Dirac's strategy.

Dirac was bothered by the negative probability density that seemed inevitable in solutions of the Klein-Gordon equation. Lore has it that he was more concerned with this than with the apparent absence of spin. This is not surprising. On physical grounds negative probability density is preposterous. Also, Pauli had already shown how spin could be introduced into the non-relativistic theory, and surely the form introduced by Pauli would emerge in any relativistic theory whose non-relativistic limit is the Pauli equation.

4.1. Interpretation

Despite its absurdity, negative probability density seemed an inevitable consequence of the mathematics. When differentiation with respect to time appears once in a quantum mechanical eigenvalue equation it yields a single sign for the energy. This is the case in Schrödinger quantum mechanics, where an energy eigenstate evolves in time according to $e^{-iE_n t/\hbar}$.

On the other hand, in the case of a wave equation that contains second derivatives with respect to time and space, $+E$ and $-E$ appear. As mentioned earlier, the problem lies in interpreting these as the kind of particle energy one gets in the non-relativistic theory. In a classical wave equation, when $+\omega$ and $-\omega$ are obtained there is no issue. These are not energies, just frequencies. The $+E$ and $-E$ have a great deal in common with such $+\omega$ and $-\omega$ parameters. For example, recall how $+\omega$ and $-\omega$ frequencies arose when we examined the quantization of lattice vibrations that yields phonons. There it was shown that the energy is always positive real, and the $+\omega$ and $-\omega$ are oscillation parameters that arise in equations of motion.

The $+E$ and $-E$ lead to a problem when interpreting the continuity equation

$$\partial_t \rho + \nabla \cdot \vec{J} = 0 . \tag{4.3}$$

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[10] Neils Bohr once encountered Dirac hard at work and asked him what he was working on, to which Dirac replied: "I am trying to take a square root."

When this is applied to the field-free Schrödinger equation, the density ρ is interpreted as the probability density: $P = \psi^*\psi$, and eqn (4.3) yields a probability flux density of $\vec{J} = (i\hbar/2m)(\psi\nabla\psi^* - \psi^*\nabla\psi)$.[11] There is no problem.

Recall Klein-Gordon

In the relativistic case, Lorentz covariance requires that the four-divergence of the probability-current density J^ν vanishes: $\partial_\nu J^\nu = 0$. Referring to the Klein-Gordon result, in the field-free case, the probability-current density J^ν consists of a 3D term like the one obtained in the Schrödinger treatment: $\vec{J} = (i\hbar/2m)(\phi\nabla\phi^* - \phi^*\nabla\phi)$, plus the zeroth component

$$J^0 = \frac{i\hbar}{2m}\left(\phi\partial_{ct}\phi^* - \phi^*\partial_{ct}\phi\right). \tag{4.4}$$

The relativistic continuity equation must be consistent with $\partial_\nu J^\nu = 0$.

Drawing on analogy with Schrödinger quantum mechanics, and in keeping with classical relativity, suppose J^0 is c times a probability density, P. This runs into difficulty in the Klein-Gordon case because of the + E and – E. Figuring out how to rationalize – E for a free particle is bad enough, but difficulty with interpretation gets worse. In the Schrödinger picture, the time evolution of an eigenstate is given by $e^{-iEt/\hbar}$, whereas with the Klein-Gordon result, it is necessary to use both positive and negative values of E. This results in what appears to be a negative probability density. That is, the parenthetic term in eqn (4.4) can assume both positive and negative values.

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[11] The inclusion of electromagnetic fields in the Schrödinger equation for a charged particle gives

$$\frac{1}{2m}\left(-i\hbar\nabla - \frac{q}{c}\vec{A}\right)\cdot\left(-i\hbar\nabla - \frac{q}{c}\vec{A}\right)\psi + V\psi = i\hbar\partial_t\psi .$$

To obtain the probability current density, we follow the same procedure as for the field-free case. First, write out the terms that arise from the dot product and then multiply from the left by ψ^*. Then take the complex conjugate of the above equation, write out the terms arising from the dot product, and multiply from the left by ψ. Finally, subtract the latter equation from the former. There is no net contribution from either V or A^2. A modest amount of algebra yields

$$-\frac{i\hbar}{2m}\nabla\cdot\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right) + \frac{q}{mc}\vec{A}\psi^*\psi = \partial_t\left(\psi^*\psi\right).$$

The term $\partial_t(\psi^*\psi)$ is $\partial_t\rho$, where ρ is the probability density, which must equal $-\nabla\cdot\vec{J}$, where $\vec{J}$ is the probability-current density. From the above, the probability-current density is

$$\vec{J} = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right) - \frac{q}{mc}\vec{A}\psi^*\psi .$$

As a result of egregious problems such as negative probability density and negative kinetic energy, the Klein-Gordon equation was abandoned shortly after its introduction. Once the Dirac equation was in place, most scientists took it to be the only correct relativistic theory: Klein-Gordon was wrong and should not be pursued further. Interestingly, despite the fact that the Dirac equation gives a positive probability density, we shall see that it also has + E and – E solutions. In other words, the negative energy issue remains. This prompted Dirac to introduce his hole theory, which shortly thereafter gave way to the field-theoretic interpretation. Nowadays Dirac's hole theory is regarded as a clever rationalization and an important piece of history, but not something to take seriously.

The problem with such offhand dismissal of the Klein-Gordon equation resides in the incautious assumption that it has wave functions as solutions. The Klein-Gordon equation was inferred on the basis of sensible arguments based on correspondence between classical and quantum mechanics. It was not derived. It can be derived, however, using relativistic quantum field theory, and when this is done, it is found that ϕ is a complex scalar field that applies to electrically charged fields. When this is taken into account, what appears as the + E and – E solutions are seen to reflect the existence of particles and antiparticles, for example, electrons and positrons. I am going over this quickly because we covered it earlier and will return to it later.

In electrodynamics it was seen that the anti-symmetric tensor $F^{\mu\nu}$ allows Maxwell's equations to be expressed as a set of first-order differential equations. Nothing is free, and the price paid for the advantage gained in dealing with first-order equations is the number of components. The same idea holds here. Namely, the set of first-order differential equations that will be derived is destined to have solutions that consist of four components. Let us now return to the approach of van der Waerden and eqn (4.2).

4.2. Dirac Equation

The form of the "interesting and suggestive" eqn (4.2) invites its separation into two coupled first-order differential equations. This is achieved by introducing the definition $\phi = \phi^L$, which paves the way for the conversion of eqn (4.2) into a pair of coupled partial differential equations. Using $\phi = \phi^L$ in eqn (4.2) yields

$$(mc)^2 \phi^L = \left(i\hbar\,\partial_{ct} + i\hbar\vec{\sigma}\cdot\nabla\right)\underbrace{\left(i\hbar\,\partial_{ct} - i\hbar\vec{\sigma}\cdot\nabla\right)\phi^L}_{\equiv\, mc\,\phi^R} .$$

Defining ϕ^R as noted yields

$$\left(i\hbar\,\partial_{ct} - i\hbar\vec{\sigma}\cdot\nabla\right)\phi^L = mc\,\phi^R \tag{4.5}$$

$$\left(i\hbar\partial_{ct} + i\hbar\vec{\sigma}\cdot\nabla\right)\phi^R = mc\,\phi^L . \tag{4.6}$$

These are each first-order differential equations. The functions ϕ^L and ϕ^R are each 2-spinors, with *L* and *R* standing for left and right. Later we will see that *L* and *R* label helicity eigenstates. Notice that eqns (4.5) and (4.6) can be written in 2×2 form

$$i\begin{pmatrix} 0 & \partial_0 - \vec{\sigma}\cdot\nabla \\ \partial_0 + \vec{\sigma}\cdot\nabla & 0 \end{pmatrix}\begin{pmatrix} \phi^R \\ \phi^L \end{pmatrix} = \frac{mc}{\hbar}\begin{pmatrix} \phi^R \\ \phi^L \end{pmatrix}. \tag{4.7}$$

Each entry in the 2×2 matrix is itself a 2×2 matrix, and ϕ^R and ϕ^L are each 2-spinors.

Recall left and right circularly polarized electromagnetic radiation, in which the tips of the electric and magnetic field vectors follow a circular trajectory whose frequency is that of the oscillating field. The same idea applies here in that $\vec{\sigma}\cdot\vec{p}$ gives two spin projections along the direction of the momentum $\vec{p}$. These are the helicity eigenstates mentioned above, though it is not yet obvious where this fits with relativistic fermions. Equations (4.5) and (4.6) [which are combined in eqn (4.8)] constitute the Dirac equation. It has been obtained via a short, efficient route. These equations are not in the form found most often in texts, but their conversion requires only modest algebraic manipulation, as discussed below.

4.3. Manipulation into a Standard Form

Manipulation of eqns (4.5) and (4.6) yields the covariant form of the Dirac equation. This is carried out here. In the next section we will go through the original derivation of Dirac. Following this, a few limiting cases will be examined: plane waves, low-energy limit, a relativistic Hamiltonian that is germane to electronic structure theory and is correct to order $(v/c)^2$, recovery of the Pauli equation, and zero mass.

To begin, alternate addition and subtraction of eqns (4.5) and (4.6) gives

$$i\hbar\left(\partial_{ct}\left(\phi^R+\phi^L\right)+\vec{\sigma}\cdot\nabla\left(\phi^R-\phi^L\right)\right) = mc\left(\phi^R+\phi^L\right) \tag{4.8}$$

$$i\hbar\left(\partial_{ct}\left(\phi^R-\phi^L\right)+\vec{\sigma}\cdot\nabla\left(\phi^R+\phi^L\right)\right) = -mc\left(\phi^R-\phi^L\right). \tag{4.9}$$

With the definitions

$$\psi_A \equiv \phi^R+\phi^L \text{ and } \psi_B \equiv \phi^R-\phi^L, \tag{4.10}$$

and using $\partial_{ct} = \partial_0$, eqns (4.8) and (4.9) become

$$i\left(\partial_0\psi_A+\left(\vec{\sigma}\cdot\nabla\right)\psi_B\right) = \frac{mc}{\hbar}\psi_A \tag{4.11a}$$

$$i\left(\partial_0\psi_B+\left(\vec{\sigma}\cdot\nabla\right)\psi_A\right) = -\frac{mc}{\hbar}\psi_B, \tag{4.11b}$$

or, in matrix form,

$$-i\begin{pmatrix} \partial_0 & \vec{\sigma}\cdot\nabla \\ -\vec{\sigma}\cdot\nabla & -\partial_0 \end{pmatrix}\begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = -\frac{mc}{\hbar}\begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}. \tag{4.12}$$

The functions ψ_A and ψ_B each have two components because they consist of linear combinations of the 2-spinors ϕ^R and ϕ^L. Thus, the column vector in eqn (4.12) has four components. Likewise, the matrix elements in the 2×2 matrix are each 2×2 matrices. With these written explicitly, eqn (4.12) becomes

$$-i\begin{pmatrix} \partial_0 & 0 & \partial_3 & \partial_1 - i\partial_2 \\ 0 & \partial_0 & \partial_1 + i\partial_2 & -\partial_3 \\ -\partial_3 & -\partial_1 + i\partial_2 & -\partial_0 & 0 \\ -\partial_1 + i\partial_2 & \partial_3 & 0 & -\partial_0 \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = -\frac{mc}{\hbar}\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}. \tag{4.13}$$

The 2-spinors ψ_A and ψ_B are assigned components ψ_1, ψ_2 and ψ_3, ψ_4, respectively.

The 4×4 matrix can be expressed as the sum of four individual matrices. Each consists of a 4×4 matrix that contains only numbers and multiplies a single partial derivative. For example, we identify the matrix that multiplies ∂_0 as diagonal with +1's in the two upper left positions and –1's in the two lower right positions, and likewise for the others. These matrices are denoted γ^ν and referred to as gamma matrices or Dirac matrices. Together with the 4-spinor ψ they yield the tidy expression

$$\left(-i\gamma^\nu \partial_\nu + \frac{mc}{\hbar}\right)\psi = 0\,. \tag{4.14}$$

Comparing eqns (4.13) and (4.14), we see that the γ^ν matrices are

$$\gamma^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad \gamma^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \quad \gamma^2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix} \quad \gamma^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \tag{4.15}$$

Equation (4.14) is the Dirac equation for a spin-½ fermion in the absence of the electromagnetic field. There are other ways to express the Dirac equation. For example, if eqn (4.14) is multiplied by $\hbar$ it reads

$$\left(\gamma^\nu p_\nu - mc\right)\psi = 0\,. \tag{4.16}$$

The matrices given by eqn (4.15) constitute one representation. This set of matrices is not unique. Unitary transformations can change the representation without affecting the physics. The best way to express the matrices is through their anti-commutation relations, as these cannot change from one representation to another. Let us do this for $\{\gamma^1,\gamma^2\}$, where the squiggly bracket denotes anti-commutation. Referring to eqn (4.15), γ^1 and γ^2 are, using the 2D form for convenience:

$$\gamma^1 = \begin{pmatrix} 0 & \sigma^1 \\ -\sigma^1 & 0 \end{pmatrix} \qquad \gamma^2 = \begin{pmatrix} 0 & \sigma^2 \\ -\sigma^2 & 0 \end{pmatrix}. \tag{4.17}$$

Taking the anti-commutator yields

$$\gamma^1\gamma^2 + \gamma^2\gamma^1 = -\begin{pmatrix} \sigma^1\sigma^2 & 0 \\ 0 & \sigma^1\sigma^2 \end{pmatrix} - \begin{pmatrix} \sigma^2\sigma^1 & 0 \\ 0 & \sigma^2\sigma^1 \end{pmatrix} = 0. \tag{4.18}$$

The fact that the Pauli matrices anti-commute, $\{\sigma^i,\sigma^j\} = 0$, gives $\{\gamma^1,\gamma^2\} = 0$.

In examining the other anti-commutators, it is easy to show that $\{\gamma^\mu,\gamma^\nu\} = 0$ whenever $\mu \neq \nu$. Alternatively, when $\mu = \nu$, the right hand side of eqn (4.18) is equal to $2\eta^{\mu\nu}$, where $\eta^{\mu\nu}$ is the Minkowski metric with signature (1,–1,–1,–1). For example, replacing σ^2 in eqn (4.18) with σ^1 yields $-2\mathbf{1}$, where $\mathbf{1}$ is the unit matrix, whereas $\{\gamma^0,\gamma^0\} = 2\mathbf{1}$. You should verify these properties for $\{\gamma^0,\gamma^1\}$, $\gamma^0\gamma^0$, $\gamma^1\gamma^1$, etc. If you are unfamiliar with the use of block forms for manipulations such as the one in eqn (4.18), you will discover that this practice is useful. The above results are summarized as

$$\boxed{\{\gamma^\mu,\gamma^\nu\} = 2\eta^{\mu\nu}\mathbf{1}.} \tag{4.19}$$

The gauge invariant Dirac equation includes the electromagnetic field. Application of minimal coupling: $\partial_\nu \to \partial_\nu + i(q/\hbar c)A_\nu$, to eqn (4.14) yields

$$\boxed{\left(-i\gamma^\nu\left(\partial_\nu + i\frac{q}{\hbar c}A_\nu\right) + \frac{mc}{\hbar}\right)\psi = 0.} \tag{4.20}$$

5. Dirac's Approach

No one alive today knows what transpired in the mind of Paul Adrien Maurice Dirac – an eccentric genius if ever there was one – during his development of a theory of relativistic quantum mechanics for spin-½ fermions. Perhaps no one other than Dirac himself appreciated the nuances of his thinking, and this assumes that Dirac was able to appreciate the nuances of his own thinking. We are left with speculation and anecdotes [2]. Though Dirac was influenced by great scientists of the day, he was fearless when it came to introducing his own ideas. As mentioned earlier, he set out to derive a theory for relativistic spin-½ fermions by enlisting a first-order differential equation. We shall follow his derivation.

A theory is sought in which time and space are assigned equal status in a partial differential equation that is first-order in both time and space derivatives. Nonetheless, one should not overlook the field-free Klein-Gordon equation

$$\left(\partial_{ct}{}^2 - \nabla^2 + \left(\frac{mc}{\hbar}\right)^2\right)\phi = \left(\partial^\nu \partial_\nu + \left(\frac{mc}{\hbar}\right)^2\right)\phi = 0\ . \tag{5.1}$$

The Klein-Gordon equation has its limitations, but when properly interpreted it serves as a useful benchmark. Specifically, in the absence of the particle's interaction with an electromagnetic field, a theory for the relativistic quantum mechanics of a spin-½ particle should recover the Klein-Gordon equation for each of its components. After all, with electromagnetism suppressed there is nothing to which spin and charged particles and antiparticles can couple.

Gauge field theory showed that it is impossible to eliminate electromagnetism from an equation of motion of an electrically charged particle if the theory is to be gauge invariant. However, at the time of Dirac's work this symbiosis of electromagnetism and quantum mechanics was not appreciated. Thus, we shall deal first with the field-free case, and later introduce the electromagnetic field through minimal coupling. There are a number of exact solutions of the field-free Dirac equation, whereas exact solutions when fields are present are relatively scarce.

Dirac realized that to have an equation in which the time derivative appears only in first order the ∂^2 term must be replaced by a term linear in ∂. The general form for such an equation for a free particle is

$$i\hbar\partial_{ct}\psi = \left(-i\hbar\alpha^i\partial_i + \beta mc\right)\psi\ . \tag{5.2}$$

With $i\hbar\partial_{ct}\psi$ on the left hand side, the parenthetic term can be interpreted as a Hamiltonian divided by c.

Being a first-order partial differential equation, eqn (5.2) differs markedly in appearance and physics from the Klein-Gordon equation. The task at hand is the determination of β and the α^i $(i = 1-3)$. In light of the previous section, it is apparent that β and α^i are matrices and ψ is a spinor. We shall see that for all practical purposes the lowest dimensional matrix representation of β and α^i that satisfies the various requirements is four. These 4×4 matrices are analogous to the γ matrices that entered in the previous section. In fact, the β and α^i matrices can be used to form the γ matrices. We shall see that a modest amount of algebraic manipulation converts eqn (5.2) to the form of the Dirac equation given by eqn (4.14).

As mentioned above, Dirac's remarkable physical insight enabled him to realize that, in the absence of interaction with an electromagnetic field, eqn (5.2) must be compatible with the Klein-Gordon equation. He used this as the basis of a strategy for deriving the forms of the matrices β and α^i. It is interesting that this compatibility, in which each spinor component satisfies the Klein-Gordon equation in the absence of the electromagnetic field, ensures that the Dirac equation (like the Klein-Gordon equation) has both positive and negative energy solutions. Unlike the Klein-Gordon case, the Dirac probability density is positive real (due to the presence of only first order derivatives) and spin is present. Nonetheless, each theory faces the challenge of interpreting the negative energies that arise in the solutions.

Relativistic quantum field theory reveals the physics that underlies the so-called negative energies quite neatly by dealing with particles and antiparticles on equal footing from the outset. This is the only reasonable way to proceed at high energy where the creation and annihilation of massive particles occurs. On the other hand, in relativistic quantum chemistry, we deal with situations where negative energy contributions are small, and the physics is cast in terms of fixed numbers of particles.

Squaring the operators in eqn (5.2) yields an expression that contains the ingredients of the Klein-Gordon equation plus a fair amount of *unwanted stuff*. This is precisely what is needed: β and α^i are chosen such that the unwanted stuff disappears. Let us carry out this exercise and then discuss the result. The expression to be dealt with is

$$\partial_{ct}{}^2\,\psi = -\left(i\alpha^i\partial_i - \beta\,\frac{mc}{\hbar}\right)^2\psi \tag{5.3a}$$

$$= \left(\alpha^i\alpha^j\partial_i\partial_j + i\frac{mc}{\hbar}\alpha^i\beta\partial_i + i\frac{mc}{\hbar}\beta\alpha^i\partial_i - \beta^2\left(\frac{mc}{\hbar}\right)^2\right)\psi\ . \tag{5.3b}$$

Use has been made of the fact that the partial derivatives commute with the β and α^i matrices because the matrix elements in β and α^i are numbers. Minor rearrangement[12] highlights the relationship between eqn (5.3b) and the Klein-Gordon equation.

[12] The first term inside the large parentheses in eqn (5.3b) ($\alpha^i\alpha^j\partial_i\partial_j$) is composed of 9 terms. Three are for $i = j$, giving the second term in eqn (5.4). The other 6 give the 3 anti-commutator terms inside the parentheses at the end of eqn (5.4).

$$\underbrace{\left(\mathbf{1}\partial_{ct}{}^2 - (\alpha^i)^2\partial_i{}^2 + \beta^2\left(\frac{mc}{\hbar}\right)^2\right.}_{\text{Klein-Gordon}} \underbrace{\left. - i\frac{mc}{\hbar}\{\alpha^i,\beta\}\partial_i - \left(\{\alpha^1,\alpha^2\}\partial_1\partial_2 + \text{c.p.}\right)\right)}_{=0}\psi = 0 \qquad (5.4)$$

where $\mathbf{1}$ is the unit matrix, {...} denotes anti-commutation, and c.p. denotes the other two cyclic permutations of the indices: $\{\alpha^2,\alpha^3\}\partial_2\partial_3 + \{\alpha^3,\alpha^1\}\partial_3\partial_1$.

Equation (5.4) reveals the conditions that β and α^i must satisfy. The first three terms must be retained because they give eqn (5.1), whereas the other terms must vanish. Setting $\beta^2 = \mathbf{1}$ and $(\alpha^i)^2 = \mathbf{1}$ recovers the Klein-Gordon equation for each component of ψ. Summarizing the above yields

$$(\alpha^i)^2 = \beta^2 = \mathbf{1} \qquad (5.5)$$

$$\alpha^i\alpha^j + \alpha^j\alpha^i = 2\delta^{ij}\mathbf{1} \qquad (5.6)$$

$$\alpha^i\beta + \beta\alpha^i = 0\ . \qquad (5.7)$$

The properties given by the above equations are sufficient to establish the lowest possible dimension of the matrices. When eqn (5.7) is multiplied from either the left or right by β, it yields $\alpha^i = -\beta\alpha^i\beta$. Taking the trace of each side and using the trace's cyclic invariance ($\mathrm{Tr\,AB} = \mathrm{Tr\,BA}$) yields $\mathrm{Tr}\,\alpha^i = -\mathrm{Tr}\,\alpha^i$. Likewise, multiplying eqn (5.7) from either the left or right by α^i yields $\mathrm{Tr}\,\beta = -\mathrm{Tr}\,\beta$. Thus, the traces of the matrices α^i and β vanish.

Equation (5.5) indicates that the eigenvalues of the matrices have magnitude of unity, and the eigenvalues are real. In other words, the eigenvalues are either +1 or –1. Because the trace is the sum of the eigenvalues, it follows that the number of +1's is equal to the number of –1's, and therefore the matrices are of even dimension. They cannot be 2×2 because no combination of the Pauli matrices and the unit matrix exists that satisfies the above anti-commutation relations. This leaves 4×4, with the understanding that higher even dimensions are allowed.

Let us now obtain a set of 4×4 α^i and β matrices that obeys the rules given by eqns (5.5) – (5.7). These matrices can be constructed by using the Pauli matrices σ^i and the unit matrix $\mathbf{1}$. An example is

$$\alpha^i = \begin{pmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}. \qquad (5.8)$$

These matrices satisfy eqns (5.5) – (5.7). This is one possible 4×4 representation of the algebra given by eqns (5.5) – (5.7), but not the only one. It is conventional to replace the symbol β with α^0. Writing the α^i and α^0 matrices in 4×4 form yields

$$\alpha^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad \alpha^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad \alpha^2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} \quad \alpha^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}. \tag{5.9}$$

We now convert the Dirac equation given by eqn (5.2) to covariant form. This brings it into registry with the result of the previous chapter. To achieve this, go back to eqn (5.2), with $\partial_{ct} = \partial_0$ and $\beta = \alpha^0$:

$$\left(i\partial_0 + i\alpha^i \partial_i - \alpha^0 \frac{mc}{\hbar} \right) \psi = 0 \,, \tag{5.10}$$

and multiply from the left by $-\alpha^0$ to obtain

$$\left(-i\big(\underbrace{\alpha^0}_{\gamma^0} \partial_0 + \underbrace{\alpha^0 \alpha^i}_{\gamma^i} \partial_i \big) + \frac{mc}{\hbar} \right) \psi = 0 \,. \quad \Rightarrow \quad \left(-i\gamma^\nu \partial_\nu + \frac{mc}{\hbar} \right) \psi = 0 \tag{5.11}$$

Standard form for field-free Dirac equation

where

$$\gamma^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad \gamma^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \quad \gamma^2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix} \quad \gamma^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \tag{5.12}$$

This is eqn (4.17). Minimal coupling yields the gauge invariant Dirac equation

$$\boxed{\left(-i\gamma^\nu \left(\partial_\nu + i\frac{q}{c} A_\nu \right) + \frac{mc}{\hbar} \right) \psi = 0 \,.} \tag{5.13}$$

Example 5.1. Free Particle at Rest

This is the simplest possible case. With $\vec{p} = 0$ and electromagnetic fields not taken into account, the term $\gamma^\nu \partial_\nu$ is reduced to the single nonzero component $\gamma^0 \partial_0$. The particle is completely delocalized. It has no wave character, only time dependence. The Dirac equation becomes four independent first-order equations, each solved by inspection:

$$\begin{pmatrix} -i\partial_0 + mc/\hbar & 0 & 0 & 0 \\ 0 & -i\partial_0 + mc/\hbar & 0 & 0 \\ 0 & 0 & i\partial_0 + mc/\hbar & 0 \\ 0 & 0 & 0 & i\partial_0 + mc/\hbar \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = 0 \tag{1}$$

The equation for ψ_1 is $(-i\partial_{ct} + mc/\hbar)\psi_1 = 0$, whose solution is $\psi_1 \propto e^{-imc^2 t/\hbar}$, and likewise for the other components. Thus, the four independent solutions are

$$\psi_1{}^{(+)} : e^{-imc^2 t/\hbar} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \psi_2{}^{(+)} : e^{-imc^2 t/\hbar} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad \psi_3{}^{(-)} : e^{imc^2 t/\hbar} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \quad \psi_4{}^{(-)} : e^{imc^2 t/\hbar} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \tag{2}$$

These are eigenfunctions of the spin projection operator:

$$\Sigma_3 = \begin{pmatrix} \sigma_3 & 0 \\ 0 & \sigma_3 \end{pmatrix}. \tag{3}$$

with respective eigenvalues +1, –1, +1, and –1. The ψ's in eqn (2) are clearly orthogonal to one another and they constitute a basis. Any free-particle-at-rest spinor can be expressed as a linear combination: $c_1\psi_1{}^{(+)} + c_2\psi_2{}^{(+)} + c_3\psi_3{}^{(-)} + c_4\psi_4{}^{(-)}$, where the c_i are complex expansion coefficients.

The (+) superscript corresponds to positive energy solutions, that is, $E = mc^2$. Recall the problem that arose with the Klein-Gordon equation, where positive and negative "energy eigenvalues" could not be interpreted as denoting energies in the same sense as in non-relativistic quantum mechanics. It turns out that the Klein-Gordon field is charged, and operating with a charge conjugation operator turns a particle wave function into an antiparticle wave function and *vice versa*. When considering an electron, the negative energy reflects the participation of a positron. However, the equation is for an electron, so we see a manifestation of antiparticle participation as viewed from within the space of one-electron functions. As we saw earlier, the field theory approach has no need for this convoluted description.

The same idea applies here. The Dirac equation should be interpreted from the perspective of relativistic quantum field theory (RQFT), in which case charge again appears and there is no problem with positive and negative energy solutions. When treated as a quantum mechanical equation with a fixed number of particles (electrons) one can expect interesting things to arise.

Example 5.2. Free Particle in Motion

Let us now turn to $\vec{p} \neq 0$ plane waves in field-free space, which is another easily solved case. When $\vec{p}$ has a single value, the particle is again delocalized throughout all of space, but this time it has wave character. A conceptually appealing way to proceed is to apply a Lorentz boost to the $\vec{p} = 0$ spinors of Example 5.1, in which case the system is then judged from a frame that can be taken as stationary with respect to the moving particle. Alternatively, use can be made of the ψ_A and ψ_B 2-spinors derived earlier. These are expressed in terms of the 2-spinors, u_A and u_B (which have no explicit spacetime dependence), each of which is multiplied by the plane wave $\exp\left(i(\vec{p}\cdot\vec{r} - Et)/\hbar\right)$. In this expression, E can be either positive or negative, *i.e.*, $E = \pm(p^2c^2 + m^2c^4)^{1/2} = \pm E_p$. This plane wave comes straight from the Klein-Gordon equation. Recall that in the absence of electromagnetic fields each Dirac 4-spinor component must satisfy the Klein-Gordon equation.

The latter route is chosen here, as it is faster. The former route (Lorentz boost) is left as an exercise. Referring to eqn (4.12), and introducing the definitions listed in the above paragraph, the 4-spinor ψ is given by

$$\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \begin{pmatrix} u_A \\ u_B \end{pmatrix} \exp\left(i(\vec{p}\cdot\vec{r} - Et)/\hbar\right). \tag{1}$$

Using this with eqn (4.11) yields expressions that relate u_A and u_B to one another:[13]

$$u_A = \frac{c}{E - mc^2}\left(\vec{\sigma}\cdot\vec{p}\right)u_B \tag{2}$$

and

$$u_B = \frac{c}{E + mc^2}\left(\vec{\sigma}\cdot\vec{p}\right)u_A . \tag{3}$$

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[13] $i\left(\partial_0\psi_A + \left(\vec{\sigma}\cdot\nabla\right)\psi_B\right) = \frac{mc}{\hbar}\psi_A \;\Rightarrow\; \frac{E}{c}\psi_A - \vec{\sigma}\cdot\vec{p}\,\psi_B = mc\,\psi_A$

$\Rightarrow \left(E - mc^2\right)u_A = c\left(\vec{\sigma}\cdot\vec{p}\right)u_B$. This is eqn (2); eqn (3) follows in a like manner .

As before, it can be assumed that for $E = +(p^2c^2 + m^2c^4)^{1/2}$ the u_A spinor is much larger than the u_B spinor. This assumption is not necessary mathematically, but it is in line with where we are headed. Thus, the two u_A spinors are chosen as

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{4}$$

The corresponding u_B spinors are obtained by using eqn (3). It is understood that normalization still needs to be added. This yields the following two 4-spinors for $E = +(p^2c^2 + m^2c^4)^{1/2} = +E_p$.

$$u^{(1)} = N \begin{pmatrix} 1 \\ 0 \\ \dfrac{cp^3}{E_p + mc^2} \\ \dfrac{cp^1 + icp^2}{E_p + mc^2} \end{pmatrix} \qquad u^{(2)} = N \begin{pmatrix} 0 \\ 1 \\ \dfrac{cp^1 - icp^2}{E_p + mc^2} \\ \dfrac{-cp^3}{E_p + mc^2} \end{pmatrix}. \tag{5}$$

Exercise: Obtain eqn (5) from eqn (3). Hint: express $\vec{\sigma} \cdot \vec{p}$ as a 2×2 matrix that operates on the spinor in eqn (4).

Alternatively, with $E = -(p^2c^2 + m^2c^4)^{1/2} = -E_p$, u_B is much larger than u_A as seen from eqn (2). Applying eqn (2) yields

$$u^{(3)} = N \begin{pmatrix} -\dfrac{cp^3}{E_p + mc^2} \\ -\dfrac{cp^1 + icp^2}{E_p + mc^2} \\ 1 \\ 0 \end{pmatrix} \qquad u^{(4)} = N \begin{pmatrix} -\dfrac{cp^1 - icp^2}{E_p + mc^2} \\ \dfrac{cp^3}{E_p + mc^2} \\ 0 \\ 1 \end{pmatrix}. \tag{6}$$

The above $u^{(i)}$ are orthogonal to one another. Note that the same N applies to each spinor. The spinors $\psi^{(i)}$ are obtained by multiplying each of the $u^{(i)}$ in eqns (5) and (6) by $\exp\left(i(\vec{p} \cdot \vec{r} - Et)/\hbar\right)$.

None of the above $u^{(i)}$ is an eigenfunction of the spin projection operator Σ_3. However, they become eigenfunctions of Σ_3 when the Σ_3 projection axis is taken along the direction of $\vec{p}$. In other words, $p^1 = p^2 = 0$, in which case $p^3 = p$, and the $u^{(i)}$ are

$$u^{(1)} = N\begin{pmatrix} 1 \\ 0 \\ \dfrac{cp}{E_p + mc^2} \\ 0 \end{pmatrix} \quad u^{(2)} = N\begin{pmatrix} 0 \\ 1 \\ 0 \\ \dfrac{-cp}{E_p + mc^2} \end{pmatrix} \quad u^{(3)} = N\begin{pmatrix} \dfrac{-cp}{E_p + mc^2} \\ 0 \\ 1 \\ 0 \end{pmatrix} \quad u^{(4)} = N\begin{pmatrix} 0 \\ \dfrac{cp}{E_p + mc^2} \\ 0 \\ 1 \end{pmatrix}. \tag{7}$$

The operator $\vec{\Sigma}\cdot\vec{p}$ is called the helicity operator.

Exercise: Verify that $\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = \begin{pmatrix} u_A \\ u_B \end{pmatrix} \exp\left(i(\vec{p}\cdot\vec{r} - Et)/\hbar\right)$ for the spinors in eqn (7) are eigenfunctions of the helicity operator $\vec{\Sigma}\cdot\vec{p}$.

Normalization

Normalization depends on convention. For example, $u^{(1)\dagger}u^{(1)} = 1$ gives

$$N = \frac{E_p + mc^2}{2E_p} \; . \ldots \text{(later)}$$

Example 5.3. Large and Small Spinor Components

It is often useful to express the Dirac 4-spinor in terms of a pair of 2-spinors. Earlier we saw that 2-spinors followed from $(mc)^2 = \big((E/c)-(\vec{\sigma}\cdot\vec{p})\big)\big((E/c)+(\vec{\sigma}\cdot\vec{p})\big)$, with quantum mechanics turned on using $E \to i\hbar\partial_t$ and $\vec{p} \to -i\hbar\nabla$. In the present example, we shall examine the case of one large 2-spinor and one small 2-spinor. In quantum mechanics, as opposed to quantum field theory, the number of particles is conserved. Thus, any particle-antiparticle physics that arises enters within the framework of a fixed number of particles. For example, if an electron in the presence of a strong field – say a core electron in the field of its heavy nucleus – is being examined, though additional particles are not introduced, their transient presence will manifest.

Separation into large and small 2-spinors is useful at energies in modest excess of mc^2, where most relativistic quantum chemistry plays out. Other separations can be found, but we will stick to large and small 2-spinors.

The starting point is eqn (4.11), which is reproduced below as eqns (1) and (2), albeit with the inclusion of the electromagnetic field. These equations enable us to obtain a closed-form expression for one of the 2-spinors. Approximations appropriate to the low-energy regime are then introduced. Sometimes this regime is referred to as the non-relativistic limit. However, important relativistic terms will be retained in a perturbation expansion, so such energies will be referred to as the low-energy regime of the Dirac equation. The present example concludes with a derivation of the terms that enter into quantum chemical calculations and short discussions of each term. We shall stop short of the many-body formulation.

To begin, consider the coupled equations obtained by introducing the electromagnetic field into eqn (4.11) and rearranging them slightly:

$$\vec{\sigma}\cdot\left(\vec{p}-\frac{q}{c}\vec{A}\right)\psi_B = \left(-mc + i\hbar\,\partial_{ct} - \frac{q}{c}V\right)\psi_A \tag{1}$$

$$\vec{\sigma}\cdot\left(\vec{p}-\frac{q}{c}\vec{A}\right)\psi_A = \left(mc + i\hbar\,\partial_{ct} - \frac{q}{c}V\right)\psi_B \,. \tag{2}$$

It is convenient to keep separate the time and space components of $A^\nu = (V, \vec{A})$. With the time dependence of wave functions given by $e^{-iEt/\hbar}$, the operation $i\hbar\,\partial_{ct}$ returns E/c. Thus, eqns (1) and (2) become

$$c\vec{\sigma}\cdot\left(\vec{p}-\frac{q}{c}\vec{A}\right)\psi_B = \left(-mc^2 + E - qV\right)\psi_A \tag{3}$$

$$c\vec{\sigma}\cdot\left(\vec{p}-\frac{q}{c}\vec{A}\right)\psi_A = \left(mc^2 + E - qV\right)\psi_B \,. \tag{4}$$

It is understood that E is positive in the above expressions.

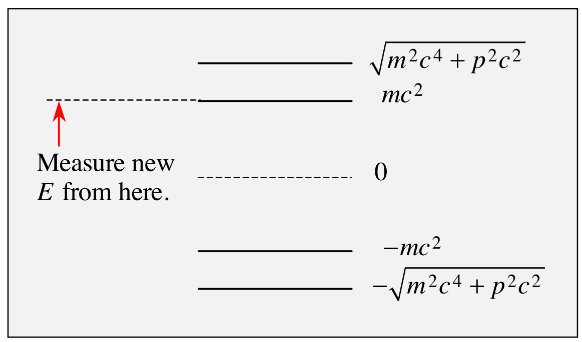
It is also understood that E is in modest excess of mc^2. Consequently, the coefficient of ψ_A in eqn (3) is much smaller than the coefficient of ψ_B in eqn (4). Referring to eqn (3), $E - mc^2$ differs from zero by an amount of order $mv^2/2$, which is small compared to the magnitude of the $c\vec{p}$ on the left hand side. This identifies ψ_A as the large component and ψ_B as the small component. A similar argument applies to eqn (4).

The small component is small indeed at energies appropriate to quantum chemistry. For E in modest excess of mc^2, and leaving aside V and $\vec{A}$, the magnitude of the right-hand side of eqn (4) is $\approx 2mc^2 |\psi_B|$, whereas the magnitude of the left hand side is $\approx pc|\psi_A|$. This yields the ratio $|\psi_B/\psi_A| \approx p/2mc$ (*i.e.*, $v/2c$). Hereafter ψ_A and ψ_B will be labeled ψ_L and ψ_S, respectively, where L and S stand for large and small.

Next, eliminating ψ_S from eqns (3) and (4) yields[14]

$$\vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A} \right) \frac{c^2}{\left(mc^2 + E - qV\right)} \vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A} \right) \psi_L = \left(-mc^2 + E - qV \right) \psi_L . \tag{5}$$

Keep in mind that ψ_L cannot be normalized such that the integral over all space of $\psi_L{}^\dagger \psi_L$ is unity because normalization must include the small component ψ_S. It is the 4-spinor that is normalized. In addition, the ψ_L's are not orthogonal to one another. The fact that solutions are sought for energies in modest excess of mc^2 makes it convenient to change the reference point for measuring energy (see sketch on right). The E in eqn (5) is therefore replaced with $mc^2 + E$. This new E is relative to mc^2 and it is much less than mc^2. Thus, eqn (5) becomes



$$\left(E - qV\right)\psi_L = \frac{1}{2m} \vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A} \right) \left(\frac{2mc^2}{2mc^2 + E - qV} \right) \vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A} \right) \psi_L . \tag{6}$$

The large parenthetic term is easily expanded:

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[14] Equation (4), with $\psi_A = \psi_L$ and $\psi_B = \psi_S$, is written

$$\psi_S = \left(mc^2 + E - qV\right)^{-1} c\vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A} \right) \psi_L ,$$

where $(mc^2 + E - qV)^{-1}$ denotes the inverse of $(mc^2 + E - qV)$. This ψ_S is now inserted into eqn (3) using

$$(mc^2 + E - qV)^{-1} = \frac{1}{mc^2 + E - qV} .$$

This yields eqn (5). This inverse is referred to as the resolvent. It is valid even when the denominator contains operators.

$$\frac{2mc^2}{2mc^2 + E - qV} = 1 - \frac{E - qV}{2mc^2} + \dots. \tag{7}$$

A free particle has $E \sim mv^2/2$, and it is assumed that $E/2mc^2$ is small. It is also assumed that $|qV| << 2mc^2$, though $|qV|$ can be large near a nucleus. For example, an electron that is $10^{-3}a_0$ from a carbon nucleus has a potential energy of ~ 6000 Hartrees[15] = $163\,\text{keV}$. At the other extreme, an electron this far from a uranium nucleus has potential energy of 2.5 MeV. And $10^{-3}a_0$ is not unreasonably small for an atom like uranium.

Pauli Limit

Before pushing onward with the large spinor component, let us take a break and recover the Pauli Hamiltonian given by eqn (2.12). This is achieved using the first term in the expansion in eqn (7) (*i.e.*, the 1). Equation (6) then yields

$$E\psi_L = \left(\frac{1}{2m}\left(\vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A} \right)\right)\left(\vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A} \right)\right) + qV \right)\psi_L. \tag{8}$$

The large parenthetic term is a Hamiltonian. As in Section 2, the identity $(\vec{\sigma}\cdot\vec{A}_1)(\vec{\sigma}\cdot\vec{A}_2)$ = $\vec{A}_1\cdot\vec{A}_2 + i\vec{\sigma}\cdot(\vec{A}_1\times\vec{A}_2)$, where $\vec{A}_1$ and $\vec{A}_2$ are arbitrary vector operators, enables this Hamiltonian to be written

$$\hat{H} = \frac{1}{2m}\left(\left(\vec{p} - \frac{q}{c}\vec{A} \right)^2 + i\vec{\sigma}\cdot\left(\vec{p} - \frac{q}{c}\vec{A} \right)\times\left(\vec{p} - \frac{q}{c}\vec{A} \right)\right) + qV. \tag{9}$$

The terms $\vec{p}\times\vec{p}$ and $\vec{A}\times\vec{A}$ vanish leaving

$$\hat{H} = \frac{1}{2m}\left(\left(\vec{p} - \frac{q}{c}\vec{A} \right)^2 - i\frac{q}{c}\vec{\sigma}\cdot\left(\vec{p}\times\vec{A} + \vec{A}\times\vec{p} \right)\right) + qV. \tag{10}$$

The second term inside the large parentheses is simplified by using $\vec{p} = -i\hbar\nabla$ and the identity $\nabla\times(\vec{A}\psi) = -\vec{A}\times(\nabla\psi) + (\nabla\times\vec{A})\psi$. Equation (10) becomes

$$\hat{H} = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A} \right)^2 - \frac{q\hbar}{2mc}\vec{\sigma}\cdot\left(\nabla\times\vec{A} \right) + qV. \tag{11}$$

The interaction of spin with the electromagnetic field (the Zeeman effect) is now explicit. Using $\vec{s} = \hbar\vec{\sigma}/2$ and $\nabla\times\vec{A} = \vec{B}$, eqn (11) becomes

[15] 1 Hartree = 27.211 eV.

$$\hat{H} = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2 - \frac{q}{mc}\vec{s}\cdot\vec{B} + qV \tag{12}$$

This result is, of course, the same as the one obtained earlier using Pauli's approach. It is a limiting case of the Dirac equation: the non-relativistic limit, not simply the low-energy limit. The correct g-factor of 2 for this level of theory is obtained. Corrections to this g-factor value are due to quantum electrodynamics (QED). Their inclusion increases g by about one part in 10^3. Precise measurements (using a Penning trap) and high-level QED calculations agree to a remarkable extent. The value recommended by NIST is: 2.0023193043622(15).

Equation (4) can be used to obtain the relative magnitudes of the large and small 2-spinors. Ignoring the fields $\vec{A}$ and V, being careful to replace E with its offset counterpart $E + mc^2$, and using $\psi_A = \psi_L$ and $\psi_B = \psi_S$, eqn (4) indicates that

$$|\psi_S| \approx \left|\frac{1}{2mc}\sigma\cdot\vec{p}\,\psi_L\right|. \tag{13}$$

This agrees with our earlier estimate: $|\psi_S / \psi_L| \sim v / 2c$.

Higher Order Terms

That ends the interlude. We now return to eqn (7) and take into account the next term in the expansion: $-(E - qV)/2mc^2$. This is tedious, so we will proceed patiently and discuss the terms after finishing the algebra. For relativistic quantum chemistry, there is no point including corrections of order higher than c^{-2}. We shall start by setting $\vec{A} = 0$, as this lessens the amount of algebra. Following this $\vec{A}$ will be introduced and its effect evaluated. The total amount of algebra is large (goes to page 307) and not enjoyable. It is the kind of thing you go through once and then move on. You might wish to jump ahead to see the result – motivation for wading through it. In any event, eqn (6) now reads

$$\frac{1}{2m}\vec{\sigma}\cdot\vec{p}\left(1 - \left(\frac{E - qV}{2mc^2}\right)\right)\vec{\sigma}\cdot\vec{p}\,\psi_L = (E - qV)\psi_L. \tag{14}$$

Despite the suppression of $\vec{A}$, this expression is still subtle. First, when $\vec{p}$ operates on qV, a non-Hermitian term proportional to $i\hbar\vec{E}\cdot\vec{p}$ arises.[16] Second, E appears on both

[16] To see how the non-Hermitian term comes about, start with

$$(\vec{\sigma}\cdot\vec{p})V(\vec{\sigma}\cdot\vec{p}) = -i\hbar(\vec{\sigma}\cdot\nabla V)(\vec{\sigma}\cdot\vec{p}) + V(\vec{\sigma}\cdot\vec{p})^2.$$

The part that gives the non-Hermitian term is

$$-i\hbar(\vec{\sigma}\cdot\nabla V)(\vec{\sigma}\cdot\vec{p}) = i\hbar(\vec{\sigma}\cdot\vec{E})(\vec{\sigma}\cdot\vec{p}).$$

The product of the parenthetic terms on the right hand side is $\vec{E}\cdot\vec{p} + i\vec{\sigma}\cdot\vec{E}\times\vec{p}$. The second of these ($i\vec{\sigma}\cdot\vec{E}\times\vec{p}$) is fine, but the first gives the non-Hermitian term: $i\hbar\vec{E}\cdot\vec{p}$.

sides of the equation, so eqn (14) is not in the form of an eigenvalue equation. Third, qV appears with no retardation to account for the time needed to transmit force via the field. Finally, ψ_L cannot itself be normalized. It is the large spinor component, but not the only spinor component. When ψ_L is altered through the inclusion of the next highest term in the expansion given by eqn (7), its relationship with the system's operators is changed. This results in the emergence of the non-Hermitian term mentioned above. Assuming that ψ_L and ψ_S start out as normalized components of the 4-spinor before the next term in the expansion is introduced, they need to be *renormalized* after the next term is introduced to ensure consistency in their relationships to the operators.

In the next few pages, manipulations are carried out that yield the Dirac Hamiltonian correct to order c^{-2}. Again, you will probably find this tedious, but give it a try. It is not the only way to achieve the desired result, but it is straightforward. Equation (13) gives the relationship between $|\psi_L|$ and $|\psi_S|$ to order c^{-2}, so the normalization condition

$$1 = \int d^3r \left(\psi_L{}^\dagger \psi_L + \psi_S{}^\dagger \psi_S \right), \tag{15}$$

can be expressed in terms of ψ_L. By using eqn (13) with $\vec{A} = 0$, eqn (15) becomes

$$1 = \int d^3r\, \psi_L{}^\dagger \left(1 + \frac{p^2}{4m^2c^2} \right) \psi_L . \tag{16}$$

To order c^{-2}, this can be written

$$1 = \int d^3r \underbrace{\left(\left(1 + \frac{p^2}{8m^2c^2} \right) \psi_L \right)^\dagger}_{\psi_L{}^\dagger \left(1 + \frac{p^2}{8m^2c^2} \right)} \underbrace{\left(1 + \frac{p^2}{8m^2c^2} \right)}_{\equiv \Omega} \psi_L . \tag{17a}$$

In other words,

$$1 = \int d^3r\, \Psi^\dagger \Psi . \tag{17b}$$

where $\Psi = \Omega \psi_L$.

The factor Ω enables normalization to be carried out in terms of the large component. Keep in mind that the above result is correct to order c^{-2}. Because $p^2 / 8m^2c^2$ is small, Ω^{-1} is given by $1 - p^2 / 8m^2c^2$. When only the first term in the expansion in eqn (7) (*i.e.*, the 1) was retained, there was no issue with normalization. We shall see that renormalization fixes the problems mentioned in the discussion that follows eqn (14), for example, the non-Hermitian term.

Next, the ψ_L in eqn (14) is replaced with $\Omega^{-1}\Psi$, and the equation is multiplied from the left by Ω^{-1}. The resulting expression is

$$E\,\Omega^{-2}\Psi \;=\left(q\Omega^{-1}V\Omega^{-1}+\Omega^{-1}\frac{1}{2m}\vec{\sigma}\cdot\vec{p}\left(1-\frac{E-qV}{2mc^2}\right)\vec{\sigma}\cdot\vec{p}\,\Omega^{-1}\right)\Psi \tag{18a}$$

$$=\left(qV-\left\{\frac{p^2}{8m^2c^2},qV\right\}\right)\Psi\;+\left(\;\Omega^{-1}\frac{1}{2m}\vec{\sigma}\cdot\vec{p}\left(1-\frac{E-qV}{2mc^2}\right)\vec{\sigma}\cdot\vec{p}\,\Omega^{-1}\right)\Psi\,. \tag{18b}$$

Going from (a) to (b), the higher order term $p^2Vp^2/(8m^2c^2)^2$ from $\Omega^{-1}V\Omega^{-1}$ is dropped, as it is proportional to c^{-4}. When the $\Omega^{-1} = (1-p^2/8m^2c^2)$ terms inside the large parentheses in (b) are written explicitly, we get eight terms. Only corrections of order c^{-2} are retained, so some of these are dropped. To see how this works, write the full expansion of the contents of the second large parentheses. Then throw out terms of higher order than c^{-2}.

$$\left(1-\frac{p^2}{8m^2c^2}\right)\vec{\sigma}\cdot\vec{p}\left(\frac{1}{2m}-\frac{E-qV}{4m^2c^2}\right)\vec{\sigma}\cdot\vec{p}\left(1-\frac{p^2}{8m^2c^2}\right)=$$

$$\frac{p^2}{2m}-\vec{\sigma}\cdot\vec{p}\left(\frac{E-qV}{4m^2c^2}\right)\vec{\sigma}\cdot\vec{p}-\frac{p^4}{8m^3c^2}+\left\{\vec{\sigma}\cdot\vec{p}\left(\frac{E-qV}{4m^2c^2}\right)\vec{\sigma}\cdot\vec{p},\frac{p^2}{8m^2c^2}\right\}$$

$$+\frac{p^2}{8m^3c^2}\vec{\sigma}\cdot\vec{p}\left(\frac{1}{2m}-\frac{E-qV}{4m^2c^2}\right)\vec{\sigma}\cdot\vec{p}\,\frac{p^2}{8m^3c^2}\,. \tag{19}$$

The anti-commutator on the second line, as well as the entire third line, each vary as c^{-4} or higher, so they are dropped. Consequently, eqn (18b) becomes

$$E\left(1-\frac{p^2}{4m^2c^2}\right)\Psi=\left(\hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}-\left\{\frac{p^2}{8m^2c^2},qV\right\}-\vec{\sigma}\cdot\vec{p}\left(\frac{E-qV}{4m^2c^2}\right)\vec{\sigma}\cdot\vec{p}\right)\Psi\,. \tag{20}$$

where $\hat{T}=p^2/2m$ and $\hat{V}=qV$ are used. Of course, there are a number of ways to work through the algebra. The one below is followed by a complementary approach in the box that follows.

Referring to eqn (20), a problematic term is $-Ep^2/4m^2c^2$ on the left hand side. However, when this is written: $-\{E,p^2\}/8m^2c^2$, and moved to the right hand side, simplification emerges. Combining it with the anti-commutator in eqn (20) gives

$$\frac{1}{8m^2c^2}\left(\{E,p^2\}-\{p^2,qV\}\right)\;=\;\frac{1}{8m^2c^2}\left\{p^2,(E-qV)\right\}, \tag{21}$$

and eqn (20) becomes

$$E\,\Psi = \left(\hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}+\frac{1}{8m^2c^2}\left(\left\{(\vec{\sigma}\cdot\vec{p})^2,(E-qV)\right\}-2\vec{\sigma}\cdot\vec{p}\,(E-qV)\,\vec{\sigma}\cdot\vec{p}\right)\right)\Psi \qquad (22)$$

where $p^2=(\vec{\sigma}\cdot\vec{p})^2$ has been used. The identity

$$\left\{A^2,B\right\} = 2ABA+\left[A,\left[A,B\right]\right] \qquad (23)$$

yields

$$E\,\Psi = \left(\hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}+\frac{1}{8m^2c^2}\underbrace{\left[(\vec{\sigma}\cdot\vec{p}),\underbrace{\left[(\vec{\sigma}\cdot\vec{p}),(E-qV)\right]}_{-iq\hbar\vec{\sigma}\cdot\vec{E}\ \text{(see earlier footnote)}}\right]}\right)\Psi \qquad (24)$$

$$-i\hbar q\Big[\underbrace{(\vec{\sigma}\cdot\vec{p}),(\vec{\sigma}\cdot\vec{E})}\Big]$$

$$\underbrace{\vec{p}\cdot\vec{E}-\vec{E}\cdot\vec{p}}_{-i\hbar(\nabla\cdot\vec{E})}+\underbrace{i\vec{\sigma}\cdot\left(\vec{p}\times\vec{E}-\vec{E}\times\vec{p}\right)}_{-2i\vec{\sigma}\cdot\vec{E}\times\vec{p}}$$

The fact that $\nabla\times\vec{E}$ varies as c^{-1} (*i.e.*, $\nabla\times\vec{E}=-\partial_{ct}\vec{B}$) results in this term being dropped as it would yield a c^{-3} contribution.

It was stated earlier that the algebra would be tedious, which has proven to be the case, and then some. The approach in the box on the next page is also tedious and I am not sure if one approach is better than the other. Regardless, rounding up terms yields the expression for the ($\vec{A}=0$) Dirac Hamiltonian to order c^{-2}:

$$\hat{H}=\hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}-\frac{q\hbar}{4m^2c^2}\vec{\sigma}\cdot\left(\vec{E}\times\vec{p}\right)-\frac{q\hbar^2}{8m^2c^2}\nabla\cdot\vec{E}\,. \qquad (25)$$

The fourth term on the right hand side of eqn (25) (see also eqn (20f) in the shaded box on the next page) is called the Thomas term. For a central potential, $\vec{E}$ is equal to $-\hat{r}\partial_r V$, where $\hat{r}$ is a unit vector, so $\vec{E}\times\vec{p}$ becomes $-(\partial_r V/r)(\vec{r}\times\vec{p}) = -(\partial_r V/r)\vec{l}$. This identifies the fourth term as spin-orbit interaction. With spin-orbit interaction now explicit, we have (for a central potential)

$$\hat{H}=\hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}+\frac{q(\partial_r V/r)}{2m^2c^2}\vec{s}\cdot\vec{l}-\frac{q\hbar^2}{8m^2c^2}\nabla\cdot\vec{E}\,. \qquad (26)$$

Alternate Derivation

Rewriting eqn (20), and highlighting cancellation of two terms with strike-throughs,

$$E\left(1-\frac{p^2}{4m^2c^2}\right)\Psi$$

$$=\left(\hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}-\frac{1}{8m^2c^2}\left(\left\{p^2,\hat{V}\right\}+2\vec{\sigma}\cdot\vec{p}\left(E-\hat{V}\right)\vec{\sigma}\cdot\vec{p}\right)\right)\Psi \tag{20a}$$

gives

$$E\Psi = \left(\hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}-\frac{1}{8m^2c^2}\left(\underline{p^2\hat{V}+\hat{V}p^2-2(\vec{\sigma}\cdot\vec{p})\hat{V}(\vec{\sigma}\cdot\vec{p})}\right)\right)\Psi . \tag{20b}$$

The algebraic part that needs attention is underlined in red. Keep in mind that this operates on Ψ. Expanding the terms that need it yields

$$p^2\hat{V}=\vec{p}\cdot\left(\vec{p}\hat{V}+\hat{V}\vec{p}\right) = \vec{p}\cdot(\vec{p}\hat{V})+2\vec{p}\hat{V}\cdot\vec{p}+\hat{V}p^2 \tag{20c}$$

$$(\vec{\sigma}\cdot\vec{p})\hat{V}(\vec{\sigma}\cdot\vec{p}) = \left(\vec{\sigma}\cdot(\vec{p}\hat{V})\right)(\vec{\sigma}\cdot\vec{p})+\hat{V}p^2 \tag{20d}$$

$$= (\vec{p}\hat{V})\cdot\vec{p}+i\vec{\sigma}\cdot\left((\vec{p}\hat{V})\times\vec{p}\right)+\hat{V}p^2 . \tag{20e}$$

Introducing these results into the red underlined term in eqn (20b) yields

$$\underbrace{\vec{p}\cdot(\vec{p}\hat{V})}_{q\hbar^2\nabla\cdot\vec{E}}+2(\vec{p}\hat{V})\cdot\vec{p}+2\hat{V}p^2-2(\vec{p}\hat{V})\cdot\vec{p}-\underbrace{2i\vec{\sigma}\cdot(\vec{p}\hat{V})\times\vec{p}}_{2q\hbar\vec{\sigma}\cdot\vec{E}\times\vec{p}}-2\hat{V}p^2 \tag{20f}$$

Thus, the Hamiltonian in eqn (20b) becomes eqn (25):

$$\hat{H} = \hat{T}+\hat{V}-\frac{p^4}{8m^3c^2}-\frac{q\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{E}\times\vec{p}-\frac{q\hbar^2}{8m^2c^2}\nabla\cdot\vec{E} . \tag{25}$$

Including the Vector Potential

Terms in the Dirac Hamiltonian to order c^{-2} that arise through $\vec{A}$ are now introduced. They were omitted earlier, while retaining terms due to qV, to lessen the algebra. Their introduction is carried out as follows: return to eqn (14), substitute $\vec{\sigma}\cdot\vec{p}\to\vec{\sigma}\cdot\vec{\pi}$ (where $\vec{\pi}=\vec{p}-(q/c)\vec{A}$), and retain terms to order c^{-2}. To emphasize connections to the $\vec{A}=0$ derivation, equations that follow from earlier counterparts are indicated using primes. For example, when eqn (14) is altered by the substitution $\vec{\sigma}\cdot\vec{p}\to\vec{\sigma}\cdot\vec{\pi}$, it becomes

$$\frac{1}{2m}\vec{\sigma}\cdot\vec{\pi}\left(1-\left(\frac{E-qV}{2mc^2}\right)\right)\vec{\sigma}\cdot\vec{\pi}\,\psi_L=\left(E-qV\right)\psi_L . \tag{14'}$$

The substitution $\vec{\sigma}\cdot\vec{p}\rightarrow\vec{\sigma}\cdot\vec{\pi}$ applies *mutatis mutandis* to all of the equations and accompanying discussions from eqn (14) to eqn (20). In places where $(\vec{\sigma}\cdot\vec{p})^2 = p^2$ was used, we now replace p^2 with $(\vec{\sigma}\cdot\vec{\pi})^2$. With these changes, eqn (20) reads

$$E\left(1-\frac{(\vec{\sigma}\cdot\vec{\pi})^2}{4m^2c^2}\right)\Psi = \left(\frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2m}+qV-\frac{(\vec{\sigma}\cdot\vec{\pi})^4}{8m^3c^2}-\left\{\frac{(\vec{\sigma}\cdot\vec{\pi})^2}{8m^2c^2},qV\right\}-\vec{\sigma}\cdot\vec{\pi}\left(\frac{E-qV}{4m^2c^2}\right)\vec{\sigma}\cdot\vec{\pi}\right)\Psi \tag{20'}$$

Now transfer $-E(\vec{\sigma}\cdot\vec{\pi})^2/4m^2c^2$ from the left hand side to the right hand side. Expressing it as the anti-commutator $(1/8m^2c^2)\{E,(\vec{\sigma}\cdot\vec{\pi})^2\}$ facilitates its inclusion in the right hand side, yielding the following expression for the Hamiltonian:

$$\hat{H} = \frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2m}+qV-\frac{(\vec{\sigma}\cdot\vec{\pi})^4}{8m^3c^2}+\frac{1}{8m^2c^2}\left(\left\{(\vec{\sigma}\cdot\pi)^2,(E-qV)\right\}-2\vec{\sigma}\cdot\vec{\pi}(E-qV)\vec{\sigma}\cdot\vec{\pi}\right). \tag{22'}$$

This is eqn (22) with $\vec{\sigma}\cdot\vec{p}$ replaced by $\vec{\sigma}\cdot\vec{\pi}$, and using $p^2=(\vec{\sigma}\cdot\vec{p})^2$ where appropriate. Let us go through eqn (22') term-by-term starting at the left. The numerator of the first term is expanded using the (by now) familiar relation:

$$(\sigma\cdot\vec{\pi})(\sigma\cdot\vec{\pi}) = \pi^2+i\sigma\cdot\left(\vec{p}-\frac{q}{c}\vec{A}\right)\times\left(\vec{p}-\frac{q}{c}\vec{A}\right). \tag{22'a}$$

The terms $\vec{p}\times\vec{p}$ and $\vec{A}\times\vec{A}$ vanish leaving

$$(\vec{\sigma}\cdot\vec{\pi})(\vec{\sigma}\cdot\vec{\pi}) = \pi^2-\frac{iq}{c}\vec{\sigma}\cdot\big(\underbrace{\vec{p}\times\vec{A}}_{-\vec{A}\cancel{\times}\vec{p}+(\vec{p}\times\vec{A})}+\vec{A}\cancel{\times}\vec{p}\big) \tag{22'b}$$

$$= \pi^2-\frac{q\hbar}{c}\vec{\sigma}\cdot(\nabla\times\vec{A}) \tag{22'c}$$

$$= \pi^2-\frac{2q}{c}\vec{s}\cdot\vec{B} \;\Rightarrow\; \frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2m}=\frac{\pi^2}{2m}-\frac{q}{mc}\vec{s}\cdot\vec{B}. \tag{22'd}$$

Next, the numerator of the third term in eqn (22') is

$$(\vec{\sigma}\cdot\vec{\pi})^2(\vec{\sigma}\cdot\vec{\pi})^2 = \left(\pi^2-\frac{2q}{c}\vec{s}\cdot\vec{B}\right)\left(\pi^2-\frac{2q}{c}\vec{s}\cdot\vec{B}\right) \tag{22'e}$$

$$= \pi^4-\frac{2q}{c}(\vec{s}\cdot\vec{B})\pi^2-\frac{2q}{c}\pi^2(\vec{s}\cdot\vec{B})+\frac{4q^2}{c^2}(\vec{s}\cdot\vec{B})^2. \tag{22'f}$$

All of the terms other than π^4, when divided by $8m^3c^2$, yield terms of order c^{-3} and higher, so they are dropped, leaving just the π^4 contribution: $\pi^4/8m^3c^2$. The field contributions ($q\vec{A}/c$) to π^4 do not meet the c^{-2} criterion, so π^4 is replaced by p^4. The last term in eqn (22') needs more attention. From its counterpart in eqn (24) we have

$$\underbrace{\frac{1}{8m^2c^2}\left[(\vec{\sigma}\cdot\vec{p}),\left[(\vec{\sigma}\cdot\vec{p}),(E-qV)\right]\right]}_{\text{from eqn (24)}} \rightarrow \frac{1}{8m^2c^2}\left[(\vec{\sigma}\cdot\vec{\pi}),\left[(\vec{\sigma}\cdot\vec{\pi}),(E-qV)\right]\right] \qquad \text{(24')}$$

Considering the rightmost commutator, the E term vanishes, leaving

$$-q\left[(\vec{\sigma}\cdot\vec{\pi}),V\right] = -q\left(\vec{\sigma}\cdot(\vec{p}V)+\cancel{V\vec{\sigma}\cdot\vec{p}}-\cancel{V\vec{\sigma}\cdot\vec{p}}\right) \qquad \text{(24'a)}$$

$$= i\hbar q\,\vec{\sigma}\cdot\nabla V \qquad \text{(24'b)}$$

$$= -i\hbar q\,\vec{\sigma}\cdot\vec{E}\,. \qquad \text{(24'c)}$$

Thus, the right hand side of eqn (24') becomes

$$\frac{-i\hbar q}{8m^2c^2}\left[(\vec{\sigma}\cdot\vec{\pi}),(\vec{\sigma}\cdot\vec{E})\right] = \frac{-i\hbar q}{8m^2c^2}\left(\vec{\pi}\cdot\vec{E}-\vec{E}\cdot\vec{\pi}+i\vec{\sigma}\cdot\vec{\pi}\times\vec{E}-i\vec{\sigma}\cdot\vec{E}\times\vec{\pi}\right) \qquad \text{(24'd)}$$

Again, $q\vec{A}/c$ does not pass the c^{-2} criterion. Thus, $\vec{\pi}\cdot\vec{E}-\vec{E}\cdot\vec{\pi}$ yields $-i\hbar\nabla\cdot\vec{E}$, which recovers $-(\hbar^2 q/8m^2c^2)\nabla\cdot\vec{E}$ in eqn (25). Likewise, $\vec{\pi}\times\vec{E}-\vec{E}\times\vec{\pi}$ yields $-2\vec{E}\times\vec{p}$.[17]

For a central potential, the $-2\vec{E}\times\vec{p}$ contribution to eqn (24'd) is:[18]

$$\frac{-i\hbar q}{8m^2c^2}i\vec{\sigma}\cdot\left(-2\vec{E}\times\vec{p}\right) = \frac{-q}{2m^2c^2}\frac{\hbar}{2}\vec{\sigma}\cdot\left(\underbrace{\vec{E}\times\vec{p}}_{-\frac{\partial_r V}{r}\vec{r}}\right) \qquad \text{(24'e)}$$

$$= \frac{q}{2m^2c^2}\frac{\partial_r V}{r}\vec{s}\cdot\vec{l} \qquad \text{(24'f)}$$

Combining the above pieces yields the Dirac Hamiltonian (to order c^{-2}) used with Ψ:

$$\hat{H} = \frac{\pi^2}{2m}+qV-\frac{p^4}{8m^3c^2}-\frac{q}{mc}\vec{s}\cdot\vec{B}\underbrace{-\frac{q\hbar}{4m^2c^2}\left(\vec{\sigma}\cdot\vec{E}\times\vec{p}+\frac{\hbar}{2}\nabla\cdot\vec{E}\right)}_{\frac{q}{2m^2c^2}\frac{\partial_r V}{r}\vec{s}\cdot\vec{l}-\frac{q\hbar^2}{8m^2c^2}\nabla\cdot\vec{E}}. \qquad \text{(27)}$$

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[17] Note: $(\nabla\times\vec{E}\psi)_3=(\partial_1E_2)\psi+E_2\partial_1\psi-(\partial_2E_1)\psi-E_1\partial_2\psi=(\nabla\times\vec{E})_3\psi-(\vec{E}\times\nabla)_3\psi$. In this case, $\nabla\times\vec{E}\psi = (\nabla\times\vec{E})\psi-\vec{E}\times\nabla\psi$. Therefore: $\vec{\pi}\times\vec{E}\rightarrow-\vec{E}\times\vec{p}-i\hbar(\nabla\times\vec{E})$. The curl term is dropped because it varies as c^{-1}, *i.e.*, $\nabla\times\vec{E}=-\partial_{ct}\vec{B}$.

[18] Had $\vec{A}$ been retained, it would have resulted in a term $(2q/c)\vec{E}\times\vec{A}$. This is proportional to the electromagnetic spin density that yields photon spin when the field is quantized.

When π^2 is expanded it gives

$$\pi^2 = p^2 - \frac{q}{c}\underbrace{\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right)}_{\vec{A}\cdot\vec{p} - i\hbar \underbrace{\nabla\cdot\vec{A}}_{\nabla\cdot\vec{A}=0 \text{ (Coulomb gauge)}}} + \frac{q^2}{c^2}A^2 . \tag{28}$$

Including the above, eqn (27) becomes

Dirac Hamiltonian (order c^{-2}) for particle interacting with fields‡

$$\hat{H} = \overbrace{\frac{p^2}{2m} + qV}^{\text{obvious}} - \overbrace{\frac{q}{mc}\vec{A}\cdot\vec{p}}^{\text{useful for spectroscopic transitions}} + \overbrace{\frac{q^2}{2mc^2}A^2}^{\text{usually ignored}} - \overbrace{\frac{p^4}{8m^3c^2}}^{\text{energy-momentum correction}}$$

$$\underbrace{-\frac{q}{mc}\vec{s}\cdot\vec{B}}_{\text{Zeeman}} - \underbrace{\frac{q\hbar^2}{8m^2c^2}\nabla\cdot\vec{E}}_{\text{Darwin}} + \underbrace{\frac{q}{2m^2c^2}\frac{\partial_r V}{r}\vec{s}\cdot\vec{l}}_{\text{spin-orbit}} \tag{29}$$

‡ Energy relative to mc^2, Coulomb gauge, central potential

Interpretation

The first two terms on the right hand side of eqn (29) need no explanation. The $\vec{A}\cdot\vec{p}$ term is the basis of much of the spectroscopy you are likely to encounter. It is often expressed as $\vec{\mu}\cdot\vec{E}$, as discussed in the chapter on photons. The A^2 term does not enter relativistic quantum chemistry. The term $p^4/8m^3c^2$ is obtained from the expansion: $(m^2c^4 + p^2c^2)^{1/2} = mc^2 + p^2/2m - p^4/8m^3c^2$ ... It is not a correction to the kinetic energy, but a term that arises through the relativistic energy-momentum relation. The $\vec{s}\cdot\vec{B}$ term is the Zeeman contribution that we found in the non-relativistic Pauli theory. The last term is spin-orbit interaction. The Zeeman and spin-orbit terms have the correct g factor value of 2.

The Darwin term is the hardest to interpret. Many texts present it *fait accompli* and say nothing about it, while some assign it to Zitterbewegung (German for jittery motion) without elaborating. Nowadays it is appreciated that Zitterbewegung is a peculiarity of the single particle picture that does not exist in the field theory description. This is another example of the challenges faced in interpreting relativistic quantum mechanics. Taking a cue from the next example, we interpret the Darwin term as also due to an effect from field theory. Namely, the creation and annihilation of e^-/e^+ pairs is viewed from the fixed particle perspective. This is revisted in Example 5.6.

Example 5.4. The Darwin Term and Zitterbewegung

The Darwin term is the least well understood of the terms in eqn (29) of Example 5.3, despite the certainty of its mathematical form and the straightforwardness of its derivation. Quoting from Bjorken and Drell: *Relativistic Quantum Mechanics* (note that they use $c = \hbar = 1$): "The last term – known as the Darwin term – may be attributed to the zitterbewegung. Because the electron coordinate fluctuates over distances $\delta r \sim 1/m$, it sees a somewhat smeared out Coulomb potential; the correction is

$$\langle \delta V \rangle = \langle V(\boldsymbol{r}+\delta\boldsymbol{r})\rangle - \langle V(\boldsymbol{r})\rangle = \left\langle \delta r \frac{\partial V}{\partial r} + \frac{1}{2}\sum_{i,j} \delta r_i \, \delta r_j \frac{\partial^2 V}{\partial r_i \partial r_j} \right\rangle = \sim \frac{1}{6}\delta r^2 \nabla^2 V \sim \frac{1}{6m^2}\nabla^2 V$$

in qualitative accord with the sign, form, and magnitude of the Darwin term." A few pages earlier these authors stated: "We have as yet no physical interpretation of these (*zitterbewegung*) solutions, but we may ask when to expect them to be added to the packet with appreciable amplitude." There are many other examples of the relationship between the Darwin term and Zitterbewegung (ZB). A sampling is given below.

Moss: "… the so-called Darwin term which is peculiar to relativistic quantum mechanics and has no classical analogue…. Except for the Darwin term all the terms in the non-relativistic approximation to the Dirac Hamiltonian can now be understood, since they can be related to electron spin or have classical relativistic counterparts. However, the Darwin term may be understood in terms of the Zitterbewegung, since it is just a correction to the electrostatic interaction between the electron and the electric potential to allow for the smearing out of the electron's charge by the Zitterbewegung."

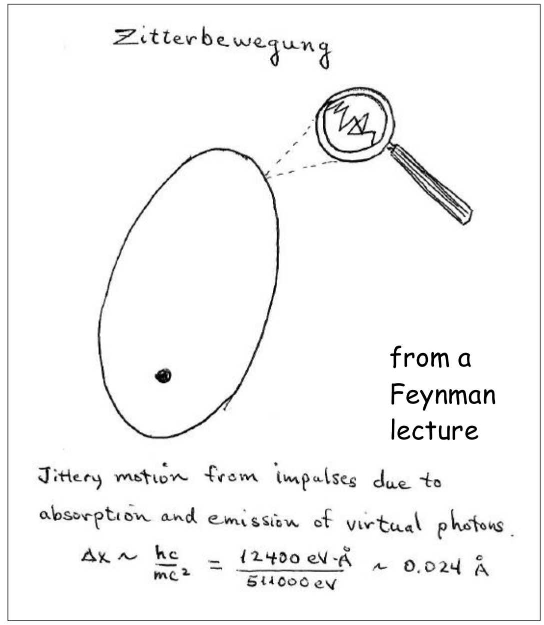
Baym: "There exists a simple explanation of the Darwin term in terms of the zitterbewegung of the electron. Really, one argues, a relativistic particle is spread out over a distance $\sim \hbar/mc$, and in fact, it samples, at any time, the potential averaged over a region $\sim \hbar/mc$ about its position. Thus the potential term $e\Phi(r)$ in the Schrödinger equation is effectively replaced by $\overline{e\Phi(\boldsymbol{r}+\delta\boldsymbol{r})}$, where one averages over values of $\delta r \sim \hbar/mc$ about $\boldsymbol{r}$. Expanding one has

$$e\Phi(\boldsymbol{r}+\delta\boldsymbol{r}) \approx e\Phi(\boldsymbol{r}) + \delta\boldsymbol{r}\cdot\nabla e\Phi(\boldsymbol{r}) + \tfrac{1}{2}\left(\delta\boldsymbol{r}\cdot\nabla\right)^2 e\Phi(\boldsymbol{r})$$

and if one averages over $\delta\boldsymbol{r}$, and assumes spherically symmetric deviations, then

$$\overline{e\Phi(\boldsymbol{r}+\delta\boldsymbol{r})} \approx e\Phi(\boldsymbol{r}) + \tfrac{1}{6}\overline{(\delta\boldsymbol{r})^2}\,\nabla^2 e\Phi(\boldsymbol{r})$$

If we write $\overline{(\delta\boldsymbol{r})^2} \approx (\hbar/mc)^2$ we find a correction term to $e\Phi$ of exactly the same form, order of magnitude, and sign as the Darwin term. The disquieting feature of this argument, however, is that the Darwin term is *absent* to this order in the spin zero case even though a spin zero particle is equally spread out. The form of the Darwin term depends critically on the spin of the particle, and a satisfactory physical explanation would have to take this into account."



Sakurai: "An immediate consequence of this is that the electron in the hydrogen atom exhibits Zitterbewegung. … Apart from a numerical factor (1/6 instead of 1/8), this is just the effective potential needed to explain the Darwin term discussed earlier in connection with the approximate treatment of the hydrogen atom." "It is very important to note that the peculiar oscillatory behavior, *Zitterbewegung*, of both $\langle \alpha_k \rangle$ and $\langle x_k \rangle$ is due solely to an interference between the positive- and negative-energy components of the wave packet. The *Zitterbewegung* is completely absent for a wave packet made up exclusively of positive- (negative-) energy plane-wave solutions."

Schwabl: "The second term contains oscillations at frequencies greater than $2mc^2/\hbar = 2 \times 10^{21}$ s^{-1}." "The Zitterbewegung stems from the interference between components with positive and negative energy."

Itzykson and Zuber: "Finally the last term in Eq. (2.82), referred to as the Darwin term $-(e/8m^2)\mathrm{div}\,\mathbf{E}$, may be traced to the zitterbewegung." … "Besides the group velocity term, there is a real, oscillating term. The frequency of these oscillations is very high, larger than $2mc^2/\hbar \approx 2 \times 10^{21}$ s^{-1}. This phenomenon, traditionally called zitterbewegung, is an example of the difficulties due to the negative energy states in the framework of a one-particle theory."

Dyall and Faegri: "The second relativistic term in the Pauli Hamiltonian is called the *Darwin* operator, and has no classical analogue."

Reiher and Wolf: "The oscillatory behavior is called zitterbewegung and is solely due to the interference of positive and negative-energy solutions."

Holstein: "Except for the factor of 1/6 rather than 1/8 this is clearly the additional term under discussion. Because of this identification, the Darwin or zitterbewegung term has no classical analogy."

Derivation

Expressions relevant to ZB are derived. Goals are to reveal its origin, determine its oscillation frequency and amplitude, and establish its relevance to the Darwin term. With a Dirac spinor, it is not feasible to create wave packets that enable easy visualization, as in Schrödinger quantum mechanics. Consequently, the Heisenberg picture, in which the state vectors are time-independent, whereas the operators are time-dependent, is used. The Schrödinger position operator $\vec{r}$ becomes $\vec{r}(t)$ by virtue of the unitary transformation that enables operators to be expressed in one or the other representation:

$$\vec{r}(t)_{\text{Heisenberg}} = e^{iHt/\hbar}(\vec{r}_{\text{Schrödinger}})e^{-iHt/\hbar}. \tag{1}$$

The Heisenberg equation of motion provides the expression for $\dot{\vec{r}}(t)$. We should probably refer to "a" velocity operator rather than "the" velocity operator, as discussed later in Example 5.5. To begin, consider the Heisenberg equation of motion:

$$\dot{\vec{r}}(t) = \frac{i}{\hbar}\left[\hat{H}, \vec{r}(t)\right], \tag{2}$$

where $\hat{H} = c\vec{\alpha}\cdot\vec{p} + \beta mc^2$. The βmc^2 term vanishes, leaving

$$\dot{\vec{r}}(t) = \frac{ic}{\hbar}\Big((\vec{\alpha}\cdot\vec{p})\vec{r} + \vec{r}\left(\vec{\alpha}\cdot\vec{p}\right) - \vec{r}\left(\vec{\alpha}\cdot\vec{p}\right)\Big) \tag{3}$$

$$= \frac{ic}{\hbar}\sum_i \alpha_i p_i \, \vec{r}(t). \tag{4a}$$

$$= c\sum_j \alpha^j \partial_j \left(x^i \hat{e}_i\right) \tag{4b}$$

Thus,

$$\boxed{\dot{\vec{r}}(t) = c\vec{\alpha}(t).} \tag{5}$$

It is interesting that $\dot{\vec{r}}(t) = c\vec{\alpha}(t)$ does not commute with $\hat{H}$ whereas $\vec{p}$ does. Because the eigenvalues of the α_i matrices are ± 1, components $c\alpha_i(t)$ have eigenvalues $\pm c$. Does this mean that the speed is $3^{1/2}c$? Also, we know that $\vec{\alpha}$ is built from Pauli matrices and now it represents velocity. Despite such curiosities, let us continue with the math. To obtain an expression for $\vec{r}(t)$, start with the Heisenberg equation of motion for $\vec{\alpha}(t)$. Integration yields $\vec{\alpha}(t) = \dot{\vec{r}}(t)$, and integration of the equation for $\dot{\vec{r}}(t)$ yields $\vec{r}(t)$.

To begin, the Heisenberg equation of motion for $\vec{\alpha}(t)$ is

$$\dot{\vec{\alpha}}(t) \;=\; \frac{i}{\hbar}\left[\hat{H},\vec{\alpha}(t)\right], \tag{6}$$

which is expressed as[19]

$$\dot{\vec{\alpha}}(t) \;=\; \frac{2i}{\hbar}\left(c\vec{p}-\vec{\alpha}(t)\hat{H}\right). \tag{7}$$

Because $\vec{p}$ and $\hat{H}$ are time independent, this is easily integrated. The order in which $\vec{\alpha}(t)$ and $\hat{H}$ are written is important, as they do not commute. The result is

$$\vec{\alpha}(t) \;=\; c\vec{p}\,\hat{H}^{-1} + \left(\vec{\alpha}(0)-c\vec{p}\hat{H}^{-1}\right)e^{-i2\hat{H}t/\hbar}, \tag{8}$$

This is verified by substituting this expression for $\vec{\alpha}(t)$ into eqn (7), and comparing the result to the $\dot{\vec{\alpha}}(t)$ obtained by differentiation of eqn (8). As stated earlier, integration of $c\vec{\alpha}(t)$ yields $\vec{r}(t)$:

$$\vec{r}(t) = \vec{\mathrm{A}} + c^2\vec{p}\,\hat{H}^{-1}t + \left(\vec{\alpha}(0)-c\vec{p}\hat{H}^{-1}\right)\frac{i\hbar c}{2}\hat{H}^{-1}e^{-i2\hat{H}t/\hbar}. \tag{7}$$

integration constant (for $\vec{\mathrm{A}}$); amplitude (for the last term)

$$\frac{c^2\vec{p}}{\gamma mc^2} = \frac{c^2\gamma m\vec{v}}{\gamma mc^2} = \vec{v}$$

To estimate the amplitude, we shall assume that v/c is small. Because $|c\vec{p}\,\hat{H}^{-1}|$ = $c\gamma mv/\gamma mc^2$ = v/c, the second term in the large parentheses will be ignored. The magnitude of the amplitude in eqn (7) is then approximately

$$|\vec{\alpha}(0)|\frac{\hbar c}{2}\frac{1}{mc^2} = \frac{\hbar}{2mc},$$

which is half the Compton radius. The second term is equal to $\vec{v}t$. It is the group velocity times time, as expected from correspondence with classical physics.

The picture is one of a group velocity $\vec{v}$ upon which is superimposed a high frequency oscillation. In eqn (7), this oscillation appears in a phase factor. When the expectation value $\langle\vec{r}(t)\rangle$ is calculated for a spinor wave packet, it is found that real sinusoidal oscillation occurs when positive and negative energy spinors are each included in the packet. For the energy regime of interest, the Hamiltonian in $e^{-i2\hat{H}t/\hbar}$ can be taken as the rest energy mc^2, in which case the value of the radian frequency $2\hat{H}/\hbar$ is $2mc^2/\hbar$ = 1.55×10^{21}. Another important quantity is the lifetime of a virtual electron-positron pair.

[19] Write $[\hat{H},\vec{\alpha}] = \hat{H}\vec{\alpha}+\vec{\alpha}\hat{H}-2\vec{\alpha}\hat{H}$, and use $\{\hat{H},\vec{\alpha}\} = \{c\vec{\alpha}\cdot\vec{p}+\beta mc^2,\vec{\alpha}\} = c\{\vec{\alpha}\cdot\vec{p},\vec{\alpha}\}$ because $\{\beta,\vec{\alpha}\}=0$. Then $c\{\vec{\alpha}\cdot\vec{p},\vec{\alpha}\} = c\{\alpha_1p_1+\alpha_2p_2+\alpha_3p_3,\alpha_1\hat{e}_1+\alpha_2\hat{e}_2+\alpha_3\hat{e}_3\}$ gives $2c\vec{p}$.

The relation $\delta E\,\delta t \sim \hbar$ indicates that an uncertainty δE of $2mc^2$ can only be tolerated for a very short time: $\delta t \sim \hbar / 2mc^2 = 6.4\times10^{-22}$ s. Note that this is the inverse of the ZB radian frequency. Some useful numbers are listed in Table 1.

Table 1

Compton radius (Compton wavelength / 2π)	$\hbar / mc$	3.86×10^{-3} Å
ZB oscillation amplitude	$\hbar / 2mc$	1.93×10^{-3} Å
ZB radian frequency	$2mc^2 / \hbar$	1.55×10^{21} s^{-1}
Lifetime of virtual e^- / e^+ pair	$\delta t \sim \hbar / 2mc^2$	6.4×10^{-22} s
Electron rest energy	mc^2	0.511 MeV

When expectation values $\langle\vec{\alpha}(t)\rangle$ and $\langle\vec{r}(t)\rangle$ are calculated for plane waves, it is found that ZB does not exist unless there are both positive and negative energy parts to the wave packet. The positive energy part is a given, and ZB occurs when, for whatever reason, a negative energy part enters. Trying to understand ZB in the context of the Darwin term has led to confusion. Some thoughts are given below.

- Suppose an electron wave packet consists of positive and negative energy waves. How they got there is another matter, but for now assume they are present. Furthermore, assume motion includes Zitterbewegung, *i.e.*, $\langle\vec{r}(t)\rangle$ undergoes standard group velocity motion, but in addition there is a superimposed sinusoidal oscillation with radian frequency 1.55×10^{21} and amplitude of ~ 0.002 Å. A packet narrowly confined in space (say ~ $\hbar / mc$) contains a large momentum spread, so negative energy contributions are inevitable. For $\vec{p} >> mc$, positive and negative energy contribute about equally.
- Were an electron to oscillate at $\omega = 1.55\times10^{21}$, it would radiate at an enormous rate. Lyman-α, whose radian frequency is 1.5×10^{16}, has a radiative lifetime of ~ 1 ns. Classically, the photon emission rate from an oscillating dipole varies as ω^3, so the rate of photon emission for $\omega = 1.55\times10^{21}$ can be expected to exceed that of Lyman-α by ~ 10^{15}. An interesting point is how a particle can undergo oscillation when there is no force. If e^+e^- pairs are created and annihilated at this rate, with forces passed on to the electron in the form of jitter, the electron needs to experience a strong potential.
- It has been suggested, as a means of rationalizing the $c\alpha_i$ eigenvalues of ± c calculated using the Heisenberg equation of motion, that the speed of an electron undergoing Zitterbewegung is close to c. Such arguments are unconvincing. Likewise, arguments about velocity components not commuting among themselves are also unconvincing. A down-to-earth interpretation of $c\vec{\alpha}$ is needed.
- The issue of positive and negative energies is confusing. It is known that when a high-energy electron encounters a scattering potential, an e^+e^- pair can be produced. Alternatively, a virtual pair can be produced below the $2mc^2$ threshold for the stable pair. Such processes are best dealt with using relativistic quantum field theory (RQFT). It handles particles and their antiparticles without the ambiguities encountered when trying to get by with quantum mechanics, where pair production is implicit. With plane waves, the argument of the exponential is $(i/\hbar)(Et + \vec{p}\cdot\vec{r})$. It is noted that negative

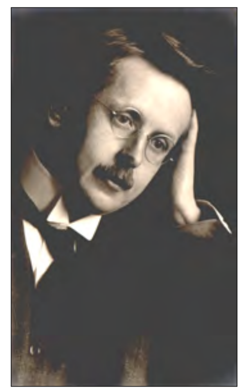
energies are needed to get wave packets to go to zero well away from the peak, and to compress them to distances less than $\hbar / mc$. The negative energy parts reflect the correct physics as much as possible within the confines of a single-particle theory.

- RQFT handles electron-positron pair production without ambiguity. Field operators create and annihilate field quanta that obey equations of motion. In the present case, the quanta are electrons and positrons and the equation of motion is the Dirac equation, albeit with the electromagnetic field treated classically. RQFT is appropriate for small systems and high energy. However, its implementation in relativistic quantum chemistry would prove untenable. So where does this leave ZB?

  The Dirac equation requires careful interpretation. Recall the case of phonons, where positive and negative oscillation frequencies have nothing to do with the energy. The latter is given by the number of quanta in a mode, summed over all modes. Likewise, in the present case, positive and negative energy parts of a wave packet might signify indirectly the participation of virtual pair production. The packet nonetheless describes an electron, not a composite electron/positron creature. A positron wave function can be obtained from the electron wave function by using charge conjugation: $i\gamma^2\psi^*_{\text{particle}} = \psi_{\text{antiparticle}}$. A positron is not a negative energy electron. Positrons and electrons are distinguished by their "good quantum numbers" $+e$ and $-e$, respectively.

Example 5.5. Chiral Representation (Bibek Presentation)

Here we shall examine a pair of waves that propagate in 1D. It is easy to work through the 1D case, and extension to 3D follows by inspection. The waves propagate in opposite directions, and in the absence of coupling between them they do so at the speed of light. These waves describe a massless Dirac fermion. Of course the fermion will be assigned mass in due course, but not right now. In addition, we shall treat the particle's spin-½ as implicit. It can project onto the momentum direction, but it cannot change its orientation relative to the momentum. This is because a massless particle always travels at the speed of light, and this eliminates any possibility of a spin flipping its orientation. This system differs significantly from the waves we have encountered so far in this chapter, leaving aside frequent references to photons.



The representation in which mass in the free-particle Dirac equation is zero is called the chiral or Weyl representation (photo of Hermann Weyl). Lord Kelvin (William Thomson): Professor of Natural Philosophy, University of Glasgow (1846-1899) introduced the term chiral into the scientific lexicon.

You might wonder why someone would set the mass to zero. It turns out that this is useful for dealing with the electron neutrino (and its antiparticle), whose mass is at most a few eV, notwithstanding the difficulty of working with the weak force. Neutrinos do not participate in electromagnetic or strong interactions. Therefore, though electromagnetic fields are always present, they can be neglected insofar as a neutrino is concerned. If the neutrino had zero mass, it would be left-handed and remain so (no spin-flip). Discovery of the small electron neutrino mass was a major experimental feat that to this day challenges theory.

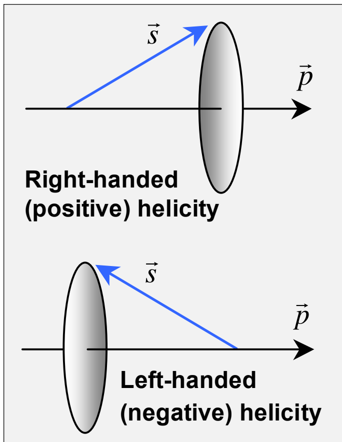


Figure 1. A particle moves with momentum $\vec{p}$. If its spin projection lies in the direction of $\vec{p}$, the system has right-handed (positive) helicity. If it lies in the direction opposite $\vec{p}$, the system has left-handed (negative) helicity. If the particle's energy E is positive, its helicity is negative. Likewise, if E is negative the particle has positive helicity.

At sufficiently high energy, a particle's mass is small compared to its energy. For example, 1 GeV exceeds the energy of the electron mass (mc^2) by a factor of ~ 2000. Electron speed is close to c in this regime, so chirality is a good approximation.

Figure 1 shows that helicity, which is defined according to the sign of $\vec{\sigma} \cdot \vec{p}$, has a great deal in common with chirality. It is interesting that the chiral representation is useful in the present context. The strategy has much in common with that used in van der Waerden's approach, which you may wish to review.

Chiral Waves

Wave propagation in opposite directions at the speed of light can be described using a pair of first order differential equations [21]:

$$\left(\partial_{ct} + \partial_r\right)\psi_R = 0 \tag{1a}$$

$$\left(\partial_{ct} - \partial_r\right)\psi_L = 0 \,. \tag{1b}$$

Figure 2. Wave fronts move toward the left and right with speed *c*.

In the present model, subscripts R and L denote waves traveling to the right and left, as indicated in Fig. 2. The terms right and left are arbitrary. Less ambiguous labeling is used in the case of helicity, as shown in Fig. 1. Right-handed helicity has spin oriented in the direction of $\vec{p}$, and left-handed helicity has spin oriented opposite the direction of $\vec{p}$. However, spin is implicit in the present example. It can be taken along a given direction, albeit with no possibility of a spin flip. Thus, we shall think of R and L as indicating spatial direction. The 1D spatial coordinate is labeled r in anticipation of extension to 3D.

You might be more familiar with the standard second-order wave equation

$$\left(\partial_{ct}{}^2 - \partial_r{}^2\right)\psi = 0 \,, \tag{2}$$

whose solutions are linear combinations of waves that travel to the right and left with speed c. Here we are interested in wave functions that have components, so eqn (1) will be used. In matrix form it can be written

$$\left(\underbrace{\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}}_{M^t}\partial_{ct} + \underbrace{\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}}_{M^r}\partial_r\right)\begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix} = 0 \,. \tag{3}$$

The matrices M^t and M^r have the following properties:

$$\left\{M^t, M^r\right\} = 0 \qquad M^t M^t = \mathbf{1} \qquad M^r M^r = -\mathbf{1} \,. \tag{4}$$

Also, note that the operator in eqn (3),

$$\begin{pmatrix} 0 & \partial_{ct} + \partial_r \\ \partial_{ct} - \partial_r & 0 \end{pmatrix}, \tag{5a}$$

when squared, yields the operator given in eqn (2):

$$\begin{pmatrix} 0 & \partial_{ct}+\partial_r \\ \partial_{ct}-\partial_r & 0 \end{pmatrix}^2 = \begin{pmatrix} \partial_{ct}{}^2-\partial_r{}^2 & 0 \\ 0 & \partial_{ct}{}^2-\partial_r{}^2 \end{pmatrix}. \tag{5b}$$

Thus, each spinor component satisfies eqn (2). Recall that each Dirac spinor component satisfies the Klein-Gordon equation in the absence of electromagnetic fields. Equation (2) is a 1D Klein-Gordon equation for massless particles.

Now add a small amount of coupling between the waves. In this case, the right hand side of eqn (3) (*i.e.*, zero) is replaced by $\varepsilon\psi$, where ε is small and ψ is the column vector in eqn (3). The resulting equation is

$$\left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\partial_{ct}+\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\partial_r\right)\begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix} = \varepsilon\begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix}, \tag{6}$$

or,

$$(\partial_{ct}+\partial_r)\psi_R = \varepsilon\psi_L \tag{7a}$$

$$(\partial_{ct}-\partial_r)\psi_L = \varepsilon\psi_R\,. \tag{7b}$$

This illustrates the fact that ψ_L is a source for ψ_R and *vice versa*. The wave that travels to the left creates the wave that travels to the right, and the wave that travels to the right creates the wave that travels to the left. Coupling is brought about through the parameter ε. At a given instant of time, a given wave [say, $\psi_R(t)$] arises from the wave ψ_L at all previous times. In other words, we take into account all ψ_L waves that originate at an earlier time and arrive at $\psi_R(t)$ at time t.[20] The net effect of each wave serving as the source of the other is a balance such that nothing escapes to the left or right. This is clear on mathematical grounds, but how are we to visualize it?

Before enlisting a balls-and-springs model to assist in visualization, recall that such equations were encountered in the context of the Dirac equation. For example, in the field-free case, each spinor component must satisfy the Klein-Gordon equation. The 3D Klein-Gordon equation is

$$(\partial_{ct}{}^2-\nabla^2)\psi = -\left(\frac{mc}{\hbar}\right)^2\psi\,. \tag{8}$$

For one spatial dimension, this is given in component form by

$$\begin{pmatrix} 0 & \partial_{ct}+\partial_r \\ \partial_{ct}-\partial_r & 0 \end{pmatrix}\begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix} = -i\,\frac{mc}{\hbar}\begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix}. \tag{9}$$

[20] Mathematically, the Green's function for the left hand side is integrated over the right hand side.

This is eqn (7) with $\varepsilon = -imc/\hbar$. It can also be obtained by factoring eqn (8):

$$(\partial_{ct} + \partial_r)\underbrace{(\partial_{ct} - \partial_r)\psi_L}_{-i\frac{mc}{\hbar}\psi_R} = -i\frac{mc}{\hbar}\psi_L .$$

The interesting feature is that mass couples waves that travel at the speed of light, slowing them in proportion to the particle's mass.

Balls and Springs

Balls-and-springs models serve to introduce the kinds of fields that arise in relativistic quantum field theory. When we examined phonons, a balls-and-springs model was used that was converted to the Klein-Gordon equation with a change of parameter values. Here we shall consider the model shown in Fig. 3.

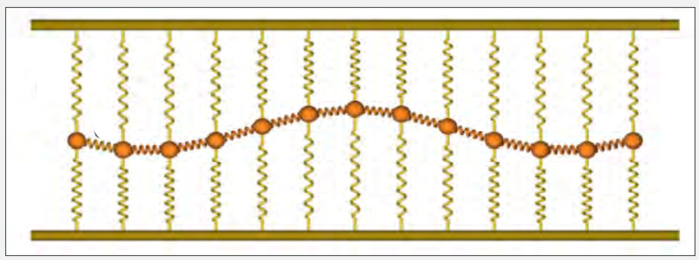


Figure 3. The horizontal springs and point masses determine the wave propagation speed. Vertical displacement is the wave's degree of freedom (amplitude). The vertical springs act to oppose the wave's propagation. (from Hans de Vries [21])

The speed with which a wave propagates, either to the left or right, is determined by the value of the mass of an individual point and the spring constant of the red (horizontal) springs. Each mass point moves vertically. This is the degree of freedom of the wave amplitude. In all cases, the forces exerted by the vertical springs oppose the wave amplitude displacements. In other words, a propagating wave is reflected. This reflection is distributed throughout the 1D lattice.

Dirac Equation in Chiral Representation

The field-free 2D Dirac equation in the chiral representation has solutions that can be expressed as a 2-spinor times a plane wave, with the plane wave satisfying the Klein-Gordon equation. The general form of the spinor for the field-free Dirac equation is

$$\begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix} = \begin{pmatrix} u_L \\ u_R \end{pmatrix} \exp\left(-iEt/\hbar + ipr/\hbar\right) . \qquad (10)$$

The spinor components u_L and u_R are functions of energy and momentum, and energy is taken to be positive. Relative values of u_L and u_R are obtained through substitution of eqn (10) into eqn (9). This yields (following the minor algebraic manipulation given in the box on the right):

$$\begin{pmatrix} 0 & \partial_{ct} + \partial_r \\ \partial_{ct} - \partial_r & 0 \end{pmatrix} \begin{pmatrix} u_L \\ u_R \end{pmatrix} \exp\left(-i\frac{Et}{\hbar} + i\frac{pr}{\hbar}\right) = -\frac{imc}{\hbar} \begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix}$$

$$\begin{pmatrix} u_R\left(-iE/\hbar c + ip/\hbar\right) \\ u_L\left(-iE/\hbar c - ip/\hbar\right) \end{pmatrix} \exp\left(-i\frac{Et}{\hbar} + i\frac{pr}{\hbar}\right) = -\frac{imc}{\hbar} \begin{pmatrix} \psi_L \\ \psi_R \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} 0 & E - pc \\ E + pc & 0 \end{pmatrix} \begin{pmatrix} u_L \\ u_R \end{pmatrix} = mc^2 \begin{pmatrix} u_L \\ u_R \end{pmatrix}$$

$$\left(E - cp\right)u_R = mc^2 u_L \tag{11a}$$

$$\left(E + cp\right)u_L = mc^2 u_R \,. \tag{11b}$$

Equation (11b) gives

$$u_R = \frac{E + cp}{mc^2} u_L \,, \tag{12}$$

and eqn (11a) yields a similar expression. When either is used with the 2-spinor, positive and negative energy spinors are obtained:[21]

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[21] Using eqn (12) yields: $\begin{pmatrix} u_L \\ u_R \end{pmatrix} = N \begin{pmatrix} 1 \\ \dfrac{E + cp}{mc^2} \end{pmatrix}$. Normalization gives: $1 = N^2\left(1 + \dfrac{(E + cp)^2}{m^2c^4}\right) =$

$$N^2\left(\frac{m^2c^4 + E^2 + p^2c^2 + 2Epc}{m^2c^4}\right) = N^2\left(\frac{2E^2 + 2Epc}{E^2 - p^2c^2}\right) = 2N^2\left(\frac{E(E + pc)}{(E + pc)(E - pc)}\right).$$

Thus $N = \dfrac{\sqrt{E - pc}}{\sqrt{2E}}$, yielding the spinor: $\dfrac{1}{\sqrt{2E}}\begin{pmatrix} \sqrt{E - pc} \\ \sqrt{E + pc} \end{pmatrix}$.

For the negative energy spinor, replacing E with $-E$ in eqn (11) yields: $u_L = -\dfrac{E + pc}{mc^2} u_R$.

Using this with the spinor gives: $\begin{pmatrix} u_L \\ u_R \end{pmatrix} = N \begin{pmatrix} -\dfrac{E + cp}{mc^2} \\ 1 \end{pmatrix}$. The algebra that yields N results in the negative energy spinor: $\dfrac{1}{\sqrt{2E}}\begin{pmatrix} -\sqrt{E + pc} \\ \sqrt{E - pc} \end{pmatrix}$.

$$\text{Positive energy:}\ \begin{pmatrix} u_L \\ u_R \end{pmatrix} = \frac{1}{\sqrt{2E}} \begin{pmatrix} \sqrt{E - pc} \\ \sqrt{E + pc} \end{pmatrix} \tag{13a}$$

$$\text{Negative energy:}\ \begin{pmatrix} u_L \\ u_R \end{pmatrix} = \frac{1}{\sqrt{2E}} \begin{pmatrix} -\sqrt{E + pc} \\ \sqrt{E - pc} \end{pmatrix} \tag{13b}$$

Wave packets are constructed by using different values of p and corresponding values of $E = \pm\ (c^2 p^2 + m^2 c^4)$.

Interpretation

In Example 5.4, the Heisenberg equation of motion yielded $\dot{\vec{r}}(t) = c\vec{\alpha}(t)$. It follows mathematically that the magnitude of the component of $\dot{\vec{r}}(t)$ along any direction is equal to c, because the eigenvalues of the α_i matrices are + 1 or – 1. This is strange in the extreme: (1) A massive particle moves at the speed of light. (2) Combining velocity components yields a speed of $c\sqrt{3}$. (3) Spin matrices represent velocity components.

The part about spin matrices is unimportant. The Pauli matrices plus the unit matrix are a basis in the space of 2D complex matrices. Consequently, 2D models can be described using them. Also, there is no implied $3^{1/2}c$, because the velocity components given by $\dot{\vec{r}}(t) = c\vec{\alpha}(t)$ do not commute among themselves. On the other hand, the part relating to the speed c needs attention.

Undaunted by the speed of light issue, continuing with the mathematics yielded the expression for $\vec{r}(t)$ that contains ZB. An estimate of the speed characteristic of ZB oscillation was obtained from the oscillation displacement amplitude ($\hbar / 2mc$) divided by the characteristic time for virtual electron-positron production obtained using the uncertainty relation: $\delta t \sim \hbar / \delta E = \hbar / 2mc^2$. This yielded a speed that is ~ c, again perplexing.

Aspects of relativistic quantum field theory (RQFT) are present in the quantum mechanical equations. The marriage of special relativity and quantum mechanics requires this for consistent physics. The quantum mechanical equations follow from RQFT, and therefore consequences of field theory must be passed on to the quantum mechanical equations. These consequences do not come with labels. It is up to us to figure out what is going on. For example, RQFT enters in the charged nature of fields, negative electron energies that reflect participation of electron-positron pairs, Klein paradox, ZB, and so on.

In the present example, the + c and – c 1D velocities are for massless particle waves. Recall that in evaluating $[\hat{H}, \vec{r}(t)]$, the βmc^2 term commutes with $\vec{r}(t)$, so mass does not enter the expression for $\dot{\vec{r}}(t)$ except through the phase of $\vec{\alpha}(t)$. This is why the speed is c. The expression $\dot{\vec{r}}(t) = c\vec{\alpha}(t)$ obtained using the Heisenberg equation of motion is the velocity of waves traveling in opposite directions at the speed of light.

The relevant velocity for a positive energy state is the expectation value of $\dot{\vec{r}}(t)$. The eigenvalue of $\dot{\vec{r}}(t)$ is not to be used, because $\dot{\vec{r}}(t)$ does not commute with the Dirac Hamiltonian, so we cannot have positive E and an eigenvalue of $\dot{\vec{r}}(t)$ simultaneously. The chiral representation provides insight and a means for evaluating the expectation value of $\dot{\vec{r}}(t)$. In the 2D chiral basis the 2×2 matrix for $\dot{r}(t)$ is $c\sigma_3$ or its negative. Thus, using the positive energy spinor given by eqn (13a), the expectation value of $\dot{r}(t)$ is

$$\langle \dot{r}(t) \rangle = \begin{pmatrix} u_L \, u_R \end{pmatrix} \begin{pmatrix} \mp c & 0 \\ 0 & \pm c \end{pmatrix} \begin{pmatrix} u_L \\ u_R \end{pmatrix} \tag{14a}$$

$$= \frac{1}{2E} \left(\sqrt{E - pc}\,, \sqrt{E + pc} \right) \begin{pmatrix} \mp c & 0 \\ 0 & \pm c \end{pmatrix} \begin{pmatrix} \sqrt{E - pc} \\ \sqrt{E + pc} \end{pmatrix} \tag{14b}$$

$$= \pm \frac{c}{2E} \left(-E + pc + E + pc \right) \tag{14c}$$

$$= \pm \frac{pc^2}{E} = \pm v \,. \tag{14d}$$

where v is the velocity that we identify with the classical problem. The choice of which entry in the 2×2 matrix is taken as negative is arbitrary. Reversing the signs of the c entries in the 2×2 matrix merely changes the velocity direction, which is not important.

This route was fast and easy because of the simplification to a single spatial direction and the convenient chiral basis. The same result is obtained using any representation. For example, the Dirac-Pauli representation (*i.e.*, the one used everywhere except in the present example) works just as well.

Equation (14) displays no ZB when the packet contains only positive energies or only negative energies. It is only present when the packet has both positive energy and negative energy contributions. Not surprisingly, the extent to which ZB is present is proportional to the product of the expansion coefficients for the $+ E$ and E contributions.

Rabi Oscillation

The 1D model shows that when a state of positive energy is constructed using waves that counter-propagate at the speed of light everything works nicely. The expectation value of $\dot{r}(t)$ accounts for particle mass and yields the usual velocity, v. Likewise for negative energy solutions. However, if the system is restricted to one velocity: $+ c$ or $- c$, but not both at the same time, it must have both $+ E$ and $- E$ contributions. It then undergoes a dynamics known as Rabi oscillation. Such oscillations have been observed experimentally under a broad range of conditions.

In the present context, the oscillation is between the positive and negative energy states of the electron, which for all practical purposes are separated by $2mc^2$. We will discuss this later, time permitting. In the meantime, note that the implicit assumption is made that $+ E$ and $- E$ are each present in the wave packet. If this is to be the case in a real system, there must be a reason.

Example 5.6. Darwin Term

Here we consider the Dirac Hamiltonian given by eqn (22'), focusing on the part of it that can be expressed using nested commutators. Equation (22'), indicating explicitly the part expressed using nested commutators, is written here as eqn (1a).

$$\hat{H} = \frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2m} + qV - \frac{(\vec{\sigma}\cdot\vec{\pi})^4}{8m^3c^2} + \underbrace{\frac{1}{8m^2c^2}\left(\left\{(\vec{\sigma}\cdot\vec{\pi})^2, E-qV\right\} - 2\vec{\sigma}\cdot\vec{\pi}(E-qV)\vec{\sigma}\cdot\vec{\pi}\right)}_{\frac{1}{8m^2c^2}\left[(\vec{\sigma}\cdot\vec{\pi}),\left[(\vec{\sigma}\cdot\vec{\pi}),(E-qV)\right]\right]} \quad (1a)$$

We shall now examine the term

$$\hat{H}' = \frac{e}{8m^2c^2}\left[\vec{\sigma}\cdot\vec{\pi},\left[\vec{\sigma}\cdot\vec{\pi},V\right]\right]. \quad (1b)$$

In going from eqn (1a) to eqn (1b), $q = -e$ and the fact that E commutes with $\vec{\sigma}\cdot\vec{\pi}$ have been used. The vector potential does not contribute to $\hat{H}'$ at order c^{-2}, so it is dropped from $\vec{\pi} = \vec{p} + e\vec{A}/c$. Thus, $\hat{H}'$ is given by

$$\hat{H}' = \frac{e}{8m^2c^2}\left[\vec{\sigma}\cdot\vec{p},\left[\vec{\sigma}\cdot\vec{p},V\right]\right]. \quad (2)$$

The inner commutator is readily simplified:

$$\left[\vec{\sigma}\cdot\vec{p},V\right]\psi = \left(\vec{\sigma}\cdot\vec{p}V\right)\psi + V\cancel{\vec{\sigma}\cdot}\vec{p}\psi - V\cancel{\vec{\sigma}\cdot}\vec{p}\psi \quad (3a)$$

$$= -i\hbar\left(\vec{\sigma}\cdot\nabla V\right)\psi \quad (3b)$$

$$= i\hbar\left(\vec{\sigma}\cdot\vec{E}\right)\psi\ . \quad (3c)$$

In going from eqn (3b) to eqn (3c), $\vec{E} = -\nabla V$ has been used, *i.e.*, the $-\partial_{ct}\vec{A}$ contribution to $\vec{E}$ is ignored, as it does not contribute at order c^{-2}. The fact that $\vec{\sigma}\cdot\vec{p}$ and V do not commute is not a surprise because $\vec{p}$ acting on V results in a force. This is also apparent from the Heisenberg equation of motion

$$\dot{\vec{p}} = \frac{i}{\hbar}\left[\hat{H},\vec{p}\right], \quad (4)$$

where $\hat{H}$ is the Dirac Hamiltonian: $c\vec{\alpha}\cdot(\vec{p}+e\vec{A}/c)+\beta mc^2-eV$. Retaining terms in $[\hat{H},\vec{p}]$ to order c^0 (to ensure $\hat{H}'$ of order c^{-2}) eliminates everything except – eV, and the expression for $\dot{\vec{p}}$ becomes

$$\dot{\vec{p}} = \frac{-ie}{\hbar}\left[V,\vec{p}\right] = e\nabla V = -e\vec{E}\,. \tag{5}$$

It is clear that a force arises, and from eqn (3c) we see that $\vec{\sigma}$ projects onto this force.

The term $\vec{\sigma}\cdot\vec{p}$ is the helicity operator, and helicity is conserved for a free particle. It clearly commutes with the free-particle Dirac Hamiltonian in its 2-spinor form. Equally clearly, it does not commute with the Dirac Hamiltonian when fields are included.

Note that for a central potential: $V = V(r)$, $\vec{p}$ acting on V yields $-i\hbar\partial_r V\,\hat{r}$ (only radial force). Using $[\vec{\sigma}\cdot\vec{p},V] = \vec{\sigma}\cdot(\vec{p}V)$, the Hamiltonian $\hat{H}'$ of eqn (2) is therefore written

$$\hat{H}' = \frac{e}{8m^2c^2}\left[\vec{\sigma}\cdot\vec{p},\vec{\sigma}\cdot\left(\vec{p}V\right)\right] \tag{6a}$$

$$= \frac{-i\hbar e}{8m^2c^2}\left[\vec{\sigma}\cdot\vec{p},\vec{\sigma}\cdot\left(\nabla V\right)\right]. \tag{6b}$$

The parentheses around ∇V indicate that the gradient acts on V, but is not passed to the right of V.

The tedious part of eqn (6b) is handling the spin projections. However, the algebra for dealing with the components of $\vec{\sigma}$ is well known, so we need only write out the commutator in eqn (6b) with the components explicit, and then apply the algebra. The resulting expressions are long but straightforward. This exercise reveals the separation into radial and angular parts, the latter yielding spin-orbit interaction.

Proceeding with the brute force approach of multiplying the component forms of $\vec{\sigma}\cdot\vec{p}$ and $\vec{\sigma}\cdot(\nabla V)$ gives

$$\begin{aligned}\left[\vec{\sigma}\cdot\vec{p},\vec{\sigma}\cdot\left(\nabla V\right)\right] &= \left(\sigma_1 p_1+\sigma_2 p_2+\sigma_3 p_3\right)\left(\sigma_1\left(\nabla V\right)_1+\sigma_2\left(\nabla V\right)_2+\sigma_3\left(\nabla V\right)_3\right)\\ &\quad - \left(\sigma_1\left(\nabla V\right)_1+\sigma_2\left(\nabla V\right)_2+\sigma_3\left(\nabla V\right)_3\right)\left(\sigma_1 p_1+\sigma_2 p_2+\sigma_3 p_3\right).\end{aligned} \tag{7}$$

Numerical subscripts denote Cartesian components. The gradient ∇V is in the radial direction, and therefore it has 3 such components. The 18 terms in eqn (7) are organized into two groups:

$$\begin{aligned}\left[\vec{\sigma}\cdot\vec{p},\vec{\sigma}\cdot\left(\nabla V\right)\right] &= \sum_{i=1}^{3}\sigma_i{}^2\left(p_i\left(\nabla V\right)_i-\left(\nabla V\right)_i\,p_i\right) +\\ &\quad \sigma_1\sigma_2 p_1\left(\nabla V\right)_2+\sigma_2\sigma_1 p_2\left(\nabla V\right)_1-\sigma_1\sigma_2\left(\nabla V\right)_1 p_2-\sigma_2\sigma_1\left(\nabla V\right)_2 p_1+\text{c.p.}\end{aligned} \tag{8}$$

where c.p. reminds us that the cyclic permutations are to be included. In writing eqn (8), use is made of the fact that p_i commutes with σ_j. Next, use is made of $\sigma_i{}^2 = 1$ and

$$p_i\left(\left(\nabla V\right)_i \psi\right) = \left(p_i\left(\nabla V\right)_i\right)\psi + \left(\nabla V\right)_i p_i\psi \,, \tag{9}$$

to write

$$\sum_{i=1}^{3}\sigma_i{}^2\left(p_i\left(\nabla V\right)_i - \left(\nabla V\right)_i p_i\right) = \sum_{i=1}^{3}\left(p_i\left(\nabla V\right)_i\right) = \left(\vec{p}\cdot\nabla V\right). \tag{10}$$

The remaining terms, *i.e.*, the second line in eqn (8), become

$$\begin{aligned}
&\sigma_1\sigma_2\left(p_1\left(\nabla V\right)_2\right) + \sigma_1\sigma_2\left(\nabla V\right)_2 p_1 + \sigma_2\sigma_1\left(p_2\left(\nabla V\right)_1\right) + \sigma_2\sigma_1\left(\nabla V\right)_1 p_2 - \sigma_1\sigma_2\left(\nabla V\right)_1 p_2 \\
&\qquad - \sigma_2\sigma_1\left(\nabla V\right)_2 p_1 + \text{c.p.} \\
&= \sigma_1\sigma_2\underbrace{\left(\left(p_1\left(\nabla V\right)_2\right) - \left(p_2\left(\nabla V\right)_1\right)\right)}_{i\hbar\left(\nabla\times\vec{E}\right)_3} + \sigma_1\sigma_2\left(\nabla V\right)_2 p_1 - \sigma_2\sigma_1\left(\nabla V\right)_2 p_1 \\
&\qquad + \sigma_2\sigma_1\left(\nabla V\right)_1 p_2 - \sigma_1\sigma_2\left(\nabla V\right)_1 p_2 + \text{c.p.}
\end{aligned} \tag{11}$$

The curl term $i\hbar\nabla\times\vec{E}$ vanishes at the present level of approximation, *i.e.*, from Maxwell's equations we have $\nabla\times\vec{E} = -\partial_{ct}\vec{B}$, which is proportional to c^{-1}. The four remaining terms are arranged to read

$$-\sigma_1\sigma_2\left(\left(\nabla V\right)_1 p_2 - \left(\nabla V\right)_2 p_1\right) + \sigma_2\sigma_1\left(\left(\nabla V\right)_1 p_2 - \left(\nabla V\right)_2 p_1\right) + \text{c.p.} \tag{12a}$$

$$= -2\sigma_1\sigma_2\left(\left(\nabla V\right)_1 p_2 - \left(\nabla V\right)_2 p_1\right) + \text{c.p.} \tag{12b}$$

$$= -2i\vec{\sigma}\cdot\left(\nabla V\right)\times\vec{p} \,. \tag{12c}$$

Notice that this term vanishes for an electron traveling only in the radial direction. This is not surprising as such an electron has no orbital angular momentum. Upon combining eqn (12c) (with $\vec{E} = -\nabla V$) and eqn (10), we see that eqn (8) becomes

$$\left[\vec{\sigma}\cdot\vec{p}, \vec{\sigma}\cdot\left(\nabla V\right)\right] = -\left(\vec{p}\cdot\vec{E}\right) + 2i\vec{\sigma}\cdot\vec{E}\times\vec{p} \,. \tag{13}$$

The same result can be obtained much more quickly from eqn (6b) by using the identity $(\vec{\sigma}\cdot\vec{\mathrm{A}})(\vec{\sigma}\cdot\vec{\mathrm{B}}) = \vec{\mathrm{A}}\cdot\vec{\mathrm{B}} + i\vec{\sigma}\cdot\vec{\mathrm{A}}\times\vec{\mathrm{B}}$, which has been enlisted frequently in the past. The more laborious route of eqns (7) – (12) was chosen because it underscores the role of $\vec{\sigma}$

in the Darwin and spin-orbit terms. Regardless, one sees that the spin-orbit and Darwin terms follow from the same physics. Putting eqn (13) into eqn (6b) gives

$$\hat{H}' = \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\vec{E} + \frac{e\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{E}\times\vec{p} \tag{14a}$$

Writing the electric field in terms of the central potential yields

$$\hat{H}' = \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\vec{E} - \frac{e\hbar}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{\sigma}\cdot\vec{r}\times\vec{p} \tag{14b}$$

$$= \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\vec{E} - \frac{e}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{s}\cdot\vec{l} \tag{14c}$$

These are the Darwin and spin-orbit terms.

Different Sides of the Same Coin

The electron that approaches the $+Ze$ charge experiences force. The field created by $+Ze$ accelerates the electron in the $-\hat{r}$ direction. Referring to Fig. 2, the particle's momentum can be separated into two components, one parallel to $\hat{r}$ and the other perpendicular to $\hat{r}$. This situation is straightforward conceptually. The Darwin term deals with the momentum component parallel to $\hat{r}$, whereas the spin-orbit term deals with the momentum component in the angular direction ($\hat{\theta}$ and $\hat{\phi}$ components). Figure 2 shows that the Darwin term is understood as the quantum version of this classical model.

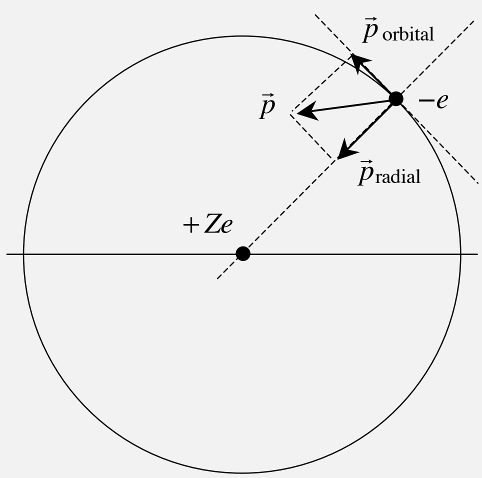

Figure 2. A charge $+Ze$ creates an electric field that accelerates the electron ($-e$). The part of the momentum that is perpendicular to $\hat{r}$, *i.e.*, $\vec{p}_{\text{orbital}}$, contributes orbital angular momentum, resulting in spin-orbit interaction. Consequently, orbital and spin angular momentum are not separately conserved, whereas their sum, $\vec{j} = \vec{l} + \vec{s}$, is conserved.

Inner and Outer Products

The natural mathematical tools for handling the separation we have just encountered are commutators and anticommutators. These return inner and outer products.

$$\left(\vec{\sigma}\cdot\vec{\mathrm{A}}\right)\left(\vec{\sigma}\cdot\vec{\mathrm{B}}\right) = \sum_{i,j}\left(\tfrac{1}{2}\left\{\sigma_i,\sigma_j\right\}+\tfrac{1}{2}\left[\sigma_i,\sigma_j\right]\right)\mathrm{A}_i\mathrm{B}_j$$

$$= \sum_{i,j}\left(\delta_{ij}+\sigma_i\sigma_j\right)\mathrm{A}_i\mathrm{B}_j$$

$$= \vec{\mathrm{A}}\cdot\vec{\mathrm{B}}+i\vec{\sigma}_k\cdot\vec{\mathrm{A}}\times\vec{\mathrm{B}}$$

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