Schiff "Quantum Mechanics"

13 Relativistic Wave Equations

In this chapter we extend the nonrelativistic Schrödinger wave equation to the description of the motion of a particle that has a speed approaching that of light. This extension can be made in many ways, each of which is consistent with the Lorentz transformation equations of the special theory of relativity.[1] A characteristic feature of relativistic wave equations is that the spin of the particle is built into the theory from the beginning and cannot be added afterward, as Pauli added the electron spin to Schrödinger's nonrelativistic equation. This feature provides a useful gauge of the applicability of a particular equation to the description of a particular kind of particle. Two relativistic equations are considered here: the spin 0 equation due to Schrödinger that has since been found to describe a π meson, and the spin $\frac{1}{2}$ equation due to Dirac that

[1] For a review of special relativity, see, for example, H. M. Schwartz, "Introduction to Special Relativity," chaps. 3, 4, 8 (McGraw-Hill, New York, 1968); P. G. Bergmann, "Introduction to the Theory of Relativity," pt. I (Prentice-Hall, Englewood Cliffs, N.J., 1946); C. Møller, "The Theory of Relativity," chaps. I–III (Oxford, London, 1952).

describes an electron. In discussing these equations, we devote our attention mainly to the deductions that can be made from them and do not attempt to establish their Lorentz invariance. We shall, therefore, continue to use three-dimensional vector notation rather than the more elegant four-dimensional notation of special relativity theory. The invariance of an equation can usually be inferred quite convincingly from its symmetry between the space coordinates and the time.

51 SCHRÖDINGER'S RELATIVISTIC EQUATION

At the time when Schrödinger developed his nonrelativistic wave equation, he also proposed an extension of it that meets the requirements of special relativity.[1] This equation follows quite naturally from the transition in classical dynamics from the nonrelativistic relation

$$E = \frac{\mathbf{p}^2}{2m} \tag{51.1}$$

between the energy and momentum of a free particle to the corresponding relativistic relation

$$E^2 = c^2\mathbf{p}^2 + m^2c^4 \tag{51.2}$$

where now E includes the rest-mass energy mc^2. We proceed by adopting the substitutions (6.13) for E and $\mathbf{p}$

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \qquad \mathbf{p} \rightarrow -i\hbar\boldsymbol{\nabla} \tag{51.3}$$

FREE PARTICLE

A relativistic wave equation for a free particle can be obtained by substituting (51.3) into (51.2) and operating on a wave function $\psi(\mathbf{r},t)$, just as the substitution of (51.3) into (51.1) yields Eq. (6.11). The result is

$$-\hbar^2\frac{\partial^2\psi}{\partial t^2} = -\hbar^2c^2\nabla^2\psi + m^2c^4\psi \tag{51.4}$$

Equation (51.4) has plane wave solutions of the form

$$\exp i(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{51.5}$$

which are eigenfunctions of the operators E and $\mathbf{p}$ in (51.3) with eigenvalues $\hbar\omega$ and $\hbar\mathbf{k}$, respectively. It is apparent that (51.5) satisfies Eq. (51.4) if

$$\hbar\omega = \pm(\hbar^2c^2\mathbf{k}^2 + m^2c^4)^{\frac{1}{2}} \tag{51.6}$$

[1] E. Schrödinger, *Ann. Physik* **81,** 109 (1926), Sec. 6.

The positive and negative square roots in (51.6) correspond to an ambiguity in the sign of the energy that also results from the classical expression (51.2). We take only the positive square root for the present and return to the negative-energy solutions at the end of Sec. 53.

Expressions for the charge and current densities can be found in analogy with those obtained in Sec. 7. The conservation equation

$$\frac{\partial}{\partial t} I'(\mathbf{r},t) + \nabla \cdot \mathbf{S}(\mathbf{r},t) = 0 \tag{51.7}$$

turns out to be invariant with respect to Lorentz transformations. We multiply (51.4) on the left by ψ^*, the complex conjugate equation on the left by ψ, and subtract one from the other. Then (51.7) results, if we define real quantities

$$\begin{aligned} P(\mathbf{r},t) &= \frac{i\hbar}{2mc^2}\left(\psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t}\right) \\ \mathbf{S}(\mathbf{r},t) &= \frac{\hbar}{2im}(\psi^* \nabla \psi - \psi \nabla \psi^*) \end{aligned} \tag{51.8}$$

This expression for $\mathbf{S}$ is identical with the nonrelativistic form (7.3), and the expression for P can be shown to reduce to (7.1) in the nonrelativistic limit (see Prob. 1). It should be noted that P given by (51.8) is not necessarily positive and hence cannot be interpreted as a position probability density. It can, however, be multiplied by e and interpreted as an electric charge density, since charge density can have either sign so long as it is real.

ELECTROMAGNETIC POTENTIALS

We can include the electromagnetic potentials $\mathbf{A}(\mathbf{r},t)$, $\phi(\mathbf{r},t)$ in the wave equation by making use of the fact that ϕ and $(1/c)\mathbf{A}$ have the same Lorentz-transformation properties as E and $\mathbf{p}$. In analogy with the nonrelativistic expression (24.29), we replace (51.2) by

$$(E - e\phi)^2 = (c\mathbf{p} - e\mathbf{A})^2 + m^2c^4 \tag{51.9}$$

for a particle of charge e. The substitutions (51.3) then give

$$\begin{aligned} &\left(-\hbar^2 \frac{\partial^2}{\partial t^2} - 2ie\hbar\phi \frac{\partial}{\partial t} - ie\hbar \frac{\partial \phi}{\partial t} + e^2\phi^2\right)\psi \\ &\quad = [-\hbar^2c^2\nabla^2 + 2ie\hbar c\mathbf{A} \cdot \nabla + ie\hbar c(\nabla \cdot \mathbf{A}) + e^2\mathbf{A}^2 + m^2c^4]\psi \end{aligned} \tag{51.10}$$

We can now find the connection between Eq. (51.10) and the similar Eq. (24.39) in the nonrelativistic limit. We make the substitution

$$\psi(\mathbf{r},t) = \psi'(\mathbf{r},t)e^{-imc^2t/\hbar} \tag{51.11}$$

in (51.10) and assume that operation with $i\hbar(\partial/\partial t)$ on ψ' gives a result that is of the same order as $e\phi\psi'$ and small in comparison with $mc^2\psi'$. This is equivalent to subtracting out the rest energy and assuming that the remaining energies are small in comparison with it. Differentiation of (51.11) gives

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \left(\frac{\partial \psi'}{\partial t} - \frac{imc^2}{\hbar}\psi'\right)e^{-imc^2t/\hbar} \\ \frac{\partial^2 \psi}{\partial t^2} &= \left(\frac{\partial^2 \psi'}{\partial t^2} - \frac{2imc^2}{\hbar}\frac{\partial \psi'}{\partial t} - \frac{m^2c^4}{\hbar^2}\psi'\right)e^{-imc^2t/\hbar} \end{aligned}$$

The first term in each of these derivatives can be neglected, as can the last two terms on the left side of (51.10), which then becomes

$$\left(2i\hbar mc^2 \frac{\partial \psi'}{\partial t} + m^2c^4\psi' - 2emc^2\phi\psi'\right)e^{-imc^2t/\hbar}$$

With these approximations, Eq. (51.10) becomes the same as (24.39) if ψ' is replaced by ψ.

There is no way in which the Pauli spin matrices (41.3) can be included in Eq. (51.10) without destroying the invariance of the theory. This is not surprising, since the spin matrices transform like the components of a three-dimensional, rather than a four-dimensional, vector and since ψ has one component rather than two components like the spin functions (33.4). Thus the Schrödinger relativistic equation represents a particle that has no spin.

The structure of Eq. (51.9) shows that a "potential-energy" term cannot be added arbitrarily to (51.10), as the term $V\psi$ was added to (24.39) to give Eq. (44.1). The Lorentz transformation properties of any such term must be investigated first. If it transforms like part of a four-dimensional vector, the rest of this vector must be included in some such manner as ϕ and $(1/c)\mathbf{A}$ were included in (51.9). If it is an invariant with respect to Lorentz transformations, it can be included as part of the rest energy mc^2.

SEPARATION OF THE EQUATION

The wave equation (51.10) can be separated with respect to $\mathbf{r}$ and t if the potentials $\mathbf{A}$, ϕ are independent of the time. We then put

$$\psi(\mathbf{r},t) = u(\mathbf{r})e^{-iEt/\hbar}$$

and substitute into (51.10) to obtain

$$\begin{aligned} (E - e\phi)^2 u = [&-\hbar^2c^2\nabla^2 + 2ie\hbar c\mathbf{A} \cdot \nabla \\ &+ ie\hbar c(\nabla \cdot \mathbf{A}) + e^2\mathbf{A}^2 + m^2c^4]u \end{aligned} \tag{51.12}$$

We now specialize to the case in which $\mathbf{A} = 0$ and $\phi(\mathbf{r})$ is spherically symmetric. Equation (51.12) then becomes

$$(-\hbar^2c^2\nabla^2 + m^2c^4)u(\mathbf{r}) = [E - e\phi(r)]^2u(\mathbf{r}) \tag{51.13}$$

which can be separated in spherical coordinates (see Sec. 14) to give

$$u(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi)$$

$$\left[-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{l(l+1)}{r^2}\right]R = \frac{(E - e\phi)^2 - m^2c^4}{\hbar^2c^2}R \qquad l = 0, 1, 2, \ldots \tag{51.14}$$

This reduces to the nonrelativistic radial equation if we put $E = mc^2 + E'$ and assume that E' and $e\phi$ can be neglected in comparison with mc^2. Then the fraction on the right side of (51.14) becomes $(2m/\hbar^2)(E' - e\phi)$, as it should.

ENERGY LEVELS IN A COULOMB FIELD

An exact solution of (51.14) can easily be obtained if we put $e\phi = -Ze^2/r$, by making use of the results of Sec. 16. This situation would represent a hydrogen atom were it not for the fact that the particle described by (51.10) has no spin and so cannot be an electron.

If we put $\rho = \alpha r$, Eq. (51.14) can be written as

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1) - \gamma^2}{\rho^2}\right]R = 0 \tag{51.15}$$

$$\gamma \equiv \frac{Ze^2}{\hbar c} \qquad \alpha^2 \equiv \frac{4(m^2c^4 - E^2)}{\hbar^2c^2} \qquad \lambda \equiv \frac{2E\gamma}{\hbar c\alpha}$$

This has precisely the form of Eq. (16.7) except that $l(l+1)$ has been replaced by $l(l+1) - \gamma^2$. The parameter λ is determined by the boundary condition on R when $\rho = \infty$, and E is expressed in terms of λ by eliminating α from the last two of Eqs. (51.15):

$$E = mc^2\left(1 + \frac{\gamma^2}{\lambda^2}\right)^{-\frac{1}{2}} \tag{51.16}$$

A study of the way in which Eq. (16.7) was solved shows that solutions of (51.15) that are finite at $\rho = 0$ and ∞ exist only if

$$\lambda = n' + s + 1 \tag{51.17}$$

where n' is zero or a positive integer and s is the nonnegative solution of the equation

$$s(s+1) = l(l+1) - \gamma^2 \tag{51.18}$$

Equation (51.18) has the two solutions

$$s = -\tfrac{1}{2} \pm \tfrac{1}{2}[(2l+1)^2 - 4\gamma^2]^{\frac{1}{2}} \tag{51.19}$$

of which one is positive and the other negative for $l > 0$.

For $l = 0$, both the s values given by (51.19) are negative, so that $R(r)$, which behaves like r^s near $r = 0$, is singular at the origin. However, γ is quite small (very nearly equal to $Z/137$ if e is the electronic charge), so that use of the upper sign in (51.19) gives a value of s that is close to zero for physically interesting values of Z, whereas the lower sign makes s close to -1. The choice between these two values of s can be made in the following way. In a physically realizable case, the source of the coulomb field has some small but finite size a that corresponds, say, to the nuclear radius, so that $\phi(r)$ is finite everywhere. Then the solution $R(r)$ that is finite at $r = 0$ can be shown to approach the point coulomb solution that corresponds to the upper sign in (51.19) when $a \to 0$ (see Prob. 3). We then use the upper sign in (51.19) for all l and obtain from (51.17)

$$\lambda = n' + \tfrac{1}{2} + [(l + \tfrac{1}{2})^2 - \gamma^2]^{\frac{1}{2}} \tag{51.20}$$

Equations (51.16) and (51.20) give a fine structure to the nonrelativistic energy levels (16.15). This can be seen by expanding the expression for the energy levels in powers of γ^2. The result to terms of order γ^4 is

$$E = mc^2\left[1 - \frac{\gamma^2}{2n^2} - \frac{\gamma^4}{2n^4}\left(\frac{n}{l + \frac{1}{2}} - \frac{3}{4}\right)\right] \tag{51.21}$$

where $n = n' + l + 1$ is the total quantum number of Eq. (16.14) and can take on positive integer values. The first term on the right side of (51.21) is the rest energy. The second term is

$$-\frac{mc^2\gamma^2}{2n^2} = -\frac{mZ^2e^4}{2\hbar^2n^2}$$

and agrees with (16.15). The third term is the fine-structure energy, which removes the degeneracy between states of the same n and different l. The total spread of the fine-structure levels for a given n is easily seen from (51.21) to be

$$\frac{mc^2\gamma^4}{n^3}\frac{n-1}{n-\frac{1}{2}} \tag{51.22}$$

This is much larger than is observed experimentally in the spectrum of hydrogen.

for a consistent nonrelativistic approximation, it cannot be dropped from the relativistic equation (52.25), where it is required to preserve Lorentz invariance.

53□DIRAC'S EQUATION FOR A CENTRAL FIELD

In the preceding section, the existence of the magnetic moment of an electron was demonstrated explicitly by showing that the expected extra magnetic energy appears in the nonrelativistic approximation. The electron spin carries no energy in itself and so can be observed only through its coupling with the orbital motion of the electron. In the first part of this section, we make this coupling apparent in two ways: through conservation of total angular momentum and through the spin-orbit energy that was introduced in Sec. 47. In both cases we work with such potentials $\mathbf{A}$, ϕ that there is no transfer of angular momentum to the electron; this implies that we have a central field ($\mathbf{A} = 0$ and ϕ spherically symmetric). In the latter part of this section, we separate the Dirac equation for a general central field and find the energy levels of the hydrogen atom.

SPIN ANGULAR MOMENTUM

With $\mathbf{A}(\mathbf{r},t) = 0$ and $\phi(\mathbf{r},t) = \phi(r)$, Eq. (52.22) can be written as

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi$$
$$H = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 + V \tag{53.1}$$

where $V = e\phi$. We might expect that the orbital angular momentum $\mathbf{L} = \mathbf{r}\times\mathbf{p}$ is a constant of the motion in such a central field. In order to investigate this point, we calculate the time rate of change of $\mathbf{L}$ in the Heisenberg picture with the help of Eqs. (24.10) and (24.31):

$$\begin{aligned} i\hbar\frac{dL_x}{dt} &= L_xH - HL_x \\ &= c\boldsymbol{\alpha}\cdot[(yp_z - zp_y)\mathbf{p} - \mathbf{p}(yp_z - zp_y)] \\ &= -i\hbar c(\alpha_zp_y - \alpha_yp_z) \end{aligned} \tag{53.2}$$

since $\mathbf{L}$ commutes with any spherically symmetric function such as $V(r)$. It is apparent that $\mathbf{L}$ does not commute with H and hence is not a constant of the motion. However, we expect on physical grounds that it is possible to define a total angular momentum that is constant in a central field of force. This means that we must find another operator such that the commutator of its x component with H is the negative of the right side of (53.2); the sum of this operator and $\mathbf{L}$ is then a constant of the motion and can be interpreted as the total angular momentum.

It is not difficult to see that the desired operator is a multiple of the $\boldsymbol{\sigma}'$ defined in (52.19). From (52.11) and (52.13), we find that σ_x' commutes with α_x and β, although not with the other components of $\boldsymbol{\alpha}$:

$$\begin{aligned} \sigma_x'\alpha_y - \alpha_y\sigma_x' &= \begin{bmatrix}\sigma_x & 0\\ 0 & \sigma_x\end{bmatrix}\begin{bmatrix}0 & \sigma_y\\ \sigma_y & 0\end{bmatrix} - \begin{bmatrix}0 & \sigma_y\\ \sigma_y & 0\end{bmatrix}\begin{bmatrix}\sigma_x & 0\\ 0 & \sigma_x\end{bmatrix} \\ &= \begin{bmatrix}0 & i\sigma_z\\ i\sigma_z & 0\end{bmatrix} - \begin{bmatrix}0 & -i\sigma_z\\ -i\sigma_z & 0\end{bmatrix} = 2i\alpha_z \end{aligned}$$

The time rate of change of $\boldsymbol{\sigma}'$ can now be obtained:

$$i\hbar\frac{d\sigma_x'}{dt} = \sigma_x'H - H\sigma_x' = 2ic(\alpha_zp_y - \alpha_yp_z) \tag{53.3}$$

It is apparent from (53.2) and (53.3) that the quantity $\mathbf{L} + \frac{1}{2}\hbar\boldsymbol{\sigma}'$ commutes with H and can therefore be taken to be the total angular momentum. We refer to the operator

$$\mathbf{S} = \tfrac{1}{2}\hbar\boldsymbol{\sigma}' \tag{53.4}$$

as the spin angular momentum of the electron.

APPROXIMATE REDUCTION; SPIN-ORBIT ENERGY

We now wish to show that the spin-orbit energy (47.13) is a consequence of the Dirac equation. This term can be shown to be of order $(v/c)^2$ times the potential energy:

$$\frac{1}{V}\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}(\mathbf{L}\cdot\mathbf{S}) \sim \frac{1}{V}\frac{1}{m^2c^2}\frac{V}{a^2}pa\hbar \sim \frac{v^2}{c^2}$$

where a represents the linear dimensions of the system, and

$$\frac{\hbar}{a} \sim p \sim mv$$

Thus the approximations that led to (52.27) are not adequate for the present purpose.

In order to obtain a consistent approximation that is expressed in terms of the more familiar two-component wave functions, we replace ψ in (53.1) by ψ_1 and ψ_2, which now represent the first two and the last two components of ψ, respectively. We assume that ψ_1, ψ_2 together constitute a nonrelativistic energy eigenfunction, which means that

$$E = E' + mc^2$$

is regarded as a number rather than an operator; E' and V are assumed to be small in comparison with mc^2. The wave equation then becomes

$$\begin{aligned} (E' - V)\psi_1 - c\boldsymbol{\sigma}\cdot\mathbf{p}\psi_2 &= 0 \\ (E' + 2mc^2 - V)\psi_2 - c\boldsymbol{\sigma}\cdot\mathbf{p}\psi_1 &= 0 \end{aligned} \tag{53.5}$$

where $\mathbf{p}$ is still an operator. It is apparent from the second of these equations that ψ_2 is of the order of v/c times ψ_1, and so we eliminate it to obtain an equation in terms of ψ_1 alone. The substitution

$$\psi_2 = (E' + 2mc^2 - V)^{-1} c\boldsymbol{\sigma} \cdot \mathbf{p}\psi_1$$

in the first of Eqs. (53.5) gives

$$E'\psi_1 = \frac{1}{2m}(\boldsymbol{\sigma} \cdot \mathbf{p})\left(1 + \frac{E' - V}{2mc^2}\right)^{-1}(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_1 + V\psi_1 \tag{53.6}$$

Thus far, no approximations have been made.

The desired approximation is obtained by keeping the lowest terms in an expansion in powers of $(E' - V)/2mc^2$. The following relations are easily established:

$$\left(1 + \frac{E' - V}{2mc^2}\right)^{-1} \approx 1 - \frac{E' - V}{2mc^2}$$

$$\mathbf{p}V = V\mathbf{p} - i\hbar\nabla V$$

$$(\boldsymbol{\sigma} \cdot \nabla V)(\boldsymbol{\sigma} \cdot \mathbf{p}) = (\nabla V) \cdot \mathbf{p} + i\boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}]$$

With the help of these, (53.6) becomes

$$E'\psi_1 = \left[\left(1 - \frac{E' - V}{2mc^2}\right)\frac{\mathbf{p}^2}{2m} + V\right]\psi_1 - \frac{\hbar^2}{4m^2c^2}(\nabla V) \cdot (\nabla\psi_1) + \frac{\hbar^2}{4m^2c^2}\boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}\psi_1] \tag{53.7}$$

Further simplications can be made if V is spherically symmetric. We use the relations

$$(\nabla V) \cdot \nabla = \frac{dV}{dr}\frac{\partial}{\partial r}$$

$$\nabla V = \frac{1}{r}\frac{dV}{dr}\mathbf{r}$$

and note that $E' - V$ is approximately equal to $\mathbf{p}^2/2m$, the accuracy being sufficient to replace the second-order term $(E' - V)\mathbf{p}^2$ in (53.7) by $\mathbf{p}^4/2m$. We can then rewrite (53.7) as

$$E'\psi_1 = \left(\frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^4}{8m^3c^2} + V - \frac{\hbar^2}{4m^2c^2}\frac{dV}{\partial r}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S} \cdot \mathbf{L}\right)\psi_1 \tag{53.8}$$

where now $\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$ and $\mathbf{L} = \mathbf{r} \times \mathbf{p}$.

The first and third terms on the right side of (53.8) give the nonrelativistic Schrödinger equation. The second term has the form of the classical relativistic mass correction, which can be obtained by expanding

the square root of (51.2):

$$E' = E - mc^2 = (c^2\mathbf{p}^2 + m^2c^4)^{\frac{1}{2}} - mc^2 \approx \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^4}{8m^3c^2}$$

The last term is the spin-orbit energy (47.14), which is now seen to appear as an automatic consequence of the Dirac equation. The fourth term is a similar relativistic correction to the potential energy, which does not have a classical analog. Since it does not involve the angular momenta, it is much more difficult to demonstrate experimentally than the spin-orbit energy.[1]

SEPARATION OF THE EQUATION

The Dirac equation for a central field can be separated without approximation in spherical coordinates. The procedure is more complicated than for either of the Schrödinger equations because of the interdependence of orbital and spin angular momenta. We start by defining radial momentum and velocity operators

$$p_r = r^{-1}(\mathbf{r} \cdot \mathbf{p} - i\hbar) \qquad \alpha_r = r^{-1}(\boldsymbol{\alpha} \cdot \mathbf{r}) \tag{53.9}$$

both of which can be shown to be hermitian. We also define an operator k that will shortly be seen to be related to the total angular momentum:

$$\hbar k = \beta(\boldsymbol{\sigma}' \cdot \mathbf{L} + \hbar) \tag{53.10}$$

where $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. It can be shown by direct substitution, with the help of (52.24), that

$$\alpha_r p_r + i\hbar r^{-1}\alpha_r\beta k = \boldsymbol{\alpha} \cdot \mathbf{p}$$

The hamiltonian (53.1) then becomes

$$H = c\alpha_r p_r + \frac{i\hbar c}{r}\alpha_r\beta k + \beta mc^2 + V \tag{53.11}$$

The following relations can be established with the help of the definitions (53.9) and (53.10) and the relations of Sec. 52:

$$\alpha_r k - k\alpha_r = 0 \qquad \beta k - k\beta = 0 \qquad p_r k - k p_r = 0$$

$$\alpha_r p_r - p_r\alpha_r = 0$$

These show that k commutes with the hamiltonian (53.11) and so is a constant of the motion. The eigenvalues of k can be inferred by squaring (53.10):

$$\hbar^2 k^2 = (\boldsymbol{\sigma}' \cdot \mathbf{L})^2 + 2\hbar(\boldsymbol{\sigma}' \cdot \mathbf{L}) + \hbar^2 = (\mathbf{L} + \tfrac{1}{2}\hbar\boldsymbol{\sigma}')^2 + \tfrac{1}{4}\hbar^2 \tag{53.12}$$

The quantity $(\mathbf{L} + \frac{1}{2}\hbar\boldsymbol{\sigma}')^2$ is the square of the total angular momentum

[1] For further discussion of this term, see E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," p. 130 (Cambridge, London, 1935).

and has eigenvalues $j(j+1)\hbar^2$, where j is half a positive odd integer. Thus k^2 has eigenvalues $(j+\frac{1}{2})^2$, so that k can be $\pm 1, \pm 2, \ldots$.

We now choose a representation in which H and k are diagonal and represented by the numbers E and k, respectively. α_r and β can then be represented by any hermitian matrices that satisfy the relations

$$\alpha_r^2 = \beta^2 = 1 \qquad \alpha_r\beta + \beta\alpha_r = 0$$

which are not difficult to verify. Such matrices can have two rows and columns; for example, we can put

$$\beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad \alpha_r = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \tag{53.13}$$

Now the angular and spin parts of the wave function are fixed by the requirement that ψ be an eigenfunction of the k operator (53.10). For such purposes as the computation of energy levels, we need be concerned only with the radial part; because of the structure of (53.13), this has two components, which we write

$$\begin{bmatrix} r^{-1}F(r) \\ r^{-1}G(r) \end{bmatrix} \tag{53.14}$$

Substitution of (53.13) and (53.14) into the wave equation with the hamiltonian (53.11) gives us the radial equations for an electron moving in a central field. We make use of the relation

$$p_r = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)$$

to obtain

$$\begin{aligned} (E - mc^2 - V)F + \hbar c\frac{dG}{dr} + \frac{\hbar ck}{r}G &= 0 \\ (E + mc^2 - V)G - \hbar c\frac{dF}{dr} + \frac{\hbar ck}{r}F &= 0 \end{aligned} \tag{53.15}$$

It is convenient to make the numerical substitutions

$$\alpha_1 = \frac{mc^2 + E}{\hbar c} \qquad \alpha_2 = \frac{mc^2 - E}{\hbar c} \qquad \rho = \alpha r$$
$$\alpha = +(\alpha_1\alpha_2)^{\frac{1}{2}} = \frac{(m^2c^4 - E^2)^{\frac{1}{2}}}{\hbar c} \tag{53.16}$$

in terms of which Eqs. (53.15) become

$$\begin{aligned} \left(\frac{d}{d\rho} + \frac{k}{\rho}\right)G - \left(\frac{\alpha_2}{\alpha} + \frac{V}{\hbar c\alpha}\right)F &= 0 \\ \left(\frac{d}{d\rho} - \frac{k}{\rho}\right)F - \left(\frac{\alpha_1}{\alpha} - \frac{V}{\hbar c\alpha}\right)G &= 0 \end{aligned} \tag{53.17}$$

THE HYDROGEN ATOM

We now find the energy eigenvalues of (53.17) when $V(r) = -Ze^2/r$; with $\gamma \equiv Ze^2/\hbar c$, the quantity $V/\hbar c\alpha$ becomes $-\gamma/\rho$. We follow a procedure that is analogous to that of Sec. 16 and put

$$F(\rho) = f(\rho)e^{-\rho} \qquad G(\rho) = g(\rho)e^{-\rho} \tag{53.18}$$

The equations for f and g are

$$\begin{aligned} g' - g + \frac{kg}{\rho} - \left(\frac{\alpha_2}{\alpha} - \frac{\gamma}{\rho}\right)f &= 0 \\ f' - f - \frac{kf}{\rho} - \left(\frac{\alpha_1}{\alpha} + \frac{\gamma}{\rho}\right)g &= 0 \end{aligned} \tag{53.19}$$

We look for solutions of (53.19) in the form of power series:

$$\begin{aligned} f &= \rho^s(a_0 + a_1\rho + \cdots) \qquad a_0 \neq 0 \\ g &= \rho^s(b_0 + b_1\rho + \cdots) \qquad b_0 \neq 0 \end{aligned} \tag{53.20}$$

Since (53.14) is supposed to be finite at $r = 0$, we expect that s is greater than or equal to 1. However, in analogy with the solution of the Schrödinger relativistic equation (51.15) for the coulomb field, we shall admit a value of s slightly less than 1.

We substitute (53.20) into (53.19) and equate the coefficients of $\rho^{s+\nu-1}$ to zero:

$$\begin{aligned} (s + \nu + k)b_\nu - b_{\nu-1} + \gamma a_\nu - \frac{\alpha_2}{\alpha}a_{\nu-1} &= 0 \\ (s + \nu - k)a_\nu - a_{\nu-1} - \gamma b_\nu - \frac{\alpha_1}{\alpha}b_{\nu-1} &= 0 \end{aligned} \tag{53.21}$$

for $\nu > 0$. When $\nu = 0$, the equations analogous to (53.21) are

$$\begin{aligned} (s + k)b_0 + \gamma a_0 &= 0 \\ (s - k)a_0 - \gamma b_0 &= 0 \end{aligned} \tag{53.22}$$

Equations (53.22) have the required nonvanishing solution for a_0 and b_0 only if the determinant of their coefficients vanishes; this gives

$$s = \pm(k^2 - \gamma^2)^{\frac{1}{2}} \tag{53.23}$$

Because of the boundary condition at the origin, we take the upper sign for s in (53.23).

A relation between a_ν and b_ν can be obtained by multiplying the first of Eqs. (53.21) by α, the second by α_2, and subtracting:

$$b_\nu[\alpha(s + \nu + k) + \alpha_2\gamma] = a_\nu[\alpha_2(s + \nu - k) - \alpha\gamma] \tag{53.24}$$

where use has been made of (53.16). We can now examine the behavior of the solution at large r. Unless both the series (53.20) terminate, this behavior is determined by their high terms, and so we can neglect constant factors in comparison with ν. We then obtain from (53.21) and (53.24)

$$a_\nu \approx \frac{2}{\nu} a_{\nu-1} \qquad b_\nu \approx \frac{2}{\nu} b_{\nu-1}$$

This means that both series have the asymptotic form $e^{2\rho}$, and regular solutions are obtained only if they terminate. Suppose that this occurs at $\nu = n'$, so that $a_{n'+1} = b_{n'+1} = 0$. Then both Eqs. (53.21) give the relation

$$\alpha_2 a_{n'} = -\alpha b_{n'} \qquad n' = 0, 1, 2, \ldots \tag{53.25}$$

We obtain energy levels by setting $\nu = n'$ in (53.24) and making use of (53.25). With the help of (53.16), we find that

$$2\alpha(s + n') = \gamma(\alpha_1 - \alpha_2) = \frac{2E\gamma}{\hbar c}$$

which incidentally shows that $E > 0$. The square of this is

$$(m^2c^4 - E^2)(s + n')^2 = E^2\gamma^2$$

which is easily solved to give

$$E = mc^2\left[1 + \frac{\gamma^2}{(s + n')^2}\right]^{-\frac{1}{2}} \tag{53.26}$$

Equations (53.23) and (53.26) are equivalent to the formula first derived by Sommerfeld[1] on the basis of the old quantum theory. This formula accounts quite well for the spectrum of hydrogen.[2] The fine structure is made evident by expanding (53.26) in powers of γ^2. The result to terms of order γ^4 resembles (51.21) but is not quite the same:

$$E = mc^2\left[1 - \frac{\gamma^2}{2n^2} - \frac{\gamma^4}{2n^4}\left(\frac{n}{|k|} - \frac{3}{4}\right)\right] \tag{53.27}$$

where $n = n' + |k|$ is the total quantum number of Eq. (16.14), and $|k|$ can take on positive integer values. The total spread in energy of the fine-structure levels for a given n is easily seen from (53.27) to be

$$\frac{mc^2\gamma^4}{n^3}\frac{n-1}{2n}$$

This is substantially less than the value (51.22) obtained from the Schrödinger relativistic equation and is in agreement with experiment.

[1] A. Sommerfeld, *Ann. Physik.* **51,** 1 (1916).

[2] There are, however, small but important deviations from this formula; see W. E. Lamb, *Rept. on Progr. Phys.* **14,** 19 (1951).

CLASSIFICATION OF ENERGY LEVELS

For $n' > 0$, all positive and negative integer values of k are permissible [we saw from (53.12) that k cannot be zero]. For $n' = 0$, however, a contradiction can arise between (53.22) and (53.25); these give

$$\frac{b_0}{a_0} = -\frac{\gamma}{s + k} \qquad \text{and} \qquad \frac{b_0}{a_0} = -\frac{\alpha_2}{\alpha} \tag{53.28}$$

respectively. Since $s < |k|$, the first of these expressions is positive or negative according as k is negative or positive, whereas the second is always negative. Thus, for $n' = 0$, k can assume only positive integer values.

Thus far we have shown only that the j value of a level is equal to $|k| - \frac{1}{2}$. In order to connect l with the level, we must make the nonrelativistic approximation that the orbital angular momentum is well defined. Since in this case F in (53.14) is much larger than G, we can replace β by -1 and $\boldsymbol{\sigma}'$ by $\boldsymbol{\sigma}$ in (53.10). In this approximation, $(\mathbf{L} + \frac{1}{2}\hbar\boldsymbol{\sigma})^2 = [l(l+1) + \frac{3}{4}]\hbar^2 + \hbar\boldsymbol{\sigma}\cdot\mathbf{L}$ and is also equal to $j(j+1)\hbar^2$. We obtain in this way

$$k = j(j+1) - l(l+1) + \tfrac{1}{4} = \begin{cases} l+1 & j = l + \frac{1}{2} \\ -l & j = l - \frac{1}{2} \end{cases}$$

As an example of the energy levels in hydrogen, we consider the case $n = 3$. The radial quantum number n' can be 0, 1, or 2, and k can be $\pm(3 - n')$ except that k can be only $+3$ when $n' = 0$. The levels with their nonrelativistic classifications are

n'	k	l	j	
0	3	2	$\frac{5}{2}$	$^2D_{\frac{5}{2}}$
1	−2	2	$\frac{3}{2}$	$^2D_{\frac{3}{2}}$
1	2	1	$\frac{3}{2}$	$^2P_{\frac{3}{2}}$
2	−1	1	$\frac{1}{2}$	$^2P_{\frac{1}{2}}$
2	1	0	$\frac{1}{2}$	$^2S_{\frac{1}{2}}$

According to (53.23) and (53.26), states with the same $|k|$ or j have the same energy; Eq. (53.27) shows that the energy increases with increasing $|k|$.

NEGATIVE ENERGY STATES

We have seen that both the Schrödinger and Dirac relativistic equations admit of solutions for which a particle has negative kinetic energy and negative rest mass. These solutions correspond to the negative square

root of the classical energy equation (51.2). The negative-energy solutions cannot be ignored in the quantum theory, as they are in the classical theory, since there is nothing to prevent a charged particle from making a radiative transition from a state of positive energy to a state of negative energy.

Dirac proposed that we regard the negative energy states of Eq. (52.22) as being full, in which case the exclusion principle prevents transitions into such occupied states. The normal state of the vacuum then consists of an infinite density of negative-energy electrons. It is assumed that there are no electromagnetic or gravitational effects of these electrons but that deviations from the norm produced by emptying one or more of the negative energy states can be observed. The absence of a negatively charged electron that has negative mass and kinetic energy would then be expected to manifest itself as a positively charged particle that has an equal positive mass and kinetic energy. In this way, a "hole" theory of *positrons* can be formulated.

With so many electrons present, however, the theory is no longer the one-particle theory contemplated when the wave equation was set up. A many-particle theory can be based on the Dirac equation in accordance with the formalism of quantized fields discussed in the next chapter, and a theory of positrons can be developed without recourse to holes.

It might at first be thought that a similar technique cannot be applied to the Schrödinger relativistic equation, since it describes a particle of zero spin, which we expect to obey Einstein-Bose statistics rather than the exclusion principle. However, Pauli and Weisskopf[1] showed that the quantized field energy is always positive in this case, even though the parameter E in the wave equation can be either positive or negative. Moreover, the charge in the quantized field can have either sign, corresponding to the ambiguity of the sign of P noted after Eq. (51.8). Thus both the theories discussed in this chapter predict the existence of particles that have positive energies and both signs of electric charge. The appearance of spin angular momentum as a consequence of the Dirac equation shows that this is the theory that describes electrons.

PROBLEMS

1. Use the nonrelativistic approximation implied in (51.11) and in the immediately following discussion to show that the expression (51.8) for P reduces to (7.1) in the proper limit.

2. Solve the Schrödinger relativistic equation for an attractive square well potential of depth V_0 and radius a, after determining the continuity conditions at $r = a$. Obtain an explicit expression for the minimum V_0 with given a that just binds a particle of mass m.

[1] W. Pauli and V. Weisskopf, *Helv. Phys. Acta* **7**, 709 (1934).

3. Find the solution of the Schrödinger relativistic equation that is finite at $r = 0$ and corresponds to the potential energy $e\phi = -Ze^2/a$ for $r < a$ and $e\phi = -Ze^2/r$ for $r > a$, when a is very small. Note that only the first two terms of each power series in r need be retained. Show that the solution for $r > a$ approaches that which corresponds to the upper sign in (51.19) when $a \to 0$.

4. Show that any matrix with two rows and columns can be expressed as a linear combination of σ_x, σ_y, σ_z, and 1. Use this result to show that there is no matrix that anticommutes with each of the first three of these.

5. Show explicitly that the wave functions (52.17) and (52.18) are not eigenfunctions of any component of the spin angular momentum $\frac{1}{2}\hbar\boldsymbol{\sigma}'$.

6. Show that the current density given by (52.20) for a free-particle wave function agrees with the corresponding nonrelativistic expression in the proper limit.

7. Make use of Eqs. (52.11), (52.13), and (52.19) to verify Eq. (52.24).

8. Prove that the operators α_r and k defined by Eqs. (53.9) and (53.10) commute with each other and that $\hbar^2k^2$ is given by the right side of (53.12).

9. Discuss the connection between the $\boldsymbol{\alpha} \cdot \mathbf{E}$ term in Eq. (52.27) and the spin-orbit energy.

10. Show that the negative square roots that could appear in arriving at Eqs. (51.16) and (53.26) actually do not correspond to bound states.

11. Use the selection rules $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$ to list the frequencies of the allowed transitions between the states with $n = 2$ and $n = 3$ for the coulomb field, in both the Schrödinger and Dirac relativistic theories. In particular, show that the latter theory gives seven lines, of which five are distinct, whereas the former gives three lines that are much more spread apart.

12. Solve the Dirac equation for an attractive square well potential of depth V_0 and radius a, after determining the continuity conditions at $r = a$. Obtain an explicit expression for the minimum V_0 with given a that just binds a particle of mass m, and compare with the answer to Prob. 2.

empirical means: For an electron in the helium atom in its ground state, $s_i = \frac{5}{16}$ (see Sect. 26 and 32). For a $1s$ electron in all atoms heavier than helium, $s_1 \approx 0.3$ is still a good approximation. For a $2s$ or $2p$ electron in neon and heavier atoms, SLATER finds $s_2 \approx 4.15$ (although s_2 should be slightly lower for $2s$ than $2p$), etc.

For light atoms, especially for the outer electrons, the outer screening constant V_{0i} is unimportant. For medium-heavy and heavy atoms, especially for inner electrons, V_{0i} is quite large. However, V_{0i} only acts as an additive constant to the energy eigenvalue, but does not affect the wave function. For a $1s$ electron in a medium or heavy atom a crude, but simple, approximation for the central potential $V_i(r)$ can be obtained as follows: The effect of the second $1s$ electron is accounted for by choosing $s_1 = 0.3$. The potential due to all the other (outer) electrons is approximately constant over the region in which the $1s$ wave function is large. We therefore take for V_{0i} the THOMAS-FERMI electrostatic potential at the origin due to all the electrons, $1.79 Z^{\frac{4}{3}}$ a.u., minus the potential at the origin due to the two $1s$ electrons, which is about $2Z$ a.u. [see Eq. (3.29)]. We then have

$$V_1(r) = -\frac{(Z-0.3)}{r} + \\ + (1.79 Z^{\frac{4}{3}} - 2Z) \Big\} \quad (17.7)$$

in atomic units. In this approximation the ionization potential of a $1s$ electron, (17.6), becomes roughly

$$I_1 = (Z^2 - 3.59 Z^{\frac{4}{3}} + \\ + 3.4 Z) \text{ Ry}. \Big\} \quad (17.8)$$

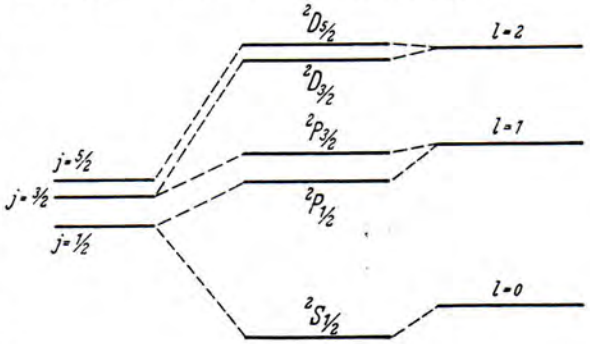

Fig. 10. Schematic level scheme for the states with $n=3$ of a DIRAC electron in an alkali atom. To the left is the level scheme for a DIRAC electron in a COULOMB potential, to the right the nonrelativistic levels in the alkali atom.

We finally return to the fine structure of energy levels in alkali atoms, containing one single electron outside closed shells. The central field approximation is then excellent for this valence electron. But, as discussed above, the shape of the effective potential $V_i(r)$ is far from the COULOMB form and, for fixed principal quantum number n, the binding energy decreases with increasing l. Thus unlike in hydrogen, there is no degeneracy between levels of different l in the nonrelativistic theory of alkali atoms. In addition, the relativistic fine structure corrections (13.8) have to be added to the nonrelativistic energy. These will result in a further splitting of any l-level (except $l=0$) into a doublet with $j = l \pm \frac{1}{2}$. The fine structure splitting of these familiar alkali doublets, being a relativistic effect, is very small compared with the (nonrelativistic) energy separation of levels of different l. The level scheme for a valence electron with $n=3$ in Li or Na is given schematically in Fig. 10.

γ) X-ray levels. For hydrogen-like atoms of reasonably low nuclear charge Z we have seen that the relativistic fine structure shifts W_1 are of order $(Z\alpha)^2 W_0$, where W_0 is the nonrelativistic energy of the level, and hence very small. Further, the difference between the exact DIRAC expression for W_1 and the PAULI approximation for it is of order $(Z\alpha)^2 W_1$, which is smaller even than the radiative corrections of order $W_1 \alpha \log \alpha$. For the heaviest atoms, however, $(Z\alpha)^2$ is not very much smaller than unity (about 0.45 for U) and the relativistic effects become very