Chapter 7

Hydrogen-like Atoms

Dirac's equation may be solved exactly in the case of a Coulomb field, leading to a relativistic theory for hydrogen-like atoms. The most important result is the so-called fine structure formula for the energy levels.

7.1 Dirac equations for a Coulomb field

The Dirac Hamiltonian (6.1) simplifies to (in ordinary units)

$$\hat{H} = c\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta m_e c^2 - e\phi \tag{7.1}$$

for an electrostatic field in the Coulomb gauge. The potential is identified here as

$$\phi(r) = \frac{Ze}{4\pi\varepsilon_0 r}. \tag{7.2}$$

The case of the hydrogen atom corresponds to $Z = 1$, and it is of interest to consider $Z > 1$ corresponding to hydrogen-like atoms, e.g., for $Z = 26$ one has an Fe-atom stripped of all but one of its electrons.

The energy eigenvalues of the Klein-Gordon equation for a hydrogen-like atom are much simpler to find than are those of the Dirac equation. The eigenvalues of the Klein-Gordon equation may be used as an intermediate step in finding the eigenvalues of the Dirac equation. The Klein-Gordon equation is

$$\left[\left(\frac{E}{c} + \frac{Z\alpha\hbar}{r}\right)^2 + \hbar^2\nabla^2 - m_e^2 c^2\right]\psi(\boldsymbol{x}) = 0, \tag{7.3}$$

where the fine structure constant is $\alpha = r_0/r_c$, where $r_0 = e^2/4\pi\varepsilon_0 m_e c^2$ is the classical radius of the electron, and $r_c = \hbar/m_e c$ is its Compton wave length.

7.2 Hydrogen-like Klein Gordon atom

One may write doen the eigenvalues of the Klein Gordon equation (7.3) by noting that it can be forced into the same form as the Schrödinger equation, for which the solution is well known.

Recall from nonrelativistic quantum mechanics that in a central potential one writes

$$\hat{\boldsymbol{p}}^2 = -\hbar^2\nabla^2 = -\hbar^2\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\boldsymbol{L}}^2}{r^2}, \tag{7.4}$$

so that Schrödinger's equation reduces to

$$\left[\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat{\boldsymbol{L}}^2}{r^2} + \frac{2m_e c\hbar Z\alpha}{r}\right]\psi(\boldsymbol{x}) = 2m_e E_{\rm NR}\psi(\boldsymbol{x}), \tag{7.5}$$

and $\hat{\boldsymbol{L}}^2$ has eigenvalues $\hbar^2 l(l+1)$. For a nonrelativistic hydrogen-like atom one has

$$(E_{\rm NR})_n = -\frac{Z^2\alpha^2 m_e c^2}{2n^2}, \qquad n-l = 1,2,\ldots. \tag{7.6}$$

Now consider the Klein Gordon equation (7.3) for the hydrogen-like atom. Using (7.4), one has

$$\left[\left(\frac{E}{c} + \frac{Z\alpha\hbar}{r}\right)^2 + \frac{\hbar^2}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hat{\boldsymbol{L}}^2}{r^2} - m_e^2c^2\right]\psi(\boldsymbol{x}) = 0. \tag{7.7}$$

One may rewrite (7.7) in the form

$$\left\{\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\hbar^2[l(l+1)-(Z\alpha)^2]}{r^2} + \frac{2EZ\hbar\alpha}{rc}\right\}\psi(\boldsymbol{x}) = \frac{E^2 - m_e^2c^4}{c^2}\psi(\boldsymbol{x}). \tag{7.8}$$

This is is equivalent to the Schrödinger equation (7.5) if one makes the replacements

$$\begin{aligned}&2m_e c^2 E_{\rm NR} \to (E^2 - m_e^2c^4), m_e c^2\alpha \to E\alpha,\\ &n \to n' = n - (l+\tfrac{1}{2}) + [(l+\tfrac{1}{2})^2 - (Z\alpha)^2]^{1/2}.\end{aligned}$$

Then $E^2 - m_e^2c^4 = -E^2(Z\alpha)^2/n'^2$ implies

$$E_{nl} = m_e c^2\left(1 + \frac{Z^2\alpha^2}{n'^2}\right)^{-1/2}, \qquad n' = n - (l+\tfrac{1}{2}) + [(l+\tfrac{1}{2})^2 - (Z\alpha)^2]^{1/2}. \tag{7.9}$$

with $n' - l' = 1,\ 2,\ \ldots,\ l'(l'+1) = l(l+1) - (Z\alpha)^2$.

According to (6.31)–(6.34), Dirac's equation, in natural units, in the presence of an electromagnetic field, $(i\not\partial + e\not A - m)\Psi = 0$, can be reduced to a Klein-Gordon like equation by introducing the ansatz $\Psi = (i\not{\partial}+e\not{A}+m)\chi$. Writing $D^\mu := \partial^\mu + iqA^\mu$ one finds

$$\left(D^\mu D_\mu + m^2 - eS^{\mu\nu}F_{\mu\nu}\right)\chi = 0. \tag{7.10}$$

One may apply (7.10) to discuss Dirac's equation for the hydrogen atom by identifying $F_{\mu\nu}$ as the Maxwell tensor for the electric field $\boldsymbol{E} = -\mathrm{grad}\,\phi$. From (6.34) we then have $S^{\mu\nu}F_{\mu\nu} = i\boldsymbol{\alpha}\cdot\boldsymbol{E}$. Now $\boldsymbol{\alpha}$ involves only the Pauli matrices, cf. (3.14), so that its eigenvalues must have the same values as those of the Pauli matrices. Moreover, the final term in (7.10) is proportional to r^{-2}, which is of the same form at the term $[l(l+1)-(Z\alpha)^2]/r^2$ in (7.8). In the presence of both orbital and spin angular momentum, only the total angular momentum is conserved, as discussed further below. The eigenvalues of the total angular momentum are $j = l \pm \frac{1}{2}$. It turns out that the only change that occurs in going from the eigenvalues of the Klein-Gordon equation to the Dirac equation involve the replacement of l in (7.9) by $j+\frac{1}{2}$.

The resulting expression for the energy levels of the hydrogen-like atom is called the *fine structure formula.* A standard form of it is

$$E_{nj} = m\left(1+\frac{Z^2\alpha^2}{n'^2}\right)^{-1/2}, \tag{7.11}$$

with the principal quantum number n related to n' by

$$n' = n - (j+\tfrac{1}{2}) + [(j+\tfrac{1}{2})^2 - (Z\alpha)^2]^{1/2}. \tag{7.12}$$

One expanding in powers of $Z^2\alpha^2$, (7.11) with (7.12) gives

$$\frac{E_{nj}-m_ec^2}{m_ec^2} = -\frac{Z^2\alpha^2}{2n^2}\left[1+\frac{Z^2\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right)+\cdots\right]. \tag{7.13}$$

The leading term in (7.13) is just the nonrelativistic formula for the energy of the hydrogen atom. This term is independent of j so that all energy levels with a given n and different j-values are degenerate. The allowed values correspond to $l = 0, 1, \ldots, n-1$ for each n, with $j = l \pm \frac{1}{2}$ except for $l = 0$ when only $j = \frac{1}{2}$ is possible. The next terms in (7.13) break the degeneracy so that there is a splitting between energy eigenvalues corresponding to different values of j. This splitting is the fine structure.

7.3 Angular momentum eigenstates

Direct solution of the Dirac equation is required to construct the wave funtions. The following discussion is an outline of some of the steps involved, concentrating on how the direct approach leads to the fine structure formula (7.11).

Using the standard representation of the Dirac matrices, it is helpful to introduce 2-spinor wave functions φ and χ. These have the same character as a Schrödinger wave function for a spin-$\frac{1}{2}$ particle in the sense that they may be written as column matrices with two elements, and interpreted (somewhat loosely) as corresponding to spin up and spin down states. The Dirac wave function, which is a 4-spinor, is then written in the form

$$\psi = \begin{pmatrix} \varphi \\ \chi \end{pmatrix}. \tag{7.14}$$

Dirac's equation with the Hamiltonian (6.1) and the form (7.14) separates into two coupled equations that may be written in the form

$$(E - m_e c^2 + e\phi)\varphi - c\boldsymbol{\sigma}\cdot\boldsymbol{p}\chi = 0, \tag{7.15}$$

$$(E + m_e c^2 + e\phi)\chi - c\boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi = 0. \tag{7.16}$$

In the nonrelativistic limit one has $E \approx m_e c^2$ and (7.16) may be approximated by $2m_e c^2\chi - c\boldsymbol{\sigma}\cdot\boldsymbol{p}\varphi = 0$; on solving for χ and substituting this into (7.15) one obtains the Schrödinger equation. The nonrelativistic limit is discussed explictly in the next lecture. Here we are concerned with finding the eigenvalues E implied by (7.15) and (7.16) in the case where no nonrelativistic assumption is made.

It is obvious on physical grounds that the angular momentum must be conserved in any central potential (because there can be no torque to change the angular momentum) and hence the total angular momentum $\boldsymbol{J}$ is a constant of the motion. Parity is also a constant of the motion for a spherically symmetric system. We look for energy eigenvalues, that is, eigenvalues of the Hamiltonian $\hat{H}$, that are also simultaneous eigenvalues of $\hat{J}_z$, $\hat{J}^2$ and of parity. Let the eigenvalues of $\hat{J}_z$ and $\hat{J}^2$ be $\hbar m$ and $\hbar^2 j(j+1)$, respectively. (Note that I denote the mass of the electron by m_e in this lecture to avoid confusion with the eigenvalue m of $\hat{J}_z$). The total angular momentum $\boldsymbol{J}$ is the sum of the orbital angular momentum $\boldsymbol{L}$ and the spin angular momentum $\boldsymbol{S}$:

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}. \tag{7.17}$$

From the theory of the addition of angular momenta, we know that the allowed values of the orbital angular momentum l (so that the eigenvalues of $\boldsymbol{L}^2$ are $\hbar^2 l(l+1)$) are $l = j \pm \frac{1}{2}$, where we use the fact that $\boldsymbol{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$ has half-integral eigenvalues. Hence any relevant simultaneous eigenvalues of $\hat{J}_z$, and $\hat{J}^2$ involve the spherical harmonic $Y_{l'}^{m'}(\theta,\phi)$, with $m' = m \pm \frac{1}{2}$ and $l' = j \pm \frac{1}{2}$. With $j = l \pm \frac{1}{2}$ defining the sign $\pm$, let us define the 2-spinors

$$\phi_{j,m}^{(\pm)} = \frac{1}{\sqrt{2l+1}} \begin{pmatrix} \pm\sqrt{l \pm m + \frac{1}{2}}\,Y_l^{m-\frac{1}{2}} \\ \sqrt{l \mp m + \frac{1}{2}}\,Y_l^{m+\frac{1}{2}} \end{pmatrix}. \tag{7.18}$$

By construction these are eigenstates of $\hat{J}_z$, $\hat{J}^2$ with eigenvalues $m\hbar$, $j(j+1)\hbar^2$, respectively. They are also eigenstates of the parity operator with eigenvlues $(-1)^l$.

We now argue that the 2-spinors in (7.15) and (7.16) can be expressed in terms of the 2-spinor eigenstates (**??**). The argument involves several steps. First, let us write

$$\boldsymbol{J}^2 = \boldsymbol{L}^2 + \hbar \boldsymbol{L} \cdot \boldsymbol{\sigma} + \tfrac{3}{4}\hbar^2, \tag{7.19}$$

and assume that the operators act on $\phi^{(\pm)}_{j,m}$. Then we may solve

$$j(j+1)\hbar^2 = (j \pm \tfrac{1}{2})(j \pm \tfrac{1}{2} + 1)\hbar^2 + \hbar \boldsymbol{L} \cdot \boldsymbol{\sigma} + \tfrac{3}{4}\hbar^2, \tag{7.20}$$

to find that the allowed eigenvalues of $\boldsymbol{L}\cdot\boldsymbol{\sigma}$. The allowed values are $(j-\frac{1}{2})\hbar$ and $(-j-\frac{3}{2})\hbar$. Second, the identification of the eigenvalues of $\boldsymbol{L}\cdot\boldsymbol{\sigma}$ allows us to determine the eigenvalues of $\boldsymbol{\sigma}\cdot\boldsymbol{p}$ in (7.15) and (7.16): one uses the identity

$$\boldsymbol{\sigma}\cdot\boldsymbol{a}\,\boldsymbol{\sigma}\cdot\boldsymbol{b} = \boldsymbol{a}\cdot\boldsymbol{b} + i\boldsymbol{\sigma}\cdot(\boldsymbol{a}\times\boldsymbol{b}) \tag{7.21}$$

first with $\boldsymbol{a} = \boldsymbol{b} = \boldsymbol{x}$, and then with $\boldsymbol{a} = \boldsymbol{x}$ and $\boldsymbol{b} = \boldsymbol{p}$ and $\boldsymbol{L} = \boldsymbol{x}\times\boldsymbol{p}$ to show

$$\boldsymbol{\sigma}\cdot\boldsymbol{p} = \frac{1}{r^2}\,(\boldsymbol{\sigma}\cdot\boldsymbol{x})(\boldsymbol{\sigma}\cdot\boldsymbol{x})(\boldsymbol{\sigma}\cdot\boldsymbol{p}) = \frac{\boldsymbol{\sigma}\cdot\boldsymbol{x}}{r^2}(\boldsymbol{x}\cdot\boldsymbol{p} + i\boldsymbol{\sigma}\cdot\boldsymbol{L}). \tag{7.22}$$

Thus the effect of the operator $\boldsymbol{\sigma}\cdot\boldsymbol{p}$, which appears in (7.15) and (7.16), on the eigenstates (7.18) may be determined in terms of the effects of the operators $\boldsymbol{\sigma}\cdot\boldsymbol{L}$, which is already determined, and of the two other operators that appear on the right hand side of (7.18). One of these is, in the coordinate representation,

$$\boldsymbol{x}\cdot\boldsymbol{p} = -i\hbar r\frac{\partial}{\partial r}. \tag{7.23}$$

Third, the effect of the remaining operator in (7.22) turns out to be simple for our choice of eigenstates. Specifically, one finds that the spinors (7.7) satisfy the identity

$$\boldsymbol{\sigma}\cdot\boldsymbol{x}\,\phi^{(\pm)}_{j,m} = -r\phi^{(\mp)}_{j,m}. \tag{7.24}$$

The proof of the identity (7.24) is given as an exercise.

The final step in the argument is to consider the effect of a parity transformation. Under $\boldsymbol{x} \to -\boldsymbol{x}$ the momentum changes sign, that is, $\boldsymbol{p} \to -\boldsymbol{p}$, and the other quantities (apart from ϕ and χ) in (7.15) and (7.16) are unchanged. It follows that if ϕ and χ are eigenstates of partiy then their eigenvalues have opposite signs. The only possibilities are that

ϕ is proportional to $\phi^{(+)}_{j,m}$ and χ is proportional to $\phi^{(-)}_{j,m}$, or vice versa. The two choices are of the form

$$\psi = \begin{pmatrix} F(r)\phi^{(+)}_{j,m} \\ -if(r)\phi^{(-)}_{j,m} \end{pmatrix} \quad \text{or} \quad \psi = \begin{pmatrix} G(r)\phi^{(-)}_{j,m} \\ -ig(r)\phi^{(+)}_{j,m} \end{pmatrix}, \tag{7.25}$$

where $F(r)$, $f(r)$, $G(r)$, $g(r)$ are radial functions that are yet to be determined. (The factors of $-i$ are introduced in (7.25) for convenience so that some subsequent equations are real.)

7.4 Radial eigenvalues

Equations (7.15) and (7.16) with the first of (7.25) reduce to

$$(E - m_e c^2 + e\phi)F - \hbar c\left(\frac{d}{dr} + \frac{j+\frac{3}{2}}{r}\right) f = 0, \tag{7.26}$$

$$(E + m_e c^2 + e\phi)f + \hbar c\left(\frac{d}{dr} - \frac{j-\frac{1}{2}}{r}\right) F = 0. \tag{7.27}$$

The corresponding set of equations for the second choice in (7.25) is

$$(E + m_e c^2 + e\phi)G - \hbar c\left(\frac{d}{dr} + \frac{j-\frac{1}{2}}{r}\right) g \;=\; 0, \tag{7.28}$$

$$(E - m_e c^2 + e\phi)g + \hbar c\left(\frac{d}{dr} - \frac{j+\frac{3}{2}}{r}\right) G = 0. \tag{7.29}$$

On introducing the Coulomb potential (7.2) and writing

$$\lambda = j + \tfrac{1}{2}, \quad \varepsilon = E/m_e c^2, \quad x = r/r_c, \quad r_c = \hbar/m_e c, \quad \alpha = e^2/4\pi\varepsilon_0\hbar c, \tag{7.30}$$

(7.26) and (7.27) reduce to

$$\left(\varepsilon - 1 + \frac{Z\alpha}{x}\right) F - \left(\frac{d}{dx} + \frac{\lambda+1}{x}\right) f = 0, \tag{7.31}$$

$$ms\left(\varepsilon + 1 + \frac{Z\alpha}{x}\right) f + \left(\frac{d}{dx} - \frac{\lambda-1}{x}\right) F = 0, \tag{7.32}$$

respectively. The other pair of equations (7.28) and (7.29) reduces to a similar pair of equations obtained from (7.31) and (7.32) by the replacements

$$F \to G \quad f \to g \quad \lambda \to -\lambda. \tag{7.33}$$

As a result it suffices to consider only the pair (7.31) and (7.32) in detail.

To proceed formally, one eliminates either F or f from (7.31) and (7.32) and obtains a second order differential equation for the other. Normalizable solutions of the resulting equation are sought. This is closely analogous to the conventional procedure for constructing the radial wave functions for the hydrogen atom in nonrelativistic quantum mechanics, in which case the normalizable solutions are generalized Laguerre polynomials. As in the nonrelativistic case there are normalizable solutions only for specific values of the energy, and these specific values are the energy eigenvalues. In the relativistic case the normalizable solutions can be written in terms of the hypergeometric function. The detailed solutions are not derived here, and the following heuristic discussion is aimed at determining the energy eigenvalues without actually solving the second order differential equation.

A prelimiary point is that we are interested in bound states, which correspond to $E < m_e c^2$ and hence to $\varepsilon < 1$. For large x the asymptotic form of the second order differential equation obtained from (7.31) and (7.32) have solutions $\propto \exp[\pm(1-\varepsilon^2)^{1/2}x]$, and clearly only the $-$ sign is consistent with the solutions being normalizable. Hence we may seek solutions of the form

$$\begin{pmatrix} F \\ f \end{pmatrix} = e^{-(1-\varepsilon^2)^{1/2}x} x^{\gamma} \sum_{\nu=0} \begin{pmatrix} a_\nu \\ b_\nu \end{pmatrix} x^{\nu}. \tag{7.34}$$

On substituting (7.34) into (7.31) and (7.32) one obtains

$$(\varepsilon-1)a_{\nu-1} + Z\alpha a_\nu + (1-\varepsilon^2)^{1/2} b_{\nu-1} - (\lambda+1+\gamma+\nu)b_\nu = 0, \tag{7.35}$$

$$(\varepsilon+1)b_{\nu-1} + Z\alpha b_\nu - (1-\varepsilon^2)^{1/2} a_{\nu-1} - (\lambda-1-\gamma-\nu)a_\nu = 0, \tag{7.36}$$

The power of γ is determined by requiring that for $\nu = 0$ the terms a_{-1} and b_{-1} in (7.35) and (7.36) be zero. This gives $Z^2\alpha^2 = \lambda^2 - (\gamma+1)^2$, which has two solutions, one of which would make the wave function too singular at $r = 0$ to be normalizable. The remaining solution is

$$\gamma = -1 + [(j+\tfrac{1}{2})^2 - Z^2\alpha^2]^{1/2}. \tag{7.37}$$

Interestingly, real solutions are possible for $j = \frac{1}{2}$ only if the nucleus is not too highly charged, specifically, only for $Z < 1/\alpha \approx 137$.

As in nonrelativistic quantum mechanics, the next step in the argument is that normalizable solutions result only if the power series expansions (7.23) terminate, so that the function multiplying $\exp[\pm(1-\varepsilon^2)^{1/2}x]$ is a polynomial. Let us suppose that the highest term is $\nu = n'$, so that we have $a_{n'+1} = b_{n'+1} = 0$. Then for $\nu = n'$ in (7.35) and (7.36) one obtains

$$\frac{b_{n'}}{a_{n'}} = \left(\frac{1-\varepsilon}{1+\varepsilon}\right)^{1/2}. \tag{7.38}$$

By multiplying (7.35) by $(1+\varepsilon^2)^{1/2}$ and (7.36) by $(1-\varepsilon^2)^{1/2}$ and adding the resulting equations, one obtains

$$\frac{b_\nu}{a_\nu} = \frac{Z\alpha(1+\varepsilon^2)^{1/2} + (\lambda - 1 - \gamma - \nu)(1-\varepsilon^2)^{1/2}}{Z\alpha(1-\varepsilon^2)^{1/2} + (\lambda + 1 + \gamma + \nu)(1+\varepsilon^2)^{1/2}}. \tag{7.39}$$

On setting $\nu = n'$ in (7.39) and comparing with (7.38), one obtains an identity that determines the energy eigenvalues. These are given by the fine structure formula (7.11).