# 232A Lecture Notes
## Hydrogen atom and relativistic corrections

In the case of hydrogen-like atoms, one can solve the Dirac equation exactly to find the energy levels. The derivation is discussed below. We find

$$E_{njlm} = mc^2 \left[ 1 + \left( \frac{Z\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - (Z\alpha)^2}} \right)^2 \right]^{-1/2} . \qquad (1)$$

The principal quantum numbers are $n = 1, 2, 3, \cdots$ as usual, and $j + 1/2 \leq n$. The important point is the degeneracy between $2s_{1/2}$ and $2p_{1/2}$ states (similarly, $3s_{1/2}$ and $3p_{1/2}$, $3p_{3/2}$ and $3d_{3/2}$, etc) persists in the exact solution to the Dirac equation. This degeneracy is lifted by so-called Lamb shifts, due to the coupling of electron to the zero-point fluctuation of the radiation field. We will come back to this point later in class when we discuss the loop diagrams.

# 1 Schrödinger Equation

Let us first review the case with the Schrödinger equation. For the radial wave function $\psi = R(r) Y_l^m e^{-iEt/\hbar}$ the non-relativistic Schrödinger equation for the hydrogen atom reads as

$$\left[ \frac{\hbar^2}{2m} \left( -\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2} \right) - \frac{Ze^2}{r} \right] R = ER. \qquad (2)$$

Note that we use $\alpha = e^2/\hbar c$ in this lecture notes following the standard notation for the non-relativistic Schrödinger equation for the hydrogen atom, *not* $\alpha = e^2/4\pi\hbar c$ as in the QED notation.

For later purposes, we allow small modifications to the equation:

$$\left[ \frac{\hbar^2}{2\mu} \left( -\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{\lambda(\lambda+1)}{r^2} \right) - \frac{Ze^2}{r} \right] R = \epsilon R. \qquad (3)$$

Here, $\lambda$ may not be an integer. We consider such a seemingly crazy modifications because Klein–Gordon and Dira equations actually reduce to this form with non-integer $\lambda$.

First, we study the behavior at small $r$. The Coulomb potential $\propto 1/r$ is less important than the centrifugal barrier $\propto 1/r^2$ or the second derivatives and we can determine the behavior using only terms in the parentheses. For $R(r) \sim r^\kappa$ for $r \to 0$,

$$\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{\lambda(\lambda+1)}{r^2}\right) r^\kappa = (-\kappa(\kappa-1) - 2\kappa + \lambda(\lambda+1)) r^{\kappa-2} = 0. \quad (4)$$

Therefore $\kappa(\kappa+1) = \lambda(\lambda+1)$ and hence $\kappa = \lambda$ or $-\lambda - 1$. The latter is singular for $r \to 0$ and is not allowed. Hence, $R(r) \sim r^\lambda$ for $r \to 0$.

Now we write $R(r) = r^\lambda \rho(r)$, where $\rho(0) \neq 0$. The equation becomes

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2(\lambda+1)}{r}\frac{d}{dr}\right) - \frac{Ze^2}{r}\right]\rho = \epsilon\rho. \quad (5)$$

We are interested in the bound state solutions, and therefore $\rho(r) \sim e^{-\beta r}$ for $r \to \infty$. The large distance behavior is dominated by the second derivative because it does not have a power suppression in $r$ and hence

$$-\frac{\hbar^2}{2\mu}\beta^2 = \epsilon. \quad (6)$$

The large distance behavior is therefore $e^{-\sqrt{-2\mu\epsilon}\, r/\hbar}$.

We can write $\rho(r) = f(r) e^{-\beta r}$. By substituting this form into the differential equation, we find

$$-\frac{\hbar^2}{2\mu}\left(\beta^2 f - 2\beta f' + f'' - \beta\frac{2(\lambda+1)}{r} f + \frac{2(\lambda+1)}{r} f'\right) - \frac{Ze^2}{r} f = \epsilon f, \quad (7)$$

and hence

$$r f'' + (2(\lambda+1) - 2\beta r) f' + \left(\frac{2Ze^2\mu}{\hbar^2} - 2(\lambda+1)\beta\right) f = 0. \quad (8)$$

To avoid $f(r)$ to diverge at infinity to overcome the wanted exponential suppression, we require $f(r)$ to be a polynomial in $r$,

$$f(r) = \sum_{k=0}^{i} c_k r^k. \quad (9)$$

The differential equation then becomes

$$\sum_{k=0}^{K} c_k \left[ k(k-1)r^{k-1} + 2(\lambda+1-\beta r)kr^{k-1} + \left( \frac{2Ze^2\mu}{\hbar^2} - 2(\lambda+1)\beta \right) r^k \right] = 0. \tag{10}$$

Collecting coefficients of $r^k$, it gives us the recursion relation

$$k(k+1)c_{k+1} + 2(\lambda+1)(k+1)c_{k+1} - 2\beta k c_k + \left( \frac{2Ze^2\mu}{\hbar^2} - 2(\lambda+1)\beta \right) c_k = 0. \tag{11}$$

Namely,

$$c_{k+1} = \frac{2}{(2\lambda+2+k)(k+1)} \left( -\frac{Ze^2\mu}{\hbar^2} + (\lambda+1+k)\beta \right) c_k. \tag{12}$$

In order for $f(r)$ to be a polynomial, $c_{K+1} = 0$ for some $K$. Therefore, we need

$$\frac{Ze^2\mu}{\hbar^2} + (\lambda+1+K)\beta = 0. \tag{13}$$

Remembering Eq. (6), we find the quantized energies

$$\epsilon = -\frac{\hbar^2}{2\mu}\beta^2 = -\frac{\hbar^2}{2\mu}\left( \frac{Ze^2\mu}{\hbar^2(\lambda+1+K)} \right)^2 = -\frac{(Ze^2)^2\mu}{2\hbar^2(\lambda+1+K)^2} = -\frac{(Z\alpha)^2\mu c^2}{2\nu^2} . \tag{14}$$

In the last step, we defined $\nu = \lambda + 1 + K = \lambda + 1, \lambda + 2, \cdots$. Note that we never had to assume that $\lambda$ is an integer in the above discussions.

When $\lambda$ *is* an integer $l$ (and $\mu = m$, $\epsilon = E$), we define $n = l + 1 + K = l + 1, l + 2, \cdots$ and obtain the usual formula

$$E_n = -\frac{(Z\alpha)^2 mc^2}{2n^2} . \tag{15}$$

# 2 Klein–Gordon Equation

It has been of interest to nuclear and atomic physicists to study bound states of charged pions to nuclei, "pi-mesic atoms." The point is that the pion is more than 200 times heavier than the electron, and hence the "Bohr radius" is correspondingly shorter, down to $10^{-11}$ cm level. Therefore pions probe much deeper structure than electrons do. Their energy levels are obtained by solving the Klein–Gordon equation in the Coulomb potential. (For realistic pi-mesic atoms, one has to consider also the strong interaction with the nucleus.)

We will see below that the time-independent field equation for the radial wave function $\phi = R(r)Y_l^m e^{-iEt/\hbar}$ has the same form as the non-relativistic Schrödinger equation for the hydrogen atom,

$$\left[\frac{\hbar^2}{2\mu}\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{\lambda(\lambda+1)}{r^2}\right) - \frac{Ze^2}{r}\right] R = \epsilon R. \tag{16}$$

We write $\mu$, $\lambda$, $\epsilon$ in terms of $E$, $m$, and $l$ starting from the Klein–Gordon equation. Note that we use $\alpha = e^2/\hbar c$ in this lecture notes following the standard notation for the non-relativistic Schrödinger equation for the hydrogen atom, *not* $\alpha = e^2/4\pi\hbar c$ as in the QED notation or $\alpha = e^2/4\pi\epsilon_0\hbar c$ in the SI system.

The Klein–Gordon field equation in the presence of the electromagnetic field is

$$D_\mu D^\mu \phi = (\partial_\mu - ieA_\mu)(\partial^\mu - ieA^\mu)\phi = 0. \tag{17}$$

In the static Coulomb field $eA_0 = -\frac{Ze^2}{r}$ and $\vec{A} = 0$, and going to the spherical coordinates and $\phi = R(r)Y_l^m e^{-iEt/\hbar}$, the field equation in the presence of the hydrogen atom is

$$\left[\frac{1}{c^2}\left(-E - \frac{Ze^2}{r}\right)^2 + \hbar^2\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right) - m^2c^2\right] R = 0. \tag{18}$$

By reorganizing terms, we find

$$\left[\frac{\hbar^2 c^2}{2E}\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1) - Z^2\alpha^2}{r^2}\right) - \frac{Ze^2}{r}\right] R = \frac{E^2 - (mc^2)^2}{2E} R. \tag{19}$$

By comparing to the Schrödinger-like equation Eq. (3), we find

$$\mu = E/c^2 \tag{20}$$

$$\lambda = \sqrt{\left(l + \frac{1}{2}\right)^2 - Z^2\alpha^2} - \frac{1}{2} \tag{21}$$

$$\epsilon = \frac{E^2 - (mc^2)^2}{2E}. \tag{22}$$

Eq. (3) has exactly the same form as the Schrödinger equation for the hydrogen atom, except that $\lambda$ is not an integer. Therefore the boundstate eigenvalues are given by

$$\epsilon = -\frac{1}{2}\frac{Z^2\alpha^2\mu c^2}{\nu^2},$$

where the "principal quantum number" $\nu$ takes values $\nu = \lambda+1, \lambda+2, \lambda+3, \cdots$. This observation allows us to solve for $E$.

$$\frac{E^2-(mc^2)^2}{2E} = -\frac{1}{2}\frac{Z^2\alpha^2 E}{\nu^2}. \tag{23}$$

Solving for $E$, we find[1]

$$E = \frac{mc^2}{\sqrt{1+Z^2\alpha^2/\nu^2}}. \tag{24}$$

We now Expand $E$ up to $O(Z^2\alpha^2)$ and see that it agrees with the result of conventional Schrödinger equation including the rest energy. By expanding Eq. (24) up to $O(Z^2\alpha^2)$, we find

$$E = mc^2\left(1-\frac{1}{2}\frac{Z^2\alpha^2}{\nu^2}+O(Z^4\alpha^4)\right). \tag{25}$$

Note that $\lambda = l+O(Z^2\alpha^2)$. Therefore, $\nu = \lambda+k$ ($k$ is a non-negative integer) and hence $\nu$ is also an integer up to an $O(Z^2\alpha^2)$ correction. Neglecting $O(Z^4\alpha^4)$ terms, we find the principal quantum number $n = \nu+O(Z^2\alpha^2)$ and hence

$$E = mc^2 - \frac{1}{2}\frac{Z^2\alpha^2 mc^2}{n^2}+O(Z^4\alpha^4). \tag{26}$$

The result agrees with conventional Schrödinger equation at this order.

We next expand $E$ in Eq. (24) up to $O(Z^4\alpha^4)$, and find

$$E = mc^2\left(1-\frac{1}{2}\frac{Z^2\alpha^2}{\nu^2}+\frac{3}{8}\frac{Z^4\alpha^4}{\nu^4}+O(Z^6\alpha^6)\right). \tag{27}$$

[1] I've read somewhere that Klein–Gordon equation was the first equation considered by Schrödinger. He actually solved the hydrogen atom problem with the Klein–Gordon equation (or maybe the "original" Schrödinger equation), and found that the result does not agree with data concerning the fine structure. He then abandoned it and took the non-relativistic limit so that the equation and the data agree within the approximation. It is sometimes a good idea to ignore the failure and forge ahead!

The difference between $\nu$ and $n$ at $O(Z^2\alpha^2)$ cannot be ignored in the second term because it gives rise to a term of $O(Z^4\alpha^4)$. By expanding $\lambda$ up to $O(Z^2\alpha^2)$,

$$\lambda = l - \frac{Z^2\alpha^2}{2l+1} + O(Z^4\alpha^4), \tag{28}$$

we can write

$$\nu = n - \frac{Z^2\alpha^2}{2l+1} + O(Z^4\alpha^4), \tag{29}$$

and hence

$$E = mc^2\left(1 - \frac{1}{2}\frac{Z^2\alpha^2}{n^2} - \frac{Z^4\alpha^4}{(2l+1)n^3} + \frac{3}{8}\frac{Z^4\alpha^4}{n^4} + O(Z^6\alpha^6)\right). \tag{30}$$

As before, the second term is the term we obtain in non-relativistic Schrödinger equation.

The question is what are the next two terms. They are the so-called "relativistic correction," obtained by expanding the relativistic kinetic energy

$$\sqrt{\vec{p}^2c^2 + (mc^2)^2} = mc^2 + \frac{\vec{p}^2}{2m} - \frac{1}{8}\frac{(\vec{p}^2)^2}{m^3c^2} + O(\vec{p}^6). \tag{31}$$

Because $|\vec{p}|/m = v = Z\alpha$ in hydrogen-like atoms, $O(\vec{p}^6) \sim O(Z^6\alpha^6)$ and these terms are beyond our interest. We can rewrite

$$\vec{p}^2|nlm\rangle = 2m\left(\frac{Ze^2}{r} - \frac{1}{2}\frac{Z^2\alpha^2mc^2}{n^2}\right), \tag{32}$$

and hence

$$\langle nlm| - \frac{1}{8}\frac{(\vec{p}^2)^2}{m^3c^2}|nlm\rangle = -\frac{1}{2mc^2}\langle nlm|\left(\frac{Ze^2}{r} - \frac{1}{2}\frac{Z^2\alpha^2mc^2}{n^2}\right)^2|nlm\rangle. \tag{33}$$

Using (see below for the derivation of these expectation values)

$$\langle nlm|\frac{1}{r}|nlm\rangle = \frac{1}{n^2a}, \qquad \langle nlm|\frac{1}{r^2}|nlm\rangle = \frac{2}{(2l+1)n^3a^2}, \tag{34}$$

with $a = \hbar^2/mZe^2 = \hbar/mcZ\alpha$, we find

$$\langle nlm| - \frac{1}{8}\frac{(\vec{p}^2)^2}{m^3c^2}|nlm\rangle = -\frac{Z^4\alpha^4}{(2l+1)n^3} + \frac{3}{8}\frac{Z^4\alpha^4}{n^4}. \tag{35}$$

This precisely reproduces the $O(Z^4\alpha^4)$ terms in Eq. (24), and hence the relativistic correction $-\frac{1}{8}\frac{\vec{p}^4}{m^3c^4}$ is their origin. Obviously, there is no spin-orbit coupling because the Klein–Gordon field does not have spin.

The energy levels of the Klein–Gordon equation in the Coulomb potential is the starting point for the study of $\pi$-mesic atoms, *i.e*, the bound states of negative pions $\pi^-$ to nuclei.

We can derive Eq. (34) without suffering through generating functions for Laguerre polynomials by using the Feynman-Hellman theorem which states[2]

$$\langle\psi|\frac{\partial H}{\partial\lambda}|\psi\rangle = \frac{\partial E}{\partial\lambda}, \tag{36}$$

quite generally when a Hamiltonian $H$, its eigenstates $|\psi\rangle$, and its eigenvalues $E$ depend on a parameter $\lambda$. (The eigenstates if degenerate must be diagonalized not to mix under infinitessimal changes in $\lambda$.) To show equation (36) start with

$$\frac{\partial}{\partial\lambda}(H|\psi\rangle) = \frac{\partial}{\partial\lambda}(E|\psi\rangle) \tag{37}$$

$$\frac{\partial H}{\partial\lambda}|\psi\rangle + H\frac{\partial}{\partial\lambda}|\psi\rangle = \frac{\partial E}{\partial\lambda}|\psi\rangle + E\frac{\partial}{\partial\lambda}|\psi\rangle, \tag{38}$$

and act on the left with $\langle\psi|$. Then $\langle\psi|H = \langle\psi|E$ so that the unwanted terms drop out:

$$\begin{aligned}\langle\psi|\frac{\partial H}{\partial\lambda}|\psi\rangle + E\langle\psi|\frac{\partial}{\partial\lambda}|\psi\rangle &= \langle\psi|\frac{\partial E}{\partial\lambda}|\psi\rangle + E\langle\psi|\frac{\partial}{\partial\lambda}|\psi\rangle \\ \Longrightarrow \langle\psi|\frac{\partial H}{\partial\lambda}|\psi\rangle &= \frac{\partial E}{\partial\lambda}.\end{aligned} \tag{39}$$

Now for the non-relativistic hydrogen atom,

$$H = \frac{\hbar^2}{2m}\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{l(l+1)}{r^2}\right) - \frac{Ze^2}{r}, \tag{40}$$

$$E = -\frac{Z^2\alpha^2mc^2}{2n^2}. \tag{41}$$

Mathematically, we can consider $Z$ to be a continuous parameter and apply the Feynman-Hellman theorem,

$$\langle nlm|\frac{1}{r}|nlm\rangle = -\frac{1}{e^2}\langle nlm|\frac{\partial H}{\partial Z}|nlm\rangle = -\frac{1}{e^2}\frac{\partial E}{\partial Z} = \frac{1}{e^2}\frac{Z\alpha^2mc^2}{n^2} = \frac{1}{n^2a}, \tag{42}$$

which is the first of (34). To find the second relation we can basically repeat the above argument with $l$ in place of $Z$, but there is one subtlety. For the Hamiltonian (40), the radial eigenvalue problem is well-defined even for non-integer $l$. But when solving for the radial wavefunction, we find a principle quantum number $n = n_r + l + 1$ where

[2] This derivation is by Ed Boyda.

$n_r = 0, 1, 2, \ldots$ must be an integer for the hypergeometric series to terminate and give a normalizable radial wavefunction. When we differentiate with respect to $l$ we must hold $n_r$, not $n$, fixed. In other words, $\frac{\partial n}{\partial l} = 1$. Then

$$\begin{aligned}\langle nlm|\frac{1}{r^2}|nlm\rangle &= \frac{2m}{\hbar^2(2l+1)}\langle nlm|\frac{\partial H}{\partial l}|nlm\rangle \\ &= \frac{2m}{\hbar^2(2l+1)}\frac{\partial E}{\partial l} \\ &= \frac{2m}{\hbar^2(2l+1)}\frac{2Z^2\alpha^2mc^2}{2n^3}\frac{\partial n}{\partial l} \\ &= \frac{2}{(2l+1)n^3a^2}. \end{aligned} \tag{43}$$

# 3 Hydrogen Atom in Dirac Equation

Now that you have seen how to obtain the energy levels for the Klein–Gordon equation, you must be wondering what we do for the Dirac equation. Here is how you do it. Starting from the Dirac equation (using Dirac's notation $\beta = \gamma^0$, $\vec{\alpha} = \gamma^0\vec{\gamma}$),

$$\left[E + \frac{Ze^2}{r} - c\vec{\alpha}\cdot\vec{p} - mc^2\beta\right]\psi = 0, \tag{44}$$

multiply by

$$\left[E + \frac{Ze^2}{r} + c\vec{\alpha}\cdot\vec{p} + mc^2\beta\right] \tag{45}$$

from the left. Then you find

$$\left[\left(E + \frac{Ze^2}{r}\right)^2 - c^2\vec{p}^2 - (mc^2)^2 + c\vec{\alpha}\cdot\left(-i\hbar\vec{\nabla}\frac{Ze^2}{r}\right)\right]\psi = 0. \tag{46}$$

The anti-commutation relation $\{\alpha^i, \alpha^j\} = 2\delta^{ij}$, $\{\alpha^i, \beta\} = 0$ had been used in simplifying the expression. Writing out the derivative acting on the Coulomb potential, we find

$$\left[\left(E + \frac{Ze^2}{r}\right)^2 - c^2\vec{p}^2 - (mc^2)^2 + i\hbar c\vec{\alpha}\cdot\hat{\vec{r}}\frac{Ze^2}{r^2}\right]\psi = 0, \tag{47}$$

using the notation $\hat{\vec{r}} = \vec{r}/r$. At this point, we also rewrite $\vec{p}^2$ using the spherical coordinates,

$$\left[\left(E + \frac{Ze^2}{r}\right)^2 + c^2\hbar^2\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1)}{r^2}\right) - (mc^2)^2 + i\hbar c\vec{\alpha}\cdot\hat{\vec{r}}\frac{Ze^2}{r^2}\right]\psi = 0. \tag{48}$$

We can block-diagonalize the matrix $\vec{\alpha}$ as

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & -\vec{\sigma} \end{pmatrix}. \tag{49}$$

Then depending on upper or lower two components, we have $\vec{\alpha}\cdot\hat{\vec{r}} = \pm\vec{\sigma}\cdot\hat{\vec{r}}$. Now the equation becomes[3]

$$\left[E^2 - (mc^2)^2 + 2E\frac{Ze^2}{r} + c^2\hbar^2\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1) - Z^2\alpha^2 \pm iZ\alpha\vec{\sigma}\cdot\hat{\vec{r}}}{r^2}\right)\right]\psi = 0. \tag{50}$$

The non-trivial point with this equation is to deal with the numerator $l(l+1) - Z^2\alpha^2 \pm iZ\alpha\vec{\sigma}\cdot\hat{\vec{r}}$. The trick is to note that it commutes with $\vec{J} = \vec{L} + \vec{\sigma}/2$. Therefore, we can look at the subspace of the Hilbert space with fixed $j$ and hence $l = j \pm 1/2$. Then $\vec{\sigma}\cdot\hat{\vec{r}}$ has a matrix element only between states of differing $l$. On the other hand, $(\vec{\sigma}\cdot\hat{\vec{r}})^2 = 1$, and hence

$$\begin{aligned} 1 &= \langle jm; l = j + \frac{1}{2}|(\vec{\sigma}\cdot\hat{\vec{r}})^2|jm; l = j + \frac{1}{2}\rangle \\ &= \langle jm; l = j + \frac{1}{2}|\vec{\sigma}\cdot\hat{\vec{r}}|jm; l = j - \frac{1}{2}\rangle\langle jm; l = j - \frac{1}{2}|\vec{\sigma}\cdot\hat{\vec{r}}|jm; l = j + \frac{1}{2}\rangle. \\ &= \left|\langle jm; l = j + \frac{1}{2}|\vec{\sigma}\cdot\hat{\vec{r}}|jm; l = j - \frac{1}{2}\rangle\right|^2. \end{aligned} \tag{51}$$

Without a loss of generality, we can adopt the phase convention that

$$\langle jm; l = j + \frac{1}{2}|\vec{\sigma}\cdot\hat{\vec{r}}|jm; l = j - \frac{1}{2}\rangle = 1. \tag{52}$$

[3]It may look like this equation violates parity because the spin $\vec{\sigma}$ is axial-vector while $\hat{\vec{r}}$ is a vector. It actually preserves parity. This is due to the fact that the intrinsic parity comes from $\gamma^0$, whose eigenvalues are $+1$ for the positive energy solutions at rest, and $-1$ for the negative energy solutions at rest.

This matrix element can be computed explicitly to verify this argument. The two states we compare have definite $j$ and $m$, where $l = j + \frac{1}{2}$

$$|j,m\rangle_+ = |j+\frac{1}{2}, m+\frac{1}{2}; \downarrow\rangle \sqrt{\frac{j+m+1}{2(j+1)}} - |j+\frac{1}{2}, m-\frac{1}{2}; \uparrow\rangle \sqrt{\frac{j-m+1}{2(j+1)}} \ , \tag{53}$$

or $l = j - \frac{1}{2}$

$$(-1)^{j+m}|j,m\rangle_- = |j-\frac{1}{2}, m+\frac{1}{2}; \downarrow\rangle \sqrt{\frac{j-m}{2j}} + |j-\frac{1}{2}, m-\frac{1}{2}; \uparrow\rangle \sqrt{\frac{j+m}{2j}} \ . \tag{54}$$

using the standard Clebsch–Gordan coefficients.

On the other hand, utilizing the identities

$$\int Y_{l_1}^{m_1} Y_{l_2}^{m_2} Y_{l_3}^{m_3} d\Omega = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \left( \begin{array}{ccc} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{array} \right), \tag{55}$$

we find

$$\langle l+1, m | \cos\theta | l, m\rangle = \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} \tag{56}$$

$$\langle l+1, m+1 | \sin\theta e^{i\phi} | l, m\rangle = -\sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}} \tag{57}$$

$$\langle l+1, m-1 | \sin\theta e^{-i\phi} | l, m\rangle = \sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}} \tag{58}$$

We rewrite

$$\vec{\sigma} \cdot \hat{\vec{r}} = \sin\theta e^{i\phi} S_- + \sin\theta e^{-i\phi} S_+ + 2\cos\theta S_z \ . \tag{59}$$

Therefore,

$$\begin{aligned}
&(-1)^{j+m} \langle j,m|_+ \vec{\sigma} \cdot \hat{\vec{r}} |j,m\rangle_- \\
&= \left[ \sqrt{\frac{j+m+1}{2(j+1)}} \langle j+\frac{1}{2}, m+\frac{1}{2}; \downarrow | - \sqrt{\frac{j-m+1}{2(j+1)}} \langle j+\frac{1}{2}, m-\frac{1}{2}; \uparrow | \right] \\
&\quad \vec{\sigma} \cdot \hat{\vec{r}} \left[ |j-\frac{1}{2}, m+\frac{1}{2}; \downarrow\rangle \sqrt{\frac{j-m}{2j}} + |j-\frac{1}{2}, m-\frac{1}{2}; \uparrow\rangle \sqrt{\frac{j+m}{2j}} \right] \\
&= \sqrt{\frac{j+m+1}{2(j+1)}} \langle j+\frac{1}{2}, m+\frac{1}{2}; \downarrow | \sin\theta e^{i\phi} S_- |j-\frac{1}{2}, m-\frac{1}{2}; \uparrow\rangle \sqrt{\frac{j+m}{2j}} \\
&\quad - \sqrt{\frac{j-m+1}{2(j+1)}} \langle j+\frac{1}{2}, m-\frac{1}{2}; \uparrow | \sin\theta e^{-i\phi} S_+ |j-\frac{1}{2}, m+\frac{1}{2}; \downarrow\rangle \sqrt{\frac{j-m}{2j}}
\end{aligned}$$

$$
\begin{aligned}
& +\sqrt{\frac{j+m+1}{2(j+1)}}\langle j+\frac{1}{2},m+\frac{1}{2};\downarrow|2\cos\theta S_z|j-\frac{1}{2},m+\frac{1}{2};\downarrow\rangle\sqrt{\frac{j-m}{2j}} \\
& -\sqrt{\frac{j-m+1}{2(j+1)}}\langle j+\frac{1}{2},m-\frac{1}{2};\uparrow|2\cos\theta S_z|j-\frac{1}{2},m-\frac{1}{2};\uparrow\rangle\sqrt{\frac{j+m}{2j}} \\
= & -\sqrt{\frac{j+m+1}{2(j+1)}}\sqrt{\frac{(j+m)(j+m+1)}{2j(2j+2)}}\sqrt{\frac{j+m}{2j}} \\
& -\sqrt{\frac{j-m+1}{2(j+1)}}\sqrt{\frac{(j-m)(j-m+1)}{2j(2j+2)}}\sqrt{\frac{j-m}{2j}} \\
& -\sqrt{\frac{j+m+1}{2(j+1)}}\sqrt{\frac{(j+m+1)(j-m)}{2j(2j+2)}}\sqrt{\frac{j-m}{2j}} \\
& -\sqrt{\frac{j-m+1}{2(j+1)}}\sqrt{\frac{(j+m)(j-m+1)}{2j(2j+2)}}\sqrt{\frac{j+m}{2j}} \\
= & -\frac{(j+m)(j+m+1)}{2j(2j+2)}-\frac{(j-m)(j-m+1)}{2j(2j+2)} \\
& -\frac{(j+m+1)(j-m)}{2j(2j+2)}-\frac{(j+m)(j-m+1)}{2j(2j+2)} \\
= & -1
\end{aligned}
\tag{60}
$$

Since this is an off-diagonal element, we can always choose the relative phase between the two states to make it always +1.

Then on this subspace of $l = j + \frac{1}{2}$ and $l = j - \frac{1}{2}$, the numerator has the form

$$
l(l+1)-Z^2\alpha^2 \pm iZ\alpha\vec{\sigma}\cdot\hat{\vec{r}} = \begin{pmatrix} (j+\frac{1}{2})(j+\frac{3}{2})-Z^2\alpha^2 & \mp iZ\alpha \\ \mp iZ\alpha & (j-\frac{1}{2})(j+\frac{1}{2})-Z^2\alpha^2 \end{pmatrix}. \tag{61}
$$

The eigenvlaues of this matrix are easily obtained, but we intentionally write the eigenvalues as $\lambda(\lambda+1)$. The motiation to do so must be clear from what we did with the Klein–Gordon equation. The two solutions are

$$
\lambda_+ = \left[\left(j+\frac{1}{2}\right)^2 - Z^2\alpha^2\right]^{1/2}, \qquad \lambda_- = \left[\left(j+\frac{1}{2}\right)^2 - Z^2\alpha^2\right]^{1/2} - 1. \tag{62}
$$

Using $\lambda$, the Dirac equation is now

$$
\left[E^2 - (mc^2)^2 + 2E\frac{Ze^2}{r} + c^2\hbar^2\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{\lambda(\lambda+1)}{r^2}\right)\right]\psi = 0. \tag{63}
$$

It has the same form as the Klein–Gordon equation except $\lambda$. By following the same arguments, we find the energy eigenvalues

$$E = \frac{mc^2}{\sqrt{1 + Z^2\alpha^2/\nu^2}}, \tag{64}$$

with $\nu = \lambda + 1, \lambda + 2, \cdots$. The solutions with both $\lambda_+$ and $\lambda_-$ give the same set of $\nu$'s, except that the smallest $\nu$ is obtained only from $\lambda_-$ with $j = 1/2$. This corresponds to the fact that $n = 1$ state has only $l = 0$ which does not mix with an $l = 1$ state. The degeneracy of the eigenvalues for two solutions is split only by Lamb shift. The principal quantum number is $\nu$ at the lowest order in $Z\alpha$, and hence

$$\nu = n + \left[\left(j + \frac{1}{2}\right)^2 - Z^2\alpha^2\right]^{1/2} - \left(j + \frac{1}{2}\right). \tag{65}$$

We finally find the energy levels of the Dirac equation

$$E = mc^2 \left[1 + \left(\frac{Z\alpha}{n - (j+1/2) + [(j+1/2)^2 - Z^2\alpha^2]^{1/2}}\right)^2\right]^{-1/2}, \tag{66}$$

showing Eq. (1).

# 4 Non-relativistic Limit

For more general background electromagnetic fields, the gauge invariance uniquely fixes the form of the interaction between the Dirac field and the electromangetic vector potential. It follows the same rule in the Schrödinger theory $\vec{p} \to \vec{p} - \frac{e}{c}\vec{A}$, or equivalently, $-i\hbar\vec{\nabla} \to -i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}$. Its Lorentz-covariant generalization also determines the time-derivative: $i\hbar\frac{\partial}{\partial t} \to i\hbar\frac{1}{c}\frac{\partial}{\partial t} - \frac{e}{c}\phi$. (The relative sign difference is due to the fact that $A_\mu = (\phi, -\vec{A})$ transforms the same way as the derivative $\partial_\mu = (\frac{1}{c}\frac{\partial}{\partial t}, \vec{\nabla})$.) Therefore, the Dirac action is now

$$\int d\vec{x}dt\psi^\dagger \left(i\hbar\frac{\partial}{\partial t} - e\phi - c\vec{\alpha}\cdot(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}) - mc^2\beta\right)\psi. \tag{67}$$

The Dirac equation is again obtained by varying it with respect to $\psi^\dagger$,

$$\left(i\hbar\frac{\partial}{\partial t} - e\phi - c\vec{\alpha}\cdot(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}) - mc^2\beta\right)\psi. \tag{68}$$

Therefore, we are interested in solving the equation

$$\left[c\vec{\alpha}\cdot\left(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}\right)+mc^2\beta+e\vec{A}^0\right]\psi=E\psi. \tag{69}$$

The way we will discuss it is by a sytematic expansion in $\vec{v}=\vec{p}/m$. It is basically a non-relativisic approximation keeping only a few first orders in the expansion. Let us write Eq. (69) explicitly in the matrix form, and further write $E=mc^2+E'$ so that $E'$ is the energy of the electron on top of the rest energy. We obtain

$$\begin{pmatrix} e\phi & c\vec{\sigma}\cdot(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}) \\ c\vec{\sigma}\cdot(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A}) & -2mc^2+e\phi \end{pmatrix}\psi=E'\psi. \tag{70}$$

The solution lives mostly in the large components, *i.e.*. the upper two components in $\psi$. The equation is diagonal in the absence of $\vec{\sigma}\cdot(-i\hbar\vec{\nabla}-\frac{e}{c}\vec{A})$, and we can regard it as a perturbation and expand systematically in powers of it. To simplify notation, we will write $\vec{p}=-i\hbar\vec{\nabla}$, even though it must be understood that we are not talking about the "momentum operator" $\vec{p}$ acting on the Hilbert space, but rather a differential operator acting on the field $\psi$. Let us write four components in terms of two two-component vectors,

$$\psi=\begin{pmatrix}\chi\\ \eta\end{pmatrix}, \tag{71}$$

where the large component $\chi$ is a two-component vector describing a spin two particle (spin up and down states). $\eta$ is the small component which vanishes in the non-relativistic limit. Writing out Eq. (70) in terms of $\chi$ and $\eta$, we obtain

$$e\phi\chi+c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\eta=E'\chi \tag{72}$$

$$c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\chi+(-2mc^2+e\phi)\eta=E'\eta. \tag{73}$$

Using Eq. (73) we find

$$\eta=\frac{1}{E'+2mc^2-e\phi}c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\chi. \tag{74}$$

Substituting it into Eq. (73), we obtain

$$e\phi\chi+c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\frac{1}{E'+2mc^2-e\phi}c\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})\chi=E'\chi. \tag{75}$$

In the non-relativistic limit, $E', e\phi \ll mc^2$, and hence we drop them in the denominator. Within this approximation (called Pauli approximation), we find

$$e\phi\chi + \frac{[\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})]^2}{2m}\chi = E'\chi. \tag{76}$$

The last step is to rewrite the numerator in a simpler form. Noting $\sigma^i\sigma^j = \delta^{ij} + i\epsilon_{ijk}\sigma^k$,

$$\begin{aligned}
[\vec{\sigma}\cdot(\vec{p}-\frac{e}{c}\vec{A})]^2 &= (\delta^{ij} + i\epsilon_{ijk}\sigma^k)(p^i - \frac{e}{c}A^i)(p^j - \frac{e}{c}A^j) \\
&= (\vec{p}-\frac{e}{c}\vec{A})^2 + \frac{i}{2}\epsilon_{ijk}\sigma^k[p^i - \frac{e}{c}A^i, p^j - \frac{e}{c}A^j] \\
&= (\vec{p}-\frac{e}{c}\vec{A})^2 + \frac{ie}{2c}\epsilon_{ijk}\sigma^k i\hbar(\nabla_i A^j - \nabla_j A^i) \\
&= (\vec{p}-\frac{e}{c}\vec{A})^2 - \frac{e\hbar}{c}\vec{\sigma}\cdot\vec{B}.
\end{aligned} \tag{77}$$

Then Eq. (76) becomes

$$\frac{(\vec{p}-\frac{e}{c}\vec{A})^2}{2m}\chi - 2\frac{e\hbar}{2mc}\vec{s}\cdot\vec{B} + e\phi\chi = E'\chi. \tag{78}$$

In other words, it is the standard non-relativistic Schrödinger equation except that the $g$-factor is fixed. The Dirac theory predicts $g = 2$! This is a great success of this theory.

# 5 Tani–Foldy–Wouthuysen Transformation

One can extend the systematic expansion further to higher orders. It is done usually with the method so-called Tani-Foldy–Wouthuysen transformation. The basic idea is keep performing unitary basis transformation on $\psi$ to eliminate small components at a given order in the expansion. The note here is based on Bjorken–Drell, "Relativisc Quantum Mechanics," McGraw-Hill, 1964.

Let us start with the free case, $H = c\vec{\alpha}\cdot\vec{p} + mc^2\beta$. The problem is to remove the mixing beween large and small components caused by the matrices $\vec{\alpha}$. Can we eliminate $\alpha$ completely from the Hamiltonian by a unitarity rotation? The answer is yes. You choose the unitarity rotation as

$$\psi' = e^{iS}\psi, \tag{79}$$

where $S = \beta\vec{\alpha}\cdot\vec{p}\theta(\vec{p})$ (it has nothing to do with the classical action). The Hamitonian is also correspondingly unitarity transformed to

$$\begin{aligned} H' &= e^{iS} H e^{-iS} \\ &= \left(\cos|\vec{p}|\theta + \frac{\beta\vec{\alpha}\cdot\vec{p}}{|\vec{p}|}\sin|\vec{p}|\theta\right)(c\vec{\alpha}\cdot\vec{p} + mc^2\beta)\left(\cos|\vec{p}|\theta - \frac{\beta\vec{\alpha}\cdot\vec{p}}{|\vec{p}|}\sin|\vec{p}|\theta\right) \\ &= c\vec{\alpha}\cdot\vec{p}\left(\cos 2|\vec{p}|\theta - \frac{mc^2}{|\vec{p}|c}\sin 2|\vec{p}|\theta\right) + \beta(mc^2\cos 2|\vec{p}|\theta + c|\vec{p}|\sin 2|\vec{p}|\theta) \end{aligned} \tag{80}$$

To eliminate the mixing between the large and small components, we choose the parameter $\theta$ so that the first term vanishes:

$$\tan 2|\vec{p}|\theta = \frac{|\vec{p}|}{mc}. \tag{81}$$

Then we find $\cos 2|\vec{p}|\theta = mc^2/\sqrt{c^2\vec{p}^2 + m^2c^4}$, $\sin 2|\vec{p}|\theta = c|\vec{p}|/\sqrt{c^2\vec{p}^2 + m^2c^4}$, and finally

$$H' = \beta\sqrt{c^2\vec{p}^2 + m^2c^4}. \tag{82}$$

This form correctly shows both positive and negative energy solutions.

Now we try to generalize this method in the presence of external radiation field, starting again from the Hamiltonian

$$H = c\vec{\alpha}\cdot(\vec{p} - \frac{e}{c}\vec{A}) + mc^2\beta + e\phi. \tag{83}$$

In this case, we must also allow ourselves to consider a time-dependent unitarity transformation. The Dirac equation

$$i\hbar\dot{\psi} = H\psi \tag{84}$$

rewritten for the unitarity transformed field $\psi' = e^{iS}\psi$ is

$$i\hbar\dot{\psi}' = \left[e^{iS}He^{-iS} - i\hbar e^{iS}\frac{\partial}{\partial t}e^{-iS}\right]\psi' = H'\psi' \tag{85}$$

which defines the transformed Hamiltonian $\psi'$. (Notice the similarity to the canonical transformations in the classical mechanics.)

We are interested in expanding $H'$ up to $O(p^4)$. To this order, we find

$$\begin{aligned} H' &= H + i[S,H] - \frac{1}{2}[S,[S,H]] - \frac{i}{6}[S,[S,[S,H]]] + \frac{1}{24}[S,[S,[S,[S,H]]]] \\ &\quad - i\hbar\dot{S} - \frac{i}{2}\hbar[S,\dot{S}] + \frac{1}{6}\hbar[S,[S,\dot{S}]]. \end{aligned} \tag{86}$$

In the free-particle case, we chose $S = -i\beta\vec{\alpha}\cdot\vec{p}\theta$ with $\theta = \frac{1}{2|\vec{p}|}\tan^{-1}\frac{|\vec{p}|}{mc} \simeq \frac{1}{2mc}$. Motivated by this, we can choose $S = -i\beta\vec{\alpha}\cdot(\vec{p} - \frac{e}{c}\vec{A})/2mc$. By calling $\mathcal{O} = \vec{\alpha}\cdot(\vec{p} - \frac{e}{c}\vec{A})$ and $\mathcal{E} = e\phi$, we find at this order

$$\begin{aligned} H' &= \beta\left(mc^2 + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3c^2}\right) + \mathcal{E} - \frac{1}{8m^2c^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i\hbar}{8m^2c^2}[\mathcal{O},\dot{\mathcal{O}}] \\ &\quad + \frac{\beta}{2mc}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2c} + i\hbar\beta\frac{\dot{\mathcal{O}}}{2mc}. \end{aligned} \tag{87}$$

The last three terms still mix large and small components because they are odd in $\mathcal{O}$. At this point, we perform another unitarity transformation using

$$S' = -i\beta\frac{\mathcal{O}'}{2mc} = -i\beta\frac{1}{2mc}\left(\frac{\beta}{2mc^2}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2c^2} + i\hbar\beta\frac{\dot{\mathcal{O}}}{2mc^2}\right). \tag{88}$$

Then the Hamiltonian is further transformed to

$$H'' = \beta\left(mc^2 + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3c^2}\right) + \mathcal{E} - \frac{1}{8m^2c^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i\hbar}{8m^2c^2}[\mathcal{O},\dot{\mathcal{O}}] + \mathcal{O}'', \tag{89}$$

where $\mathcal{O}''$ is still odd in $\alpha$, but is suppressed by $1/m^2$. Finally, using another unitarity transformation with $S'' = -i\beta\mathcal{O}''/2mc$ eliminates the last term and we find

$$H''' = \beta\left(mc^2 + \frac{\mathcal{O}^2}{2m} - \frac{\mathcal{O}^4}{8m^3c^2}\right) + \mathcal{E} - \frac{1}{8m^2c^2}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{i\hbar}{8m^2c^2}[\mathcal{O},\dot{\mathcal{O}}] \tag{90}$$

to this order. Now we write it out explicitly and find

$$\begin{aligned} H''' &= \beta\left(mc^2 + \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} - \frac{\vec{p}^4}{8m^3c^2}\right) + e\phi - \frac{e\hbar}{2mc}\beta\vec{\Sigma}\cdot\vec{B} \\ &\quad - \frac{ie\hbar^2}{8m^2c^2}\vec{\Sigma}\cdot(\vec{\nabla}\times\vec{E}) - \frac{e\hbar}{4m^2c^2}\vec{\Sigma}\cdot(\vec{E}\times\vec{p}) - \frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E}. \end{aligned} \tag{91}$$

The first term is nothing but the rest energy, and the second the non-relativistic kinetic term. The third term is the relativistic correction to the kinetic energy. The Coulomb potential term is there as desired, and the next term is the magnetic momentum coupling with $g = 2$ as we saw before. $\vec{\nabla}\times\vec{E} = 0$ for the Coulomb potential, while

$$-\frac{e\hbar}{4m^2c^2}\vec{\Sigma}\cdot(\vec{E}\times\vec{p}) = \frac{e\hbar}{4m^2c^2}\vec{\Sigma}\cdot\frac{1}{r}\frac{dV}{dr}(\vec{x}\times\vec{p}) = \frac{e\hbar}{4m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{\Sigma}\cdot\vec{L} \tag{92}$$

is the spin-orbit coupling (with the correct Thomas precession factor, where I assumed a central potential). The last term $-\frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E}$ is called Darwin term, in honor of the first person who solved the hydrogen atom problem exactly with the Dirac equation.[4]

The physical meaning of the relativistic correction, the spin-orbit couping, and the magnetic moment coupling are probably familiar to you. What is the Darwin term? It is attribtuted to a perculiar motion of a Dirac particle called *Zitterbewegung* (Schrödinger). One way to see it is by using Heisenberg equation of motion (well, we shouldn't use the "Hamiltonian" $\vec{\alpha}\cdot\vec{p}+m\beta$ too seriously because we abandoned the single-particle wave mechanics interpretation, but it is still instructive). The velocity operator is

$$i\hbar\frac{d}{dt}\vec{x} = [\vec{x}, H] = i\hbar c\vec{\alpha}. \tag{93}$$

This is already quite strange. The velocity operator $\dot{\vec{x}} = c\vec{\alpha}$ has eigenvalues $\pm c$ and velocities in different directions do not commute (*i.e.* not simultaneously observable). Clearly, this velocity is not the motion of the particle as a whole, but something rather different. To see this, we further consider the Heisenberg equation for the velocity operator when the particle is at rest $\vec{p}=0$ ($H = mc^2\beta$). Then,

$$i\hbar\frac{d^2}{dt^2}\vec{x} = [c\vec{\alpha}, H] = 2mc^3\vec{\alpha}\beta, \tag{94}$$

while its further derivative is

$$-\hbar^2\frac{d^3}{dt^3}\vec{x} = [2mc^3\vec{\alpha}\beta, H] = 4m^2c^5\vec{\alpha} = 4m^2c^4\frac{d}{dt}\vec{x}. \tag{95}$$

Therefore,

$$\frac{d}{dt}\vec{x}(t) = c\vec{\alpha}\cos\frac{2mc^2t}{\hbar} - ic\vec{\alpha}\beta\sin\frac{2mc^2t}{\hbar}, \tag{96}$$

which oscillates very rapidly with the period $\hbar/2mc^2 = 6\times 10^{-22}$ sec. (Note that $-i\vec{\alpha}\beta$ is hermitean, because $(-i\vec{\alpha}\beta)^\dagger = i\beta\vec{\alpha} = -i\vec{\alpha}\beta$ due to the anti-commutation relation.) The position is then obtained by integrating it:

$$\vec{x}(t) = \vec{x}(0) + \frac{\hbar}{2mc}\left(\vec{\alpha}\sin\frac{2mc^2t}{\hbar} + i\vec{\alpha}\beta\cos\frac{2mc^2t}{\hbar}\right). \tag{97}$$

This rapid motion of an "electron at rest" is the Zitterbewegung, a peculiarity in the relevatistic quantum mechanical motion of spin 1/2 particle. Because of this rapid motion of the electron, the net electric field the electron experiences is averaged over its "blur,"

[4]Dirac himself did not do this. An anecdote I've read is that Dirac was so proud of his equation that he was afraid of doing any tests which might falsify it. Of course he was technically capable enough to solve it exactly, but he didn't do it because of this fear. Interesting insight into the psychology of a genius.

and hence is somewhat different from the electric field at the position itself. The averaging of the electric field gives rise to the correction

$$\langle V \rangle = \frac{1}{2}\langle(\delta x^i)(\delta x^j)\rangle \frac{\partial^2 V}{\partial x^i \partial x^j}, \tag{98}$$

where the isotropy tells us that $\langle(\delta x^i)(\delta x^j)\rangle = \frac{1}{3}\delta^{ij}\langle(\delta x^i)^2\rangle = \delta^{ij}(\hbar/2mc)^2$, where I used the time average of the Zitterbewegung at the last step. Then the correction to the potential energy is

$$\langle eV \rangle = e\frac{1}{2}\frac{\hbar^2}{4m^2c^2}\Delta V = -\frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E}, \tag{99}$$

reproducing the Darwin term.

Now let us specialize to the case of the hydrogen atom $\vec{A} = 0$ and $e\phi = -Ze^2/r$. The energy levels of a hydrogen-like atom are perturbed by the additional terms in Eq. (91). The sum of the relativistic correction and the spin-orbit coupling gives a correction

$$(Z\alpha)^4 mc^2 \left(\frac{3}{8n^4} + \frac{j(j+1) - 3l(l+1) - \frac{3}{4}}{2l(l+1)(2l+1)n^3}\right) \tag{100}$$

Due to some magical reason I don't understand, for both possible cases where $l = j \pm \frac{1}{2}$ allowed by the addition of angular momenta, it simplifies to

$$(Z\alpha)^4 mc^2 \left(\frac{3}{8n^4} - \frac{1}{(2j+1)n^3}\right). \tag{101}$$

Therefore states with the same principal quantum number $n$ and the total angular momentum $j$, even if they come from different $l$, remain degenerate.

The case $l = 0$ is special and deserves attention. For this case, the spin-orbit interaction vanishes identically. The relativisic correction to the kinetic energy gives $(Z\alpha)^4 mc^2(\frac{3}{8n^4} - \frac{1}{n^3})$. However, for $s$-waves only, the Darwin term also contributes. For hydrogen-like atoms, the Darwin term is

$$-\frac{e\hbar^2}{8m^2c^2}\vec{\nabla}\cdot\vec{E} = \frac{e\hbar^2}{8m^2c^2}Ze4\pi\delta(\vec{x}) = \frac{Z\alpha\hbar^3}{8m^2c}4\pi\delta(\vec{x}). \tag{102}$$

The first-order perturbation in the Darwin term gives

$$\frac{Z\alpha\hbar^3}{8m^2c}4\pi|\psi(0)|^2 = (Z\alpha)^4 mc^2\frac{1}{2n^3}. \tag{103}$$

Therefore the sum of the relativistic correction and the Darwin term gives

$$(Z\alpha)^4 mc^2\left(\frac{3}{8n^4} - \frac{1}{2n^3}\right) = (Z\alpha)^4 mc^2\left(\frac{3}{8n^4} - \frac{1}{(2j+1)n^3}\right), \tag{104}$$

because $j = 1/2$ for $l = 0$, and hence happens to have the same form as Eq. (101) which is valid for $l \neq 0$

The principal quantum numbers are $n = 1, 2, 3, \cdots$ as usual, and $j+1/2 \leq n$. Expanding it up to $O(Z\alpha)^4$, we find

$$E_{njlm} = mc^2 \left[ 1 - \frac{(Z\alpha)^2}{2n^2} + \frac{(Z\alpha)^4}{n^3} \left( \frac{3}{8n} - \frac{1}{2j+1} \right) \right] \tag{105}$$

and agrees with the results based on Tani–Foldy–Wouthuysen transformation. One important point is the degeneracy between $2s_{1/2}$ and $2p_{1/2}$ states (similarly, $3s_{1/2}$ and $3p_{1/2}$, $3p_{3/2}$ and $3d_{3/2}$, etc) persists in the exact solution to the Dirac equation. This degeneracy is lifted by so-called Lamb shifts, due to the coupling of electron to the zero-point fluctuation of the radiation field. We will come back to this point later in class.