A Relativistic Electron in a Coulomb Potential

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The Problem

Solve the Dirac Equation for an electron in a Coulomb potential. Identify the conserved quantum numbers. Specify the degeneracies. Compare with solutions of the Schrödinger equation including relativistic and spin corrections.

Approach

My approach follows that taken by Dirac in [1] closely. A few modifications taken from [2] and [3] are included, particularly in regards to the final quantum numbers chosen.

The general strategy is to first find a set of transformations which turn the Hamiltonian for the system into a form that depends only on the radial variables r and p_r. Once this form is found, I solve it to find the energy eigenvalues and then discuss the energy spectrum.

The Radial Dirac Equation

We begin with the electromagnetic Hamiltonian

$$\mathcal{H} = p_0 - c\rho_1\vec{\sigma} \cdot \left(\vec{p} - \frac{q}{c}\vec{A}\right) + \rho_3 mc^2 \tag{1}$$

with

$$\rho_1 = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \tag{2}$$

$$\rho_3 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{3}$$

$$\vec{\sigma} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}, \begin{bmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{bmatrix}, \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{4}$$

We note that, for the Coulomb potential, we can set (using cgs units):

$$p_o = -e\Phi = -\frac{Ze^2}{r}$$

$$\vec{A} = 0$$

This leads us to this form for the Hamiltonian:

$$\mathcal{H} = -\frac{-Ze^2}{r} - c\rho_1 \vec{\sigma} \cdot \vec{p} + \rho_3 mc^2 \tag{5}$$

We need to get equation 5 into a form which depends not on $\vec{p}$, but only on the radial variables r and p_r. We do this by looking for quantities that commute with the terms of the Hamiltonian.

In order to find the first, we consider the total angular momentum

$$\vec{J} = \vec{L} + \frac{1}{2}\hbar\vec{\sigma} \tag{6}$$

$$\vec{L} = \hat{x} \times \hat{p} \tag{7}$$

By assumption, we assume that we can write

$$(j\hbar)'^2 = J_1^2 + J_2^2 + J_3^2 + \frac{1}{4}\hbar^2 = J^2 + \frac{1}{4}\hbar^2 \tag{8}$$

We have created the left-hand side arbitrarily. The variable j' is a non-zero integer, and (we will find later) is related to (but not the same ase) the total angular momentum quantum number j. The right-hand side is arbitrary at this point, but will later be shown to be of use.

In general, if $\vec{B}$ and $\vec{C}$ are operators that commute with $\vec{\sigma}$, it can be shown that

$$\left(\vec{\sigma} \cdot \vec{B}\right)\left(\vec{\sigma} \cdot \vec{C}\right) = \left(\vec{B} \cdot \vec{C}\right) + i\vec{\sigma} \cdot \left(\vec{B} \times \vec{C}\right) \tag{9}$$

where we have defined

$$\vec{\sigma} \cdot \left(\vec{B} \times \vec{C}\right) = \sum_{i,j,k} \epsilon_{ijk}\sigma_k B_i C_j \tag{10}$$

which is something like a cross product for our operators. In particular, due to the fact that $[L_1, L_2] = L_3$ (and cyclic permutations), it can be shown that

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$$\vec{L} \times \vec{L} = i\hbar\vec{L} \tag{11}$$

We can thus combine equations 9 and 11 to find

$$
\begin{aligned}
\left(\vec{\sigma} \cdot \vec{L}\right)^2 &= \left(\vec{L} \cdot \vec{L}\right) + i\vec{\sigma} \cdot \left(\vec{L} \times \vec{L}\right) && (12)\\
&= L^2 - \hbar\left(\vec{\sigma} \cdot \vec{L}\right) && (13)
\end{aligned}
$$

By clever rearrangement, this is equivalent to

$$\left(\vec{\sigma} \cdot \vec{L}\right)^2 = \left(\vec{L} + \frac{1}{2}\hbar\vec{\sigma}\right)^2 - 2\hbar\left(\vec{\sigma} \cdot \vec{L}\right) - \frac{3}{4}\hbar^2$$

$$\left[\left(\vec{\sigma} \cdot \vec{L}\right) + \hbar\right]^2 = J^2 + \frac{1}{4}\hbar^2 = (j'\hbar)^2 \tag{14}$$

where I have used equation 6 to simplify. Note that we could identify $j'\hbar$ with the quantity in the bracket on the left. Unfortunately, this does not have the desired commutation properties. We can make further headway by continued use of equation 9:

$$\left(\vec{\sigma} \cdot \vec{L}\right)\left(\vec{\sigma} \cdot \vec{p}\right) = \left(\vec{L} \cdot \vec{p}\right) + i\vec{\sigma} \cdot \left(\vec{L} \times \vec{p}\right) = i\vec{\sigma} \cdot \left(\vec{L} \times \vec{p}\right)$$

$$\left(\vec{\sigma} \cdot \vec{p}\right)\left(\vec{\sigma} \cdot \vec{L}\right) = \left(\vec{p} \cdot \vec{L}\right) + i\vec{\sigma} \cdot \left(\vec{p} \times \vec{L}\right) = i\vec{\sigma} \cdot \left(\vec{p} \times \vec{L}\right)$$

(where we have used $\vec{p} \cdot \vec{L} = \vec{L} \cdot \vec{p} = 0$.)

Adding these two expressions:

$$\left(\vec{\sigma} \cdot \vec{L}\right)\left(\vec{\sigma} \cdot \vec{p}\right) + \left(\vec{\sigma} \cdot \vec{p}\right)\left(\vec{\sigma} \cdot \vec{L}\right) = i\sum_{123} \sigma_1 \left(L_2 p_3 - L_3 p_2 + p_2 L_3 - p_3 L_2\right)$$

where the summation $\sum_{123}$ denotes cyclic permuation of the indices 1, 2 and 3 (a notation used often by Dirac). By re-ordering the terms in the bracket inside the sum, we can see that they are, in fact, twice the commutator $[\vec{L}, \vec{p}] = i\hbar\vec{p}$. That means

$$\left(\vec{\sigma} \cdot \vec{L}\right)\left(\vec{\sigma} \cdot \vec{p}\right) + \left(\vec{\sigma} \cdot \vec{p}\right)\left(\vec{\sigma} \cdot \vec{L}\right) = -2\hbar\left(\vec{\sigma} \cdot \vec{p}\right)$$

We can redistribute the right hand side into the left hand side, giving

$$\left(\vec{\sigma} \cdot \vec{L} + \hbar\right)\left(\vec{\sigma} \cdot \vec{p}\right) + \left(\vec{\sigma} \cdot \vec{p}\right)\left(\vec{\sigma} \cdot \vec{L} + \hbar\right) = 0 \tag{15}$$

This proves that $\vec{\sigma} \cdot \vec{L} + \hbar$ anti-commutes with $\vec{\sigma} \cdot \vec{p}$, which is in some ways similar to the Runge-Lenz vector $\vec{p} \times \vec{L} - mk\hat{r}$, up to the constant term. Due to the fact that $c\rho_1$ is a constant (see equation 2), $\vec{\sigma} \cdot \vec{L} + \hbar$ also anti-commutes with $c\rho_1\left(\vec{\sigma} \cdot \vec{p}\right)$, which is a term in the Hamiltonian, equation 5.

Furthermore, it can be shown by direct computation that $\vec{\sigma} \cdot \vec{L} + \hbar$ also commutes with the other two terms in tha Hamiltonian ($-\frac{Ze^2}{r}$ and $\rho_3 mc^2$).

We would very much like this quantity to commute with all three terms. This can be accomplished by noticing that $\rho_1 \rho_3 = 0$. Therefore, $\rho_3 \left(\vec{\sigma} \cdot \vec{L} + \hbar \right)$ must commute with $c\rho_1 \left(\vec{\sigma} \cdot \vec{p} \right)$, since the ρs enforce a zero commutator. We have only multiplied by a constant (see equation 3), which does not change the existing commutation with the other two terms.

Now we attempt to relate this to j' by squaring the quantity $\rho_3 \left(\vec{\sigma} \cdot \vec{L} + \hbar \right)$:

$$\left[\rho_3 \left(\vec{\sigma} \cdot \vec{L} + \hbar \right) \right]^2 = \rho_3^2 \left(\vec{\sigma} \cdot \vec{L} + \hbar \right)^2 = \left(\vec{\sigma} \cdot \vec{L} + \hbar \right)^2 = J^2 + \frac{1}{4}\hbar^2$$

where I have used $\rho_3^2 = I_4$.

This is the same expression we had in equation 14. We can now define $j'\hbar$ as so:

$$j'\hbar = \rho_3 \left(\vec{\sigma} \cdot \vec{L} + \hbar \right) \tag{16}$$

and rest assured that it is a constant of motion, commuting with everything in the Hamiltonian. Note that j' is free to take any non-zero integral value.

We now have one constant of motion. Equation 9 can yield still more results, by application to the x and p operators:

$$
\begin{aligned}
\left(\vec{\sigma} \cdot \vec{x} \right) \left(\vec{\sigma} \cdot p \right) &= \left(\vec{x} \cdot \vec{p} \right) + i\vec{\sigma} \cdot \left(\vec{x} \times \vec{p} \right) \\
&= \left(\vec{x} \cdot \vec{p} \right) + i\vec{\sigma} \cdot \vec{L} \\
&= rp_r + i\hbar \left(\rho_3 j' - 1 \right)
\end{aligned}
$$

where I have used equation 16 and the fact that ρ_3 is its own inverse. Note that I have used the fact that

$$\left(\vec{x} \cdot \vec{p} \right) = rp_r$$

where

$$p_r = r^{-1} \left(xp_x + yp_y + zp_z \right) = \frac{\hbar}{i} \frac{\partial}{\partial r} \tag{17}$$

We now define a new linear operator ϵ:

$$r\epsilon = \rho_1 \left(\vec{\sigma} \cdot \vec{x} \right) \tag{18}$$

The square of ϵ has the convenient property

$$
\begin{aligned}
r^2 \epsilon^2 &= \rho_1^2 \left(\vec{\sigma} \cdot \vec{x} \right)^2 = \left(\vec{\sigma} \cdot \vec{x} \right)^2 = \left(\vec{x} \cdot \vec{x} \right) + i\vec{\sigma} \cdot \left(\vec{x} \times \vec{x} \right) = |\vec{x}|^2 = r^2 \\
\implies \epsilon^2 &= 1
\end{aligned}
$$

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where I have used $\rho_1^2 = I_4$, $\vec{x} \cdot \vec{x} = r^2$ and $\vec{x} \times \vec{x} = 0$.

Note that $\rho_1 (\vec{\sigma} \cdot \vec{p})$ commutes with j'. The angular momentum operators in j' don't discriminate between $\vec{p}$ and $\vec{x}$, so $\rho_1 (\vec{\sigma} \cdot \vec{x})$ must also commute with j'. Therefore, ϵ also commutes with p_r.

This fact can be exploited:

$$
\begin{aligned}
[(\vec{\sigma} \cdot \vec{x}), (\vec{x} \cdot \vec{p})] &= (\vec{\sigma} \cdot \vec{x})(\vec{x} \cdot \vec{p}) - (\vec{x} \cdot \vec{p})(\vec{\sigma} \cdot \vec{x}) \\
&= \sigma \cdot [\vec{x}(\vec{x} \cdot \vec{p}) - (\vec{x} \cdot \vec{p})\vec{x}] \\
&= i\hbar (\vec{\sigma} \cdot \vec{x})
\end{aligned}
$$

where I have used the fact that the interior of the bracket in the second line is itself a known commutator.

We can write this result in terms of ϵ:

$$
r\epsilon r p_r - r p_r r \epsilon = i\hbar r \epsilon \tag{19}
$$

Now looking at

$$
\begin{aligned}
(\vec{\sigma} \cdot \vec{x})(\vec{\sigma} \cdot \vec{p}) &= r\epsilon \rho_1 (\vec{\sigma} \cdot \vec{p}) \\
&= r p_r + i\hbar (\rho_3 j' - 1)
\end{aligned}
$$

where I have used a previous result. Dividing through by $r\epsilon$, we obtain:

$$
\rho_1 (\vec{\sigma} \cdot \vec{p}) = \epsilon p_r - \frac{\epsilon i\hbar}{r} + \frac{\epsilon i\hbar \rho_3 j'}{r} \tag{20}
$$

This expression is in terms only of the radial variables, and ϵ and j'. It is also the only term in the Hamiltonian (equation 5) containing non-radial variables! By making this substitution, we are left with

$$
\mathcal{H} = -\frac{Ze^2}{r} + c\epsilon \left(p_r - i\frac{\hbar}{r} \right) + \frac{ci\epsilon \rho_3 j' \hbar}{r} + \rho_3 mc^2 \tag{21}
$$

which is the radial form of the Hamiltonian.

A quick check shows that ϵ and ρ_3 commute with all other terms, and that they anti-commute with one another. This means that we can transform to a representation in which ρ_3 is a diagonal matrix and ϵ has the simple form shown below.

$$
\rho_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{22}
$$

$$
\epsilon = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \tag{23}
$$

This transformation is done by reducing ρ_3 to a 2×2 matrix, and then finding ϵ via the commutation and anti-commutation relations.

In this form, the Dirac Equation for stationary states is:

$$H\psi = E\psi$$

$$\begin{bmatrix} -\frac{Ze^2}{r} + mc^2 & -icp_r - c\frac{\hbar}{r} - c\frac{j'\hbar}{r} \\ icp_r + c\frac{\hbar}{r} - c\frac{j'\hbar}{r} & -\frac{Ze^2}{r} - mc^2 \end{bmatrix} \begin{bmatrix} \psi_a(r) \\ \psi_b(r) \end{bmatrix} = \lambda \begin{bmatrix} \psi_a(r) \\ \psi_b(r) \end{bmatrix} \tag{24}$$

Solution for the Coulomb Potential

Unfortunately, we cannot simply take the determinant of the Hamiltonian matrix in equation 24, as the derivative terms brought in by the momentum coordinate are present. We will instead reduce the system to 2 coupled differential equations, and solve them by substituting an unknown function in the form of a (potentially) infinite series.

Rewriting $(H - \lambda I) = 0$ as a system of coupled equations and substituting in p_r from equation 17, we have:

$$\left(-\lambda - \frac{Ze^2}{r} + mc^2\right)\psi_a + c\hbar\left(-\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r} - \frac{j'}{r}\right)\psi_b = 0$$

$$\left(-\lambda - \frac{Ze^2}{r} - mc^2\right)\psi_b - c\hbar\left(-\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{r} + \frac{j'}{r}\right)\psi_a = 0$$

This can be simplified in form using three substitutions:

$$\alpha = \frac{e^2}{\hbar c} \tag{25}$$

$$a_1 = \frac{\hbar}{mc - \frac{\lambda}{c}} \tag{26}$$

$$a_2 = \frac{\hbar}{mc + \frac{\lambda}{c}} \tag{27}$$

α is identically the fine structure constant, as we are working in cgs units.

This makes our equations, with appropriate rearrangement and factoring

$$\left(\frac{1}{a_1} - \frac{Z\alpha}{r}\right)\psi_a - \left(\frac{\mathrm{d}}{\mathrm{d}r} + \frac{j'+1}{r}\right)\psi_b = 0 \tag{28}$$

$$\left(\frac{1}{a_2} + \frac{Z\alpha}{r}\right)\psi_b - \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{j'-1}{r}\right)\psi_a = 0 \tag{29}$$

We now assume solutions exist of the form

$$\psi_a(r) = r^{-1}e^{-\frac{r}{a}}f(r) \tag{30}$$

$$\psi_b(r) = r^{-1}e^{-\frac{r}{a}}g(r) \tag{31}$$

With $f(r)$ and $g(r)$ representing unknown functions. The variable a is defined as

$$a = \sqrt{a_1 a_2} = \hbar \left(m^2 c^2 - \frac{\lambda^2}{c^2} \right)^{-\frac{1}{2}} \tag{32}$$

By substituting expressions 30 and 31 into equations 28 and 29 and simplifying, we find:

$$\left(\frac{1}{a_1} - \frac{Z\alpha}{r} \right) f(r) - \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{a} + \frac{j'}{r} \right) g(r) = 0 \tag{33}$$

$$\left(\frac{1}{a_2} + \frac{Z\alpha}{r} \right) g(r) - \left(\frac{\mathrm{d}}{\mathrm{d}r} - \frac{1}{a} - \frac{j'}{r} \right) f(r) = 0 \tag{34}$$

Next we expand the unknown functions $f(r)$ and $g(r)$ as series:

$$f(r) = \sum_s f_s r^s \tag{35}$$

$$g(r) = \sum_s g_s r^s \tag{36}$$

These are then substituted into our system of equations. In order for the equation to go to zero as required, each term in the resulting series must separately go to zero.

The coefficient of the r^s terms are:

$$\frac{f_s}{a_1} - Z\alpha f_{s+1} - (s + 1 + j') g_{s+1} + \frac{g_s}{a} = 0 \tag{37}$$

$$\frac{g_s}{a_2} - Z\alpha g_{s+1} - (s + 1 - j') f_{s+1} + \frac{f_s}{a} = 0 \tag{38}$$

These can be combined by multiplying equation 37 by a and equation 38 by a_2 and then subtracting the former from the latter. This gives us an expression directly relating the f_s coefficients with the g_s coefficients:

$$[Z\alpha a - a_2(s - j')] f_s + [Z\alpha a_2 + a(s + j')] g_s = 0 \tag{39}$$

We can begin to obtain the values of the coefficients by considering the boundary conditions. The functions $f(r)$ and $g(r)$ must go to zero at $r = 0$, because the $\psi(r)$ functions would otherwise diverge there due to the r^{-1} term. This means that there is some smallest s below which the series does not continue. We call this s_0, and it has the property:

$$f_{s_0 - 1} = g_{s_0 - 1} = 0$$

Plugging this into equations 37 and 38, we find:

$$Z\alpha f_{s_0} + (s_0 + j') g_{s_0} = 0$$

$$Z\alpha g_{s_0} - (s_0 - j') f_{s_0} = 0$$

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Combining these and equation 39, we can write the value s_0 in a very simple form

$$s_0 = \sqrt{j'^2 - Z^2\alpha^2} \tag{40}$$

This places a lower bound on the series. Note that this bound becomes imaginary if $Z\alpha > j'$. This will be discussed in more detail shortly.

The upper bound of the series is also useful. It can be shown that the series must terminate if the energy eigenvalue λ is to be less than mc^2 (see, for example, [1]). The implication of this result is that if the series terminates at index s_1 such that

$$f_{s_1+1} = g_{s_1+1} = 0$$

then, using equations 37, 38 and 39, we have

$$\frac{s_1}{a} = \frac{1}{2}\left(\frac{1}{a_2} - \frac{1}{a_1}\right)Z\alpha = \frac{\lambda}{\hbar c}Z\alpha$$

(where we have used equations 26 and 27 to expand a_1 and a_2.)

Squaring this expression and expanding a using equation 32, we get

$$s_1^2\left(m^2c^2 - \frac{\lambda^2}{c^2}\right) = Z^2\alpha^2\frac{\lambda^2}{c^2}$$

This can be solved for the energy eigenvalues λ:

$$\lambda = \pm mc^2\left[1 + \frac{(Z\alpha)^2}{s_1^2}\right]^{-\frac{1}{2}} \tag{41}$$

Note that the "negative energy" solution doesn't imply negative energy. What we are seeing are positron energy levels. From here forward, I drop the negative root and look only at the electron solution.

The two end points of the series indices s_0 and s_1 are separated by an integer number of steps. If we call this integer n', then we can write

$$\begin{aligned} s_1 &= n' + s_0 \\ &= n' + \sqrt{j'^2 - Z^2\alpha^2} \end{aligned}$$

Plugging this in gives a result for the energy eigenvalues in terms of only the two quantum numbers n' and j':

$$E_{n'j'} = mc^2\left\{1 + \frac{(Z\alpha)^2}{\left[n' + \sqrt{j'^2 - Z^2\alpha^2}\right]^2}\right\}^{-\frac{1}{2}} \tag{42}$$

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This is the final result quoted for the energy eigenvalues of the hydrogenic atom by Dirac in [1]. It turns out that later developments in the field (such as [2, 3]) prefer to use an equivalent set of quantum numbers that maps more closely to the familiar ones we have used in our class.

The number j' is closely related to the total angular momentum quantum number j. j' has the range $1, 2, 3, \ldots$ while j has the range $1/2, 3/2, 5/2, \ldots$. It is natural, and in fact correct, to make the identification

$$j' = j + \frac{1}{2} \tag{43}$$

The principal quantum number n is a bit more tricky. The value of n' we have chosen is simply any arbitrary integer whose value is positive (since it represents the length of the non-zero elements of the series expansion of $f(r)$ and $g(r)$). While this is correct, it does not deal well with how that series obtains the length that it does. A more careful calculation, presented by Greiner in [2], shows that we should identify n' with the more familiar n thusly:

$$n' = n - j' = n - j - \frac{1}{2} \tag{44}$$

This has the same range of values as Dirac's solution, but is more careful in handling the degeneracy of each level.

Combining these two adjustments with equation 42, we get the Sommerfeld Fine-Structure Formula:

$$E_{nj} = mc^2 \left\{ 1 + \frac{(Z\alpha)^2}{\left[n - j - \frac{1}{2} + \sqrt{\left(j + \frac{1}{2} \right)^2 - Z^2 \alpha^2} \right]^2} \right\}^{-\frac{1}{2}} \tag{45}$$

The derivation of the form of the actual wave functions $\psi_a(r)$ and $\psi_b(r)$ is very tedious and unenlightening. Greiner addresses this in detail in [2], and the interested reader is directed there.

It was earlier noted that equation 40 has no solution if $Z\alpha > j' = j + \frac{1}{2}$. This means that the s states start to be destroyed above $Z = 137$, and that the p states begin being destroyed above $Z = 274$. Note that this differs from the result of the Klein-Gordon equation, which predicts s states being destroyed above $Z = 68$ and p states destroyed above $Z = 82$ (see, for example, problem set #1 from the first quarter of class).

Energy Spectrum of the Dirac Hydrogen Atom

We are interested in the spectrum of photons emitted by a hydrogen atom when an electron transfers from one energy level to another. This means that the rest mass of the electron is not of concern. I define the observed energy levels of the hydrogen atom to be (taking $Z = 1$):

$$\mathcal{E}_{nj} = E_{nj} - mc^2 = mc^2 \left(\left\{ 1 + \frac{\alpha^2}{\left[n - j - \frac{1}{2} + \sqrt{\left(j + \frac{1}{2} \right)^2 - \alpha^2} \right]^2} \right\}^{-\frac{1}{2}} - 1 \right) \tag{46}$$

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This can be expanded in α as a Taylor Series:

$$\mathcal{E}_{nj} \approx -\frac{mc^2\alpha^2}{2}\left\{\frac{1}{n^2} + \frac{\alpha^2}{n^2}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]\right\} \tag{47}$$

Using the numerical values

$$
\begin{aligned}
mc^2 &= 511004.1\text{eV} \\
\alpha &= \frac{1}{137.04}
\end{aligned}
$$

this can be written as

$$\mathcal{E}_{nj} \approx -13.605\text{eV}\left\{\frac{1}{n^2} + \frac{(137.04)^{-2}}{n^2}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]\right\}$$

The first term is clearly recognisable as the energy spectrum of the non-relativistic hydrogen atom, ignoring the fine structure. The second term contains all of the detail of the fine structure. This expression can be found identically by taking the first-order perturbation of the Schrödinger hydrogen atom solution with the perturbing Hamiltonian

$$\mathcal{H}_1 = -\frac{p^4}{8m^3c^2}$$

which is the first relativistic correction to the kinetic energy of the electron. An excellent derivation of this result is given by Fitzpatrick in [4].

We are now in a position to compute the energy spectrum and the degeneracies. The principal quantum number n defines the large-scale energy levels. Within each large-scale level, the orbital angular momentum quantum number ℓ can take on values of $0, 1, \ldots, n$ and its azimuthal number m runs from $-\ell, -\ell + 1, \ldots, \ell - 1, \ell$. For each of these values of ℓ, we compute the total angular momentum j by combining ℓ with the electron spin quantum number m_s, which can be $\pm 1/2$.

I performed these computations using equation 46 and the numerical values of mc^2 and α listed above. The result is tabulated below:

n	ℓ	j	$\mathcal{E}$ (eV)	Label	Degeneracy
1	0	1/2	-13.6052	$1s_{1/2}$	2
2	0	1/2	-3.40132	$2s_{1/2}$	2
2	1	1/2	-3.40132	$2p_{1/2}$	2
2	1	3/2	-3.40127	$2p_{3/2}$	4
3	0	1/2	-1.51169	$3s_{1/2}$	2
3	1	1/2	-1.51169	$3p_{1/2}$	2
3	1	3/2	-1.51168	$3p_{3/2}$	4
3	2	3/2	-1.51168	$3d_{3/2}$	4
3	2	5/2	-1.51167	$3d_{5/2}$	6

This confirms the previously determined degeneracies found by using only the first-order relativistic correction. Note that the Lamb Shift and the effect of spin-orbit coupling are not present in our result, and the hyperfine structure thus does not appear. These effects require the use of a more sophisticated Hamiltonian (such as one with $\vec{A} \neq 0$).

References

[1] P. Dirac, *The Principles Of Quantum Mechanics*, 4th ed.   Oxford University Press, 1982.

[2] W. Greiner, *Relativistic Quantum Mechanics: Wave Equations*, 2nd ed.   Springer, 1987.

[3] F. Gross, *Relativistic Quantum Mechanics and Field Theory.*   Wiley, 1999.

[4] R.   Fitzpatrick.   (2006)   The   fine   structure   of   hydrogen.   [Online].   Available: http://farside.ph.utexas.edu/teaching/qmech/lectures/node107.html