Dirac's Hydrogen Atom

We start with the hamiltonian

$$H = -eA^0 - (c\vec{p} + e\vec{A})\cdot\gamma^0\vec{\gamma} + i\,mc^2\gamma^0. \qquad 1$$

The field of the proton has $\vec{A} = 0$ and A^0 spherically symmetric. So H is

$$H = -eA^0 - c\,\vec{p}\cdot\gamma^0\vec{\gamma} + i\,mc^2\gamma^0 \qquad 2$$

or since

$$\gamma^0\vec{\gamma} = \vec{\Sigma} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & -\vec{\sigma} \end{pmatrix} \qquad 3$$

$$H = -eA^0 - c\,\vec{p}\cdot\vec{\Sigma} + i\,mc^2\gamma^0. \qquad 4$$

We have seen that

$$\vec{J} = \vec{L} + \frac{\hbar}{2}\vec{\sigma_4} \qquad 5$$

is the conserved total angular momentum. Its e-vals are $j(j+1)\hbar^2$ where $j = \ell \pm \frac{1}{2} > 0$. (6)

Let's compute

$$\Sigma\, \sigma_4\cdot L\; \sigma_4\cdot p = \begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix}\begin{pmatrix} \sigma_j & 0 \\ 0 & \sigma_j \end{pmatrix} L_i p_j = \begin{pmatrix} \sigma_i\sigma_j & 0 \\ 0 & \sigma_i\sigma_j \end{pmatrix} L_i p_j. \qquad (7)$$

Since

$$\sigma_i \sigma_j = \delta_{ij} + i \epsilon_{ijk} \sigma_k \tag{8}$$

it follows that

$$\sigma_4 \cdot L \, \sigma_4 \cdot p = L \cdot p + i \epsilon_{ijk} \sigma_{4k} L_i p_j$$

$$= i \, \vec{\sigma}_4 \cdot (L \times p) \tag{9}$$

since

$$L \cdot p = \epsilon_{ijk} r_j p_k p_i = 0. \tag{10}$$

Similarly,

$$\sigma_4 \cdot p \, \sigma_4 \cdot L = i \, \vec{\sigma}_4 \cdot (p \times L). \tag{11}$$

Classically $L \times p + p \times L = 0$, so

$$(L \times p)_i + (p \times L)_i = \epsilon_{ijk} [p_j, \epsilon_{klm} r_l p_m]$$

$$= -i\hbar \, \delta_{jl} \, \epsilon_{ijk} \epsilon_{klm} p_m \tag{12}$$

$$= -i\hbar \, \epsilon_{ilk} \epsilon_{klm} p_m = i\hbar \, \epsilon_{kli} \epsilon_{klm} p_m,$$

Since

$$\sum_{klm} \epsilon_{kli} \epsilon_{klm} = \delta_{ll} \delta_{im} - \delta_{lm} \delta_{il}$$

$$= 3 \delta_{im} - \delta_{im} = 2 \delta_{im}, \tag{13}$$

we have

$$\vec{L \times p} + \vec{p \times L} = -2 i \hbar \, \vec{p}. \tag{14}$$

So the anti-commutator $\{\sigma_4 \cdot L, \sigma_4 \cdot p\}$ is

$$\sigma_4 \cdot L\, \sigma_4 \cdot p + \sigma_4 \cdot p\, \sigma_4 \cdot L = i\, \sigma_4 \cdot (L \times p + p \times L)$$
$$= i\, \sigma_4 \cdot (2 i \hbar \vec{p}) = -2\hbar\, \vec{\sigma_4} \cdot \vec{p}. \qquad 15$$

Thus this anti-commutator

$$(\sigma_4 \cdot L + \hbar)\, \sigma_4 \cdot p + \sigma_4 \cdot p\, (\sigma_4 \cdot L + \hbar) = 0 \qquad 16$$

vanishes. Also, since

$$\gamma^0 = -i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad 17$$

$$\gamma^0 \vec{\sigma_4} = -i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix} = -i \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \qquad 18$$

and

$$\sigma_4 \gamma^0 = -i \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -i \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \qquad 19$$

so

$$[\vec{\sigma_4}, \gamma^0] = 0. \qquad 20$$

Thus $\sigma_4 \cdot L + \hbar$ commutes with the first and last terms of H — with $-eA^0$ and $i mc^2 \gamma^0$. It also anti-commutes with the other term $-c p \cdot \Sigma$ because

$$\vec{\Sigma} = \vec{\sigma_4} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \vec{\sigma_4} = \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & -\vec{\sigma} \end{pmatrix}. \qquad 21$$

Thus (16) & (21) imply

$$(\sigma_4 \cdot L + \hbar)\,\sigma_4 \cdot p \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \sigma_4 \cdot p\,(\sigma_4 \cdot L + \hbar)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 0$$

$$(\sigma_4 \cdot L + \hbar)\,\Sigma \cdot p + \Sigma \cdot p\,(\sigma_4 \cdot L + \hbar) = 0. \qquad (22)$$

Now $\gamma^0(\sigma_4 \cdot L + \hbar)$ commutes with $-eA^0$ and with $i\,mc^2\gamma^0$. And γ^0 anti-commutes with Σ

$$\gamma^0 \vec{\Sigma} = -i \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \vec{\sigma} & 0 \\ 0 & -\vec{\sigma} \end{pmatrix} = -i \begin{pmatrix} 0 & -\vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}$$

$$\Sigma \gamma^0 = -i \begin{pmatrix} \sigma & 0 \\ 0 & -\sigma \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = -i \begin{pmatrix} 0 & \sigma \\ -\sigma & 0 \end{pmatrix}$$

so

$$\{\gamma^0, \Sigma\} = 0, \qquad 23$$

Thus (22) & (23) imply

$$\gamma^0 (\sigma_4 \cdot L + \hbar)\,\Sigma \cdot p + \gamma^0 \Sigma \cdot p\,(\sigma_4 \cdot L + \hbar) = 0$$

or

$$\gamma^0(\sigma_4 \cdot L + \hbar)\,\Sigma \cdot p - \Sigma \cdot p\,\gamma^0(\sigma_4 \cdot L + \hbar) = 0. \qquad 24$$

Thus $i\gamma^0(\sigma_4 \cdot L + \hbar) \equiv j_D \hbar$ commutes with H and is conserved.

One may show that

$$\left[i\gamma^0(\sigma_4 \cdot L + \hbar)\right]^2 = \left(\vec{L} + \tfrac{\hbar}{2}\vec{\sigma}_4\right)^2 + \frac{\hbar^2}{4} = \vec{J}^2 + \frac{\hbar^2}{4} \equiv j_D^2 \hbar^2. \qquad (25)$$

Note that this j_D is not the j_A we use for the total angular momentum. If

$$\vec{J}^2 \, |j_A m\rangle = \hbar^2 j_A(j_A+1)\, |j_A m\rangle \qquad 26$$

then

$$j_D = \pm (j_A + \tfrac{1}{2}). \qquad 27$$

The e-vals j_D are all positive and negative integers, excluding zero.

Now

$$\sigma_4 \cdot x \, \sigma_4 \cdot p = x_i p_j \sigma_{4i} \sigma_{4j}$$

$$= x_i p_j (\delta_{ij} + i \epsilon_{ijk} \sigma_{4k})$$

$$= \vec{x} \cdot \vec{p} + i \, \vec{\sigma}_4 \cdot \vec{L}. \qquad 28$$

But since

$$j_D \hbar = i\gamma^0 (\sigma_4 \cdot L + \hbar) \qquad 29$$

so

$$\sigma_4 \cdot L = i\gamma^0 j_D \hbar - \hbar \qquad 30$$

whence

$$\sigma_4 \cdot x \, \sigma_4 \cdot p = x \cdot p - \gamma^0 j_D \hbar - i\hbar \qquad 31$$

$$= r \cdot p_r - \gamma^0 j_D \hbar - i\hbar. \qquad 32$$

Dirac then defines ϵ by

$$r\epsilon = -\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \sigma_4 \cdot x \qquad 33$$

$$r^2\epsilon^2 = \begin{pmatrix}1&0\\0&-1\end{pmatrix}\sigma_4\cdot x \begin{pmatrix}1&0\\0&-1\end{pmatrix}\sigma_4\cdot x$$

$$= (\sigma_4\cdot x)^2 = \vec{x}^{\,2} = r^2 \qquad 34$$

whence $\qquad \epsilon^2 = 1 \qquad 35$

Now we have seen in (24) that

$$0 = \left[-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\sigma_4\cdot p, j_D\hbar\right]$$

$$= -i\left[\begin{pmatrix}1&0\\0&-1\end{pmatrix}\sigma_4\cdot p, \gamma^0(\sigma_4\cdot L+\hbar)\right] \qquad 36$$

$$= -i\left[\Sigma\cdot p, \gamma^0(\sigma_4\cdot L+\hbar)\right].$$

Since $\vec{x}$ and $\vec{p}$ play similar algebraic roles in $\vec{L}$, one may show that $\Sigma\cdot x$ commutes with j_D

$$[\vec{\Sigma}\cdot\vec{x}, \gamma^0(\sigma_4\cdot L+\hbar)] = 0 \qquad 37$$

So $\qquad [\epsilon, j] = 0. \qquad 38$

Also $\qquad [\epsilon, p_r] = 0 \qquad$ because $\qquad 39$

$$\sigma_4\cdot x\ \vec{x}\cdot\vec{p} - \vec{x}\cdot\vec{p}\ \sigma_4\cdot x = \vec{\sigma}_4\cdot\left(\vec{x}(x\cdot p) - (x\cdot p)\vec{x}\right)$$

$$= -\sigma_{4i}\ x_j\frac{\hbar}{i}\partial_j x_i = i\hbar\,\sigma_{4i}\,x_j\,\delta_{ij} = i\hbar\,\sigma_4\cdot x \qquad 40$$

So

$$-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\left[\sigma_4\cdot x\ x\cdot p - x\cdot p\ \sigma_4\cdot x\right] = -\begin{pmatrix}1&0\\0&-1\end{pmatrix}i\hbar\,\sigma_4\cdot x \qquad 41$$

or

$$r\epsilon\, r p_r - r p_r\, r\epsilon = i\hbar\, r\epsilon \qquad 42$$

or $\qquad 43$

$$r^2\epsilon p_r - r^2 p_r\epsilon = 0.$$

By (32)

$$\sigma_4 \cdot x \; \sigma_4 \cdot p = \left[-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\right]\sigma_4\cdot x \left[-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\right]\sigma_4\cdot p$$

$$= r p_r - \gamma^0 j_D \hbar - i\hbar \qquad 44$$

so

$$r\epsilon\left[-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\right]\sigma_4\cdot p = r p_r - \gamma^0 j_D \hbar - i\hbar$$

$$\epsilon\left[-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\right]\sigma_4\cdot p = p_r - \frac{i\hbar}{r} - \frac{\gamma^0}{r} j_D \hbar \qquad 45$$

or since $\epsilon^2 = 1$ by (35)

$$-\begin{pmatrix}1&0\\0&-1\end{pmatrix}\sigma_4\cdot p = \epsilon\left(p_r - \frac{i\hbar}{r}\right) - \epsilon\gamma^0 j_D \hbar/r \qquad 46$$

So, the hamiltonian in these polar coordinates is by (3-4)

$$\frac{H}{c} = -\frac{e}{c}A^0 - p\cdot\begin{pmatrix}1&0\\0&-1\end{pmatrix}\sigma_4 + i m c \gamma^0 \qquad 47$$

$$= -\frac{e}{c}A^0 + \epsilon\left(p_r - \frac{i\hbar}{r}\right) - \epsilon\gamma^0 j_D \hbar/r + i m c \gamma^0.$$

Now ϵ and γ^0 commute with all the other variables — A^0, p_r, $\hbar/r$, j_D/r — in H. Also

$$\{\epsilon, \gamma^0\} = 0 \qquad 48$$

because

by (33) and (3)

$$\epsilon = -\frac{1}{r}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\sigma_4 \cdot x$$

$$= -\frac{1}{r}\,\Sigma \cdot x$$

$$= -\frac{1}{r}\gamma^0 \vec{\gamma} \cdot x \qquad 49$$

So since

$$\{\gamma^\mu, \gamma^\nu\} = 2\eta^{\mu\nu} \qquad 50$$

$$\{\epsilon, \gamma^0\} = 0 . \qquad 51$$

So one may choose a representation in which γ^0 is diagonal and

$$\epsilon = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad i\gamma^0 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \qquad 52$$

since $\epsilon^2 = 1$ and $\gamma^{0\,2} = -1$, so now (47) is

$$\frac{M}{c} = -\frac{e^2}{cr} + \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\left(p_r - \frac{i\hbar}{r}\right)$$

$$- \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\left[-i\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right]\frac{j_D\hbar}{r} + mc\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}. \qquad 53$$

That is,

$$\frac{H}{c} = -\frac{e^2}{cr} + \hbar \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{j_D \hbar}{r} + mc \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \qquad (54)$$

This is a 2×2 matrix. So letting

$$\langle r a | \psi \rangle = \psi_a(r) \qquad 55$$
$$\langle r b | \psi \rangle = \psi_b(r)$$

we find

$$0 = \langle r a | \frac{H' - H}{c} | \psi \rangle = \left(\frac{H'}{c} + \frac{e^2}{cr} \right) \psi_a + \hbar \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) \psi_b + \frac{j\hbar}{r} \psi_b - mc\psi_a$$

$$0 = \langle r b | \frac{H' - H}{c} | \psi \rangle = \left(\frac{H'}{c} + \frac{e^2}{cr} \right) \psi_b - \hbar \left(\frac{\partial}{\partial r} + \frac{1}{r} \right) \psi_a + \frac{j\hbar}{r} \psi_a + mc\psi_b \qquad 56$$

in which $j \equiv j_D$. Let

$$\frac{\hbar}{mc - \frac{H'}{c}} = a_1 , \qquad \frac{\hbar}{mc + \frac{H'}{c}} = a_2 , \qquad 57$$

Then Eqs. (56) become

$$\left(\frac{1}{a_1} - \frac{\alpha}{r} \right) \psi_a - \left(\frac{\partial}{\partial r} + \frac{j+1}{r} \right) \psi_b = 0$$

$$\left(\frac{1}{a_2} + \frac{\alpha}{r} \right) \psi_b - \left(\frac{\partial}{\partial r} - \frac{j-1}{r} \right) \psi_a = 0 \qquad 58$$

where $\alpha = e^2/\hbar c \simeq 1/137$. 59

Let

$$\psi_a = r^{-1} e^{-r/a} f \qquad \psi_b = r^{-1} e^{-r/a} g \qquad 60$$

where

$$a = \sqrt{a_1 a_2} = \frac{\hbar}{\sqrt{m^2c^2 - H'^2/c^2}} \qquad 61$$

Then (58) reduce to

$$\left(\frac{1}{a_1} - \frac{\alpha}{r}\right) f - \left(\frac{\partial}{\partial r} - \frac{1}{a} + \frac{j}{r}\right) g = 0$$

$$62$$

$$\left(\frac{1}{a_2} + \frac{\alpha}{r}\right) g - \left(\frac{\partial}{\partial r} - \frac{1}{a} - \frac{j}{r}\right) f = 0 .$$

Set

$$f = \sum_s c_s r^s \qquad g = \sum_s c'_s r^s \qquad 63$$

and put f & g into (62) and identify coefficients of r^{s-1}

$$c_{s-1}/a_1 - \alpha c_s - (s+j) c'_s + c'_{s-1}/a = 0 \qquad 64$$

$$c'_{s-1}/a_2 + \alpha c'_s - (s-j) c_s + c_{s-1}/a = 0 , \qquad 65$$

Note by (61)

$$\frac{a}{a_1} = \frac{a_2}{a} \qquad 66$$

so that

$$a\,(64) - a_2\,(65) = 0 \quad \text{gives} \qquad 67$$

$$[a\,\alpha - a_2(s-j)]\,c_s + [a_2\alpha + a(s+j)]\,c'_s = 0. \qquad 68$$

Now at $r=0$, we need

$$r\,\psi_a \to 0 \quad \text{and} \quad r\,\psi_b \to 0 \qquad 69$$

so by (60) we need

$$f \to 0 \quad \text{and} \quad g \to 0 \quad \text{as} \quad r \to 0, \qquad 70$$

So there must be a minimum value s_0 for which $c_{s_0}\,c'_{s_0} \neq 0.$ 71

So

$$c_{s_0-1} = 0 = c'_{s_0-1} \qquad 72$$

and by (64–65)

$$\alpha c_{s_0} + (s+j)\,c'_{s_0} = 0 \qquad 73$$

$$\alpha\, c'_{s_0} - (s-j)\,c_{s_0} = 0 \qquad 74$$

which give

$$\alpha^2 c'_{s_0} = (s-j)\,\alpha\, c_{s_0} = +(j^2 - s_0^2)\,c'_{s_0} \qquad 75$$

So

$$\alpha^2 = j^2 - s_0^2. \qquad 76$$

So

$$s_0^2 = j^2 - \alpha^2 \qquad 77$$

and since $f, g \to 0$ as $r \to 0$

$$s_0 = +\sqrt{j^2 - \alpha^2}\,. \qquad 78$$

Now by (68) and (65), we find approximately for large s

$$+a_2 c_s \cong a\, c'_s \qquad 79$$

and

$$s c_s \simeq \frac{c_{s-1}}{a} + \frac{c'_{s-1}}{a_2} \qquad 80$$

neglecting α.

Now (79) and (80) imply that

$$\frac{c_s}{c_{s-1}} \cong \frac{2}{as} \qquad 81$$

So the series (63) f & g go as

$$\sum c_s r^s \sim \sum \frac{1}{s!}\left(\frac{2r}{a}\right)^s = e^{2r/a} \qquad 82$$

which is not normalizable. So the series (63) must terminate.

Series (67) must terminate so that

$$c_{s+1} = c'_{s+1} = 0, \tag{83}$$

Now (64) + (65) give

$$\frac{c_s}{a_1} + \frac{c'_s}{a} = 0 \tag{84}$$

$$\frac{c'_s}{a_2} + \frac{c_s}{a} = 0 \tag{85}$$

which are equivalent by (66). Now (68) gives

$$a_1 [a\alpha - a_2(s-j)] = a[a_2\alpha + a(s+j)] \tag{86}$$

or

$$2 a_1 a_2 s = a(a_1 - a_2)\alpha \tag{87}$$

or

$$\frac{s}{a} = \frac{1}{2}\left(\frac{1}{a_2} - \frac{1}{a_1}\right)\alpha = \frac{M'}{c\hbar}\alpha . \tag{88}$$

Using (61), we find

$$s^2 (m^2c^2 - M'^2/c^2) = \alpha^2 M'^2/c^2 \tag{89}$$

or

$$\frac{M'}{mc^2} = \left(1 + \frac{\alpha^2}{s^2}\right)^{-\frac{1}{2}} \tag{90}$$

Let

$$s = n + s_0 \tag{91}$$

$$= n + \sqrt{j^2 - \alpha^2} \tag{92}$$

where n is an integer. Then

$$\frac{H'}{mc^2} = \left\{ 1 + \frac{\alpha^2}{(n_D + \sqrt{j_D^2 - \alpha^2})^2} \right\}^{-\frac{1}{2}} . \tag{93}$$

Here $$j_D = \pm (j_A + \tfrac{1}{2}) \tag{94}$$

is a non-zero integer, not a half-integer.

The formula (93) is expressed in terms of Dirac's notation in which n_D is not the principal quantum number n, and j_D is not the j of the total angular momentum. In terms of n_D and j_D, the quantum number j of the total angular momentum is

$$j = |j_D| - \tfrac{1}{2} \tag{95}$$

and the principal quantum number n is

$$n = n_D + j + \tfrac{1}{2} . \tag{96}$$

So $n_D = n - j - \frac{1}{2}$ and $|j_D| = j + \frac{1}{2}$ (97)

and the energy E_{nj} is

$$E_{nj} = \frac{mc^2}{\sqrt{1 + \left(\frac{Z\alpha}{n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - (Z\alpha)^2}}\right)^2}} \tag{98}$$

in which Z is the charge of the nucleus.

If instead of an electron, the orbiting spin-1/2 particle had charge $-Z'$ and mass m', then E_{nj} would be

$$E_{nj} = \frac{m'c^2}{\left[1 + \left(\frac{ZZ'\alpha}{n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - (ZZ'\alpha)^2}}\right)^2\right]^{1/2}} \tag{99}$$

which would be complex for $Z' = 2$ and $Z \geq 69$. It would be interesting to make the nucleus of anti-helium-3 and to aim a low-energy beam of it at a uranium target.