Dirac Theory of the H Atom (and Electron)

What have we omitted?

1) electron spin (fine structure)
2) proton spin (hyperfine structure)
3) relativistic corrections
4) radiative (quantum electrodynamic) corrections

We will address 1) and 3) together by looking at the relativistic Dirac equation, which describes a spin $\frac{1}{2}$ particle. The other small effects, 2) and 4), will be deferred until later. (Hyperfine structure can be dealt with using the present methods, but we'll need more angular momentum theory to get very far.)

Dirac Equation (WARNING: cgs units used for 4-vectors!)

The Schrödinger eqn can be developed by using the relation,

$$\frac{p^2}{2m} = E$$

and substituting $E \to i\hbar \frac{2}{\hbar} \vec{p} \to -i\hbar \vec{\nabla}$. An obvious way to get a relativistic equivalent is to do the same for,$

$$c^2 p^2 + m^2 c^4 = E^2$$

To get,

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

or

$$\Box \psi = \frac{m^2 c^2 \psi}{\hbar^2}$$

d'Alambertian

$$\Box = \nabla^2 - \frac{\hbar^2}{c^2} \frac{\partial^2}{\partial t^2}$$

Klein-Gordon Eqn.
This turns out to describe spinless particles accurately, though the interpretation of the probability density is problematic (not understood until 1930).

It was to avoid the problem of negative probability density that Dirac sought a modified equation in 1928. It was invented totally as the theoretical entity that satisfied the obvious criteria for a relativistic Hamiltonian--

1. No time derivatives in the expression for probability density, so it can be positive definite.
2. \(x, y, z\) and \(ct\) treated symmetrically, for relativistic invariance \(\Rightarrow\) all appear in 1st order.
3. Must be linear for superposition principle to work.
4. \(c^2 p^2 + m^2 c^4 = E^2\), or some equivalent. (quadratic!)

This is like the situation in \(\mathbb{E} \mathbb{M}\), where Maxwell's equations are 1st order & linear, but each component of the field obeys a 2nd order wave eqn.

In the same way we satisfy all of the above requirements with a 4-component wave function. The simplest possible equation is the Dirac equation,

\[
\text{vector of matrices } \begin{pmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{pmatrix}
\]

\[
\begin{align*}
\begin{pmatrix} \mathbf{0} & \mathbf{1} \\ \mathbf{1} & \mathbf{0} \end{pmatrix}
\end{align*} \left( c \mathbf{\hat{x}} \cdot \mathbf{\hat{p}} + \beta m c^2 \right) \Psi &= 0
\]

For stationary state solutions the eigenvalue eqn is,

\[
(E - c \mathbf{\hat{x}} \cdot \mathbf{\hat{p}} + \beta m c^2) \Psi = 0
\]

The form of \(\mathbf{\hat{x}}\) and \(\beta\) is determined by requiring \((E^2 - c^2 p^2 - m^2 c^4) \Psi = 0\).

By multiplying \(\Psi\) by \(E + c \mathbf{\hat{x}} \cdot \mathbf{\hat{p}} + \beta m c^2\) and requiring this, it can be shown,
\[ \begin{align*}
\alpha_i \alpha_j + \alpha_j \alpha_i &= 2 \delta_{ij} \quad \text{identity matrix} \\
\alpha_i \beta + \beta \alpha_i &= 0 \\
(\alpha_i)^2 &= \beta^2 = I
\end{align*} \]

Several representations satisfy this; the simplest and most usual is,

\[ \alpha_i = \begin{bmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{bmatrix}, \quad i = 1, 2, 3 \]

\[ \beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \text{ or } \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \]

where the \( \sigma_i \) are the 2x2 Pauli spin matrices,

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

The \( \Psi \)'s are then 4-component column vectors, or 4-spinors,

\[ \Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} \]

So like the Maxwell equations, the solutions have internal degrees of freedom. There it's polarization; here it's spin, as we'll see.

**Free-particle solutions**

The Dirac eqn, like Maxwell's eqn's, has plane wave solutions. I think it's useful (following Mizushima) to make things concrete by finding the solutions along the \( z \) axis --

\[ \Psi = \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} e^{(kz - \omega t)} \]
Putting this into (1),
\[ \left( \begin{array}{c} A \\ B \\ C \\ D \end{array} \right) e^{ikz} = \left( \begin{array}{c} A \\ B \\ C \\ D \end{array} \right) e^{ikz} + mc^2 \left( \begin{array}{c} A \\ B \\ -C \\ -D \end{array} \right) e^{ikz} \]
\[ \frac{1}{\hbar} \left( \begin{array}{c} A \\ B \\ C \\ D \end{array} \right) = \frac{1}{\hbar} \left( \begin{array}{c} C \\ -D \\ -A \\ -B \end{array} \right) + mc^2 \left( \begin{array}{c} A \\ B \\ -C \\ -D \end{array} \right) \]
So,
\[ \left( \frac{1}{\hbar} \omega - mc^2 \right) A = c \hbar k \left( \begin{array}{c} C \\ -D \\ -A \\ -B \end{array} \right) \]
\[ \left( \frac{1}{\hbar} \omega - mc^2 \right) B = -c \hbar k \left( \begin{array}{c} D \\ C \\ A \\ B \end{array} \right) \]
\[ \left( \frac{1}{\hbar} \omega + mc^2 \right) C = c \hbar k \left( \begin{array}{c} A \\ B \\ -C \\ -D \end{array} \right) \]
\[ \left( \frac{1}{\hbar} \omega + mc^2 \right) D = -c \hbar k \left( \begin{array}{c} B \\ C \\ A \\ D \end{array} \right) \]
(because we picked an axis)
So there are two classes of solutions, of type
\[ \Psi_+ = \left( \begin{array}{c} A \\ B \\ C \\ D \end{array} \right), \quad \Psi_- = \left( \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array} \right) \]

**Spin**

Why? If we take the spin operator from ordinary quantum mechanics and generalize,
\[ \hat{s} = \frac{1}{2} \hbar \left( \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right), \quad \hat{s}_z = \frac{1}{2} \hbar \left( \begin{array}{cc} -1 & 0 \\ 0 & 1 \end{array} \right) \]
we find,
\[ \hat{s}_z \Psi_+ = \frac{1}{2} \hbar \Psi_+ \]
and \[ \hat{s}_z \Psi_- = -\frac{1}{2} \hbar \Psi_- \]
So \( \Psi_+ \) has spin \( \frac{1}{2} \); \( \Psi_- \) spin \( -\frac{1}{2} \).

The Dirac equation can describe spin-\( \frac{1}{2} \) particles (electrons, etc.)

If we go back to (1), we can confirm this interpretation ---
\[ \frac{d^2 \xi}{dt^2} = -\frac{i}{\hbar} \left[ \hat{L}, \hat{H} \right] \neq 0 \]
checked, say, for \( L \xi \).
So $\mathbf{J}$ is not a constant of motion.

But if we take $\dot{\mathbf{J}} = \dot{\mathbf{L}} + \dot{\mathbf{s}}$, we can confirm that

$$\frac{d}{dt}(\mathbf{J}) = 0,$$

so

$$\mathbf{J} = \mathbf{L} + \mathbf{s}$$

is the total angular momentum of the Dirac particle.

And

$$\mathcal{S}^2 \psi = \frac{\hbar^2}{4} \left( \sigma^2 \right) \psi = \frac{7 \hbar^2}{4} \psi = 5 \left( 5 + 1 \right) \psi \quad \text{for} \quad \hbar = \frac{1}{2},$$

(confirming that spin $\frac{1}{2}$ is what's described)

Solutions

Going back to (8) and solving for $\psi_+$, we must have determinant of coefficients = 0,

$$\begin{vmatrix} \hbar w - mc^2 & -ckt \\ -ckt & \hbar w + mc^2 \end{vmatrix} = 0$$

$$\Rightarrow \hbar w = E = \pm \sqrt{m^2 c^4 + c^2 k^2 \hbar^2} = \pm \sqrt{m^2 c^4 + c^2 p^2}$$

(11)

2 independent solutions --

1. + sign (positive energy) interpret as electrons

If particle moves slowly, (8) gives

$$\frac{A}{c} = \frac{cp}{\sqrt{m^2 c^4 + p^2 c^2}} - mc^2 \approx 2 \frac{mc}{p} \text{ (large)}$$

$$\gamma_+ = \begin{pmatrix} \text{large} \\ 0 \\ 0 \end{pmatrix}$$

2. - sign (negative energy) interpret as positron

Now $\psi_+ = \begin{pmatrix} \text{small} \\ 0 \\ \text{large} \end{pmatrix}$

Finally, there are two analogous independent solutions for $\psi_-$, with spin $\hbar z = -\frac{1}{2}$. 
Dirac Equation in an Electromagnetic Field

How do we introduce the field?

Since \( (\mathbf{A}, i\phi) \) form a 4-vector just as \((\mathbf{p}, i\frac{\psi}{c})\), we can retain Lorentz invariance by substituting

\[
\mathbf{p} \rightarrow \mathbf{\pi} = \mathbf{p} - e\mathbf{A} \quad \text{(cgs units!)}
\]

and \( E \rightarrow E - q\phi \)

where \( \mathbf{\pi} = \mathbf{p} \times \mathbf{A} \) and \( E = -\frac{1}{c^2} \frac{\partial \mathbf{A}}{\partial t} - \nabla \phi \)

This gives the stationary state Dirac equation,

\[
(E - q\phi - c^2 \mathbf{\pi} \cdot \mathbf{\pi} - \beta mc^2) \psi = 0
\]

Obviously other forms are possible, but this is the simplest (and works)!

Magnetic moments -- a factor of the electron, etc.

Before solving the H atom, consider an electron in a pure \( \mathbf{B} \) field. For a homogeneous \( \mathbf{B} \) field, can write

\[ \mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}, \quad \text{and} \quad \phi = 0 \]

It will be sufficient to solve the Dirac equation up to order \( v^2/c^2 \); beyond this the radiative corrections from QED are \( \gg \) the remaining relativistic corrections.

To do this, motivated by our free electron solution, divide the Dirac wave function into two components (spinors):

\[
\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}
\]

\[
\psi_A = \begin{pmatrix} \psi_{A1} \\ \psi_{A2} \end{pmatrix}
\]

\[
\psi_B = \begin{pmatrix} \psi_{B1} \\ \psi_{B2} \end{pmatrix}
\]
Equation (13) then becomes, using the Pauli matrix representation,

\[
\begin{bmatrix}
0 & I \\
I & 0
\end{bmatrix} \begin{bmatrix}
\mathbf{\sigma} \\
\mathbf{\pi}
\end{bmatrix} + \begin{bmatrix}
I & 0 \\
0 & -I
\end{bmatrix} mc^2 \begin{bmatrix}
\psi_A \\
\psi_B
\end{bmatrix} = (E - q\Phi)(\psi_A \\
\psi_B)
\]

or,

\[
\begin{align*}
(E - q\Phi - mc^2) \psi_A &= \begin{bmatrix}
\mathbf{\sigma} \\
\mathbf{\pi}
\end{bmatrix} \psi_B \\
(E - q\Phi + mc^2) \psi_B &= \begin{bmatrix}
\mathbf{\sigma} \\
\mathbf{\pi}
\end{bmatrix} \psi_A
\end{align*}
\]

2 coupled eq's

(14a, b)

gives,

\[
\psi_B = \frac{1}{E - q\Phi + mc^2} \begin{bmatrix}
\mathbf{\sigma} \\
\mathbf{\pi}
\end{bmatrix} \psi_A
\]

So from (10),

\[
(E - q\Phi - mc^2) \psi_A = \left( \begin{bmatrix}
\mathbf{\sigma} \\
\mathbf{\pi}
\end{bmatrix} \psi_B \right) \frac{1}{E - q\Phi + mc^2} \left( \begin{bmatrix}
\mathbf{\sigma} \\
\mathbf{\pi}
\end{bmatrix} \psi_A \right)
\]

(15)

A "Schrödinger eqn" for \( \psi_A \) thus results.

Now specialize to the lowest order term for the \( \Phi \) field (we don't even need the next order for this problem!)

For a non-relativistic particle, write energies in terms of \( \frac{E'}{E - mc^2} \) (\( E' \ll mc^2 \))

And setting \( \Phi = 0 \) in (15), expand the denominator, (16)

\[
\frac{1}{E' + 2mc^2} \approx \frac{1}{2mc^2} \left( 1 - \frac{E'}{2mc^2} + \cdots \right) \approx \frac{1}{2mc^2}
\]

Also from (14b), we see \( \psi_B \approx \frac{\psi_A}{2mc} \approx \frac{\psi_A}{2mc} \)

So \( \psi_A \) is the large 50% We'll thus be able to expand (15) to get the non-relativistic result and lowest order corrections. We get,

\[
E' \psi_A \approx \frac{1}{2m} \begin{bmatrix}
\mathbf{\sigma} \\
\mathbf{\pi}
\end{bmatrix} \psi_A
\]

(17)

It is easily verified that in general,

\[
(\mathbf{\sigma} \cdot \mathbf{\pi})^2 = \mathbf{\sigma}^2 + i \mathbf{\sigma} \cdot \mathbf{\pi} \times \mathbf{\pi}
\]

so \( (\mathbf{\sigma} \cdot \mathbf{\pi})^2 = \mathbf{\sigma}^2 + i \mathbf{\sigma} \cdot (\mathbf{p} - \frac{\Phi}{\mathbf{A}})^2 \times (\mathbf{p} - \frac{\Phi}{\mathbf{A}}) \)
Using $\hat{p} \times \hat{A} = -i\hbar \nabla \times \hat{A} - \hat{A} \times \hat{p}$,

$$ (\vec{\sigma} \cdot \hat{A})^2 = \vec{\pi}^2 - \vec{\sigma} \cdot \frac{\hbar}{c} \vec{B} $$

Expand $\vec{\pi}^2$ to finish up:

$$ \vec{\pi}^2 = (\vec{p} - \frac{\hbar}{c} \vec{A})^2 = \vec{p}^2 + \frac{\hbar^2}{c^2} \vec{A}^2 - \frac{\hbar}{c} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) $$

and using $\vec{A} = \frac{1}{2} \vec{B} \times \vec{r}$,

$$ \vec{\pi}^2 = \vec{p}^2 + \frac{\hbar^2}{c^2} \vec{A}^2 - \frac{\hbar}{2c} (\vec{p} \cdot \vec{B} \times \vec{r} + \vec{B} \times \vec{r} \cdot \vec{p}) $$

$$ = 2 \vec{B} \cdot (\vec{r} \times \vec{p}) = 2 \vec{L} \cdot \vec{B} $$

Eqn. (17) now becomes,

$$ E' \gamma_A = \left( \frac{\hbar^2}{2m} - \vec{\sigma} \cdot \frac{\hbar}{2mc} \vec{B} - \frac{\hbar}{2mc} \vec{L} \cdot \vec{B} + \frac{\hbar^2}{2mc^2} \vec{A}^2 \right) \gamma_A $$

Writing $q = -e$ for the electron (e positive),
the Hamiltonian is thus, for eigenvalue $E'$,

$$ H' = \frac{\hbar^2}{2m} + \frac{\hbar^2}{2} + \frac{e}{mc} \vec{B} + \frac{e}{2mc} \vec{L} \cdot \vec{B} + \frac{e^2}{2mc^2} \vec{A}^2 $$

$$ = \frac{\hbar^2}{2m} + \frac{e}{2mc} (\vec{L} + 2\vec{S}) \cdot \vec{B} + \frac{e^2}{2mc^2} \vec{A}^2 \quad \text{cgs} $$

$$ H' = \frac{\hbar^2}{2m} + \frac{e}{2m} (\vec{L} + 2\vec{S}) \cdot \vec{B} + \frac{e^2}{2m} \vec{A}^2 \quad \text{(SI)} $$

Bohr magneton $\times \frac{1}{\hbar}$ diamagnetic term (very small)

Paramagnetic terms —

If we measure $\vec{L}$ and $\vec{S}$ in units of $\hbar$,

$$ H'_{\text{mag}} = -\vec{\mu} \cdot \vec{B} \quad \text{with} \quad \vec{\mu} = \frac{-e}{2m} (\vec{L} + 2\vec{S}) = \text{magnetic moment operator} $$

$$ M_B = 1.400 \text{ MHz/gauss} \quad \text{or} \quad 5.05 \times 10^{-31} \text{ J/ gauss} $$

We see that the electron has an intrinsic magnetic moment. Going back to our "usual" units,

$$ \vec{M}_s = -g_s M_B \left( \frac{\hbar}{c} \right) \quad \text{where} \quad g_s \quad \text{(Dirac)} = 2 $$