1. Fine By Me

The final expression we obtained for the fine structure of the hydrogen atom had two contributions, that just happened to be of the same size: a relativistic correction, and the effects of spin-orbit coupling. Combining these two pieces, though, takes a bit of algebra. Supply that algebra here, and show explicitly that the relativistic term (Eq. 6.57) and the spin-orbit term (Eq. 6.65) can be added to yield the fine-structure term given in Eq. 6.66. Rewrite this last expression to obtain the result for the hydrogen energy levels given in Eq. 6.67. Hint: note that the final expression does not depend on the quantum number $\ell$, so step one is to express $\ell$ in terms of other quantum numbers.

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**SOLUTION**

As indicated, our job here is to “supply that algebra” needed to combine the relativistic and spin-orbit contributions to the hydrogen atom energy levels into a single expression that we observe in nature as fine structure. In this case, the algebra is very easy once we develop a strategy, but there is still a lot of it.

To start, let’s collect our two contributions. From Eq. 6.57, we have

$$E_{\text{rel}}^1 = \left(\frac{E_n}{2mc^2}\right)^2 \left[ 3 - \frac{4n}{\ell + 1/2} \right]$$

For the spin-orbit piece, Eq. 6.65 gives us

$$E_{\text{s.o.}}^1 = \left(\frac{E_n}{2mc^2}\right)^2 \left[ \frac{2n [j(j+1) - \ell(\ell + 1) - 3/4]}{\ell(\ell + 1/2)(\ell + 1)} \right]$$

The only real trick here is to figure out how to add these two terms in such a way that the quantum number $\ell$ no longer appears in the sum. The easiest approach is to realize that there are only two possibilities: either $j = \ell + 1/2$ or $j = \ell - 1/2$. While we could try to do these two cases together, making extensive use of $\pm$ and $\mp$ notation, I find it much easier to just work out each case separately. If we start with the first case, $j = \ell + 1/2$, then $\ell = j - 1/2$. Using this substitution, the two expressions above become
\[ E_{\text{rel}}^1 = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j} \right] \]

and
\[ E_{\text{s.o.}}^1 = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n[j(j+1) - (j-1/2)(j+1/2) - 3/4]}{(j-1/2)(j)(j+1/2)} \right] \]
\[ = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n[j^2 + j - j^2 + 1/4 - 3/4]}{(j-1/2)(j)(j+1/2)} \right] \]

Doing some housecleaning inside the square brackets in the numerator, we see that this reduces to just \( 2n(j - 1/2) \), and so we get the much more compact result
\[ E_{\text{s.o.}}^1 = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n}{j(j+1/2)} \right] \]

Adding these two contributions together, we find that for \( j = \ell + 1/2 \):
\[ E_{\text{fs}}^1 = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j} + \frac{2n}{j(j+1/2)} \right] \]
\[ = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n(j+1/2)}{j(j+1/2)} + \frac{2n}{j(j+1/2)} \right] \]
\[ = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1/2} \right] \]

So at least for this case, we have confirmed Eq. 6.66 in the text.

We now consider the other possibility, that \( j = \ell - 1/2 \), and so \( \ell = j + 1/2 \). As before, we first write down our two contributions for this case, giving us
\[ E_{\text{rel}}^1 = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1} \right] \]

and
\[ E_{\text{s.o.}}^1 = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n[j(j+1) - (j+1/2)(j+3/2) - 3/4]}{(j+1/2)(j+1)(j+3/2)} \right] \]
\[ = \frac{(E_n)^2}{2mc^2} \left[ \frac{2n[j^2 + j - j^2 - 2j - 3/4 - 3/4]}{(j+1/2)(j+1)(j+3/2)} \right] \]
\[ = \frac{(E_n)^2}{2mc^2} \left[ \frac{-2n}{(j+1)(j+1/2)} \right] \]
Adding these together, we find that for $j = \ell - 1/2$:

$$E_{ls}^1 = \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1} \frac{2n}{(j+1)(j+1/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n(j+1/2)}{(j+1)(j+1/2)} \frac{2n}{(j+1)(j+1/2)} \right]$$

$$= \frac{(E_n)^2}{2mc^2} \left[ 3 - \frac{4n}{j+1/2} \right]$$

So we confirm Eq. 6.66 for this case as well, and hence conclude that this equation is valid under all conditions.

Our last step is to use this result to derive a complete expression for the hydrogen energy levels, at least to this level of accuracy. Recalling that for the unperturbed solutions we have $E_n = E_1/n^2$, we find

$$E_{nj} = \frac{E_1}{n^2} + \frac{(E_1)^2}{(n^2)2mc^2} \left[ 3 - \frac{4n}{j+1/2} \right]$$

$$= \frac{E_1}{n^2} \left\{ 1 + \frac{(E_1)}{(n^2)2mc^2} \left[ 3 - \frac{4n}{j+1/2} \right] \right\}$$

Defining the fine structure constant $\alpha \equiv ke^2/(\hbar c)$, we can express $E_1$ as

$$E_1 = -mc^2 \frac{(ke^2)^2}{2\hbar^2c^2} = -\frac{1}{2}mc^2\alpha^2$$

and then rewrite the previous expression in the form

$$E_{nj} = \frac{E_1}{n^2} \left\{ 1 - \frac{\alpha^2}{4n^2} \left[ 3 - \frac{4n}{j+1/2} \right] \right\}$$

Just to set the scale, we can replace $E_1$ by its approximate value of $-13.6$ eV, do some trivial algebra, and arrive at our final result in the desired form:

$$E_{nj} = -\frac{13.6}{n^2} \left\{ 1 + \frac{\alpha^2}{n^2} \left[ \frac{n}{j+1/2} - \frac{3}{4} \right] \right\}$$

3
2. You May Walk the Walk, But Do You Rock Dirac? (15 pts)

In class, I argued that the similarity in size we noted between the first-order relativistic correction to the hydrogen atom and its spin-orbit interaction (the two contributions to fine structure considered in the previous problem) would have to be viewed as just a “coincidence” in the Schrödinger picture, but emerges “naturally” in a fully relativistic treatment. To see this, here is Dirac’s exact expression for the energy levels of hydrogen:

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

Taking \( \alpha \approx 1/137 \) to be a small number, expand this to order \( \alpha^4 \). If you do it right, your final answer should look an awful lot like Eq. 6.67 in the text.

**SOLUTION**

The goal for this problem is to take Dirac’s equation for the hydrogen atom energy levels and show that it reduces non-relativistically to the Schrödinger result plus fine structure. This indicates that Dirac’s equation not only correctly accounts for the relativistic nature of the electron, but also its interaction with the magnetic field generated by the relative orbital motion between the electron and the proton.

We can attack this either from the inside-out or from outside-in. I’ll do the latter. Note that the term inside the large parentheses is of the order of \( \alpha \), since the denominator is on the order of unity or “a few.” If we denote this term by \( \varepsilon \), then the whole equation is just

\[ E_{nj} = mc^2 \left\{ \left[ 1 + \varepsilon^2 \right]^{-1/2} - 1 \right\} \]

Working to order \( \varepsilon^4 \) (same size as \( \alpha^4 \)), we do a quick Taylor’s series expansion to find

\[ (1 + x^2)^{-1/2} = 1 - \frac{1}{2} x^2 + \frac{3}{8} x^4 + \ldots \]

and so we see that to this order

\[ E_{nj} = mc^2 \left\{ \left[ 1 - \frac{1}{2} \varepsilon^2 + \frac{3}{8} \varepsilon^4 + \ldots \right] - 1 \right\} = -\frac{mc^2}{2} \left\{ \varepsilon^2 - \frac{3}{4} \varepsilon^4 + \ldots \right\} \]
Putting this aside for a moment, we turn to evaluating \( \varepsilon \). For convenience, I’ll define \( a \equiv (j + 1/2) \gg \alpha \). With this substitution, we note that in the denominator

\[
\sqrt{(j + 1/2)^2 - \alpha^2} \equiv \sqrt{a^2 - \alpha^2} = a \sqrt{1 - (\alpha/a)^2} \approx a \left[ 1 - (\alpha/a)^2/2 \right] = a - \alpha^2/(2a)
\]

We now do the messiest part, and work out \( \varepsilon \). We have

\[
\varepsilon \equiv \frac{\alpha}{n - (j + 1/2) + \sqrt{(j + 1/2)^2 - \alpha^2}} = \frac{\alpha}{n - a + \sqrt{a^2 - \alpha^2}} = \frac{\alpha}{n - a + a - \alpha^2/(2a)} = \frac{\alpha}{n - \alpha^2/(2a)} = \frac{\alpha}{n \left[ 1 - \alpha^2/(2na) \right]}
\]

Armed with this expression, we can easily work out that to order \( \alpha^4 \) we have

\[
\varepsilon^2 = \frac{\alpha^2}{n^2} \left[ 1 + \frac{\alpha^2}{2na} \right]^2 \approx \frac{\alpha^2}{n^2} \left[ 1 + \frac{\alpha^2}{na} \right]
\]

and to the same order

\[
\varepsilon^4 \approx \frac{\alpha^4}{n^4}
\]

Finally, we stick these back into our expression for the energy given at the bottom of the previous page, and we find

\[
E_{nj} = -\frac{mc^2}{2} \left\{ \frac{\alpha^2}{n^2} \left[ 1 + \frac{\alpha^2}{na} \right] - \frac{3 \alpha^4}{4 n^4} + \ldots \right\}
\]

\[
= -\frac{mc^2}{2} \left\{ \frac{\alpha^2}{n^2} + \frac{\alpha^4}{n^3a} - \frac{3 \alpha^4}{4 n^4} + \ldots \right\}
\]

\[
= -\frac{\alpha^2 mc^2}{2n^2} \left\{ 1 + \frac{\alpha^2}{na} - \frac{3 \alpha^2}{4 n^2} + \ldots \right\}
\]

\[
\approx -\frac{\alpha^2 mc^2}{2n^2} \left[ 1 + \frac{\alpha^2}{n^2 \left( \frac{n}{a} - \frac{3}{4} \right)} \right]
\]

Recognizing that \( \alpha^2 mc^2/2 \approx 13.6 \text{ eV} \), and recalling our definition of \( a = j + 1/2 \), we can now rewrite this in the desired form as

\[
E_{nj} = -\frac{13.6 \text{ eV}}{n^2} \left[ 1 + \frac{\alpha^2}{n^2 \left( \frac{n}{j + 1/2} - \frac{3}{4} \right)} \right]
\]
3. A Devilish Derivation (15 pts)

Please do Problem 6.22, found on page 280 in the text. To get started, realize that the goal here is to figure out how to express the energy level shifts due to fine structure using the basis states in which the atom’s orbital and spin angular momentum are uncoupled. Most of this is just bookkeeping and rearranging constants, which is a boring but very useful exercise to do (every once in a while).

**SOLUTION**

In this problem, we are asked to work out some of the steps in the algebra to derive an expression for the first-order correction to the hydrogen atomic energy levels in the presence of a strong external magnetic field (the “strong-field Zeeman effect” or so-called “Paschen-Bach effect”). As we argued in class, in this regime ($B_{ext} \gg B_p$) the external field provides sufficient torque on $\mathbf{L}$ and $\mathbf{S}$ to break their coupling, so that total angular momentum $J$ is not conserved. This means that $j$ and $m_j$ are no longer good quantum numbers, but $m_\ell$ and $m_s$ will be.

Once we understand this, then it should be clear that we need to choose states of good $n, \ell, s, m_\ell, m_s$ for our basis states. Using these states, we can then calculate the ‘fine structure’ energy level shifts by evaluating the expectation values

$$ (E_{fs}^1)_{m_\ell m_s} = \langle n \ell m_\ell m_s | H_{rel}' + H_{so}' | n \ell m_\ell m_s \rangle $$

where, by convention, we usually do not list the quantum number $s = 1/2$.

We start by breaking this down into two pieces, one for each of our perturbations. For the first term, the relativistic correction, we note that we have already worked through this problem using the ‘uncoupled’ angular momentum states, and so we already have the answer. Eq. 6.57 in the text reminds us that

$$ (E_{rel}^1)_{m_\ell m_s} = -\frac{1}{8m^3c^2} \langle n \ell m_\ell m_s | p^4 | n \ell m_\ell m_s \rangle = \frac{(E_n^0)^2}{2mc^2} \left[ 3 - \frac{4n}{\ell + 1/2} \right] $$

For the second piece, the spin-orbit term, we derived an expression for the energy shift, but this was in the absence of any external magnetic field. Once the external field is sufficiently strong to break this coupling, we must evaluate the expectation value of the same perturbation, but now in the uncoupled basis states, *i.e.*, we must evaluate (using Eq. 6.61)

$$ (E_{so}^1)_{m_\ell m_s} = \frac{k e^2}{2m^2c^2} \langle n \ell m_\ell m_s | r^{-3} (\mathbf{L} \cdot \mathbf{S}) | n \ell m_\ell m_s \rangle $$
The radial integral (for the \( r^{-3} \) operator) is the same as before – because it involves integrals of the radial wave function \( R_{n\ell}(r) \), it is unaffected by our choice of angular momentum coupling – and so we know from Eq. 6.64 that

\[
\langle r^{-3} \rangle = \frac{1}{\ell(\ell + 1/2)(\ell + 1)n^3a_0^3}
\]

For the \( \mathbf{L} \cdot \mathbf{S} \) operator, we exploit the fact that we are working with basis states that are eigenstates of \( L_z \) and \( S_z \). This means that it is useful to express this in the form

\[
\langle \mathbf{L} \cdot \mathbf{S} \rangle = \langle L_x \rangle \langle S_x \rangle + \langle L_y \rangle \langle S_y \rangle + \langle L_z \rangle \langle S_z \rangle = 0 + 0 + \hbar^2 m_\ell m_s
\]

In the above, we know that the expectation values of all transverse angular momentum components will be zero, as there is no preferred direction perpendicular to \( \mathbf{B}_{ext} \propto \hat{z} \). We also know that our basis states are eigenstates of \( L_z \) and \( S_z \).

We now have all the pieces we need, and we just gather them together. So far, we have

\[
(E_{fs})_{m_\ell m_s} = \left( \frac{E_n^0}{2mc^2} \right)^2 \left[ 3 - \frac{4n}{\ell + 1/2} \right] + \frac{ke^2}{2m^2c^2} \left[ \frac{\hbar^2 m_\ell m_s}{\ell(\ell + 1/2)(\ell + 1)n^3a_0^3} \right]
\]

We need to play around with some constants. Note that

\[
\left( \frac{E_n^0}{2mc^2} \right)^2 = \left( -\frac{2E_1}{mc^2} \right) \left( -\frac{E_1}{4n^4} \right) = \frac{\alpha^2}{4n^4} (13.6 \text{ eV})
\]

and, using \( a_0 = \hbar^2/(mke^2) = \hbar/(\alpha mc) \), that

\[
\frac{ke^2}{2m^2c^2} \frac{\hbar^2}{n^3a_0^3} = \frac{\alpha \hbar}{2m^2c} \frac{(\alpha mc)^3}{hn^3} = \left( \frac{1}{2} \alpha^2 mc^2 \right) \frac{a_0^2}{n^3} = \frac{\alpha^2}{n^3} (13.6 \text{ eV})
\]

Inserting these into our previous expression, we arrive at the desired result

\[
(E_{fs})_{m_\ell m_s} = \frac{(13.6 \text{ eV})}{n^3} \alpha^2 \left\{ \frac{3}{4n} - \frac{1}{\ell + 1/2} + \frac{m_\ell m_s}{\ell(\ell + 1/2)(\ell + 1)} \right\}
\]

We’re done! In summary: to calculate the actual energy levels of the hydrogen atom in the presence of a strong external magnetic field, the above must be added to the unperturbed energy level, plus the energy shift due to the external field. To this order, we have

\[
(E)_{n\ell m_\ell m_s} \approx -\frac{E_1}{n^2} + \mu_B B_0 (m_\ell + 2m_s) + (E_{fs})_{m_\ell m_s}
\]