Relativistic Kinetic Energy Effect

The relation of relativistic kinetic energy of the electron of hydrogen-like atoms is as follows

\[ K = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \]

\[ \approx mc^2 \left( 1 + \frac{1}{2} \frac{p^2 c^2}{m^2 c^4} - \frac{1}{8} \frac{p^4 c^4}{m^4 c^8} \right) \]

The perturbed term that we would consider is:

\[ H_1 = -\frac{1}{2} \left( \frac{p^2}{2m} \right)^2 \frac{1}{mc^2} \]
We may consider the magnitude of this perturbation on the energy levels:

\[ \frac{H_1}{K_0} = \frac{1}{2} \left( \frac{p^2}{2m} \right)^2 \frac{1}{mc^2} = \frac{1}{2} \left( \frac{p^2}{2m} \right) \frac{1}{mc^2} \]

\[ \left\langle \frac{H_1}{H_0} \right\rangle \approx \frac{1}{2} \frac{\langle p^2 \rangle}{2m} \frac{1}{mc^2} \approx \frac{1}{2} \frac{1}{2} mc^2 \frac{(z\alpha)^2}{n^2} \frac{1}{mc^2} \approx (z\alpha)^2 \]

\[ H_0 = \frac{p^2}{2m} - \frac{Ze^2}{r} \]

\[ \alpha = \frac{e^2}{\hbar c} = \frac{1}{137} \]
The existence of the electron spin gives rise to another correction that is of the same order of magnitude.

It may be qualitatively understood as follows:

If the electron were at rest relative to the proton (we are discussing this on a classical level), it would only see an electric field due to the proton charge.

This is the Coulomb potential term that appears in $H_0$. 
Because the electron is moving, there are additional effects.

In the electron rest frame, the proton is moving, so there is a current present, and the electron sees a magnetic field.

If the relativistic motion were rectilinear, the magnetic filed, as seen by the electron, would be $\mathbf{v} \times \mathbf{E}/c$.

This magnetic field interacts with the spin of the electron, or more precisely, with the magnetic moment of the electron.
We might expect an interaction of the form:

\[ -\mathbf{M}.\mathbf{B} = -\left(-\frac{eg}{2mc}\right)\mathbf{S}.\mathbf{B} = \frac{e}{mc}\mathbf{S}.\mathbf{B}, \quad g = 2 \]

\[ = \frac{e}{mc^2}\mathbf{S}.\mathbf{v} \times \mathbf{E} \quad \quad = -\frac{e}{m^2c^2}\mathbf{S}.\mathbf{p} \times \nabla \Phi \]

\[ = -\frac{e}{m^2c^2}\mathbf{S}.\mathbf{p} \times \mathbf{r} \frac{1}{r} \frac{d\Phi}{dr} \quad \quad = \frac{1}{m^2c^2}\mathbf{S}.\mathbf{r} \times \mathbf{p} \frac{1}{r} \frac{d(e\Phi)}{dr} \]

where \( \phi(r) \) is the potential due to the nuclear charge.

Actually this is not correct.
It turns out that relativistic effects associated with
the fact that the electron does not move in a straight
line (the Thomas precession effect) reduce the
above by a factor of 2.

Thus correct perturbation is

\[ H_2 = \frac{1}{2m^2c^2} S \cdot L \frac{1}{r} \frac{d(e\Phi)}{dr} \]
Let us now use first order-perturbation theory to calculate the effects of $H_1$ and $H_2$ on the spectrum of hydrogen-like atoms.

We may rewrite $H_1$ in the form

$$H_1 = -\frac{1}{2} \left( \frac{p^2}{2m} \right)^2 - \frac{1}{mc^2} = -\frac{1}{2} \frac{1}{mc^2} \left( H_0 + \frac{ze^2}{r} \right)^2$$
\[
\langle \phi_{nlm} | H_1 | \phi_{nlm} \rangle = -\frac{1}{2} \frac{1}{mc^2} \langle \phi_{nlm} | \left( H_0 + \frac{ze^2}{r} \right)^2 | \phi_{nlm} \rangle
\]

\[
= -\frac{1}{2} \frac{1}{mc^2} \left[ E_n^2 + 2E_n ze^2 \langle \frac{1}{r} \rangle_{nl} + (ze^2)^2 \langle \frac{1}{r^2} \rangle_{nl} \right]
\]

\[
\langle \frac{1}{r} \rangle_{nl} = \langle \phi_{nlm} | \frac{1}{r} | \phi_{nlm} \rangle = \frac{Z}{a_0 n^2}
\]

\[
E_n = -\frac{1}{2} mc^2 \left( \frac{Z\alpha}{n^2} \right)^2
\]

\[
\langle \frac{1}{r^2} \rangle_{nl} = \langle \phi_{nlm} | \frac{1}{r^2} | \phi_{nlm} \rangle = \frac{Z^2}{a_0 n^3 (l + 1/2)}
\]

\[
a_0 = \frac{1}{\alpha mc}
\]

\[
\langle \phi_{nlm} | H_1 | \phi_{nlm} \rangle = -\frac{1}{2} mc^2 (Z\alpha)^2 \left[ \frac{(Z\alpha)^2}{n^3 (l + 1/2)} - \frac{3(Z\alpha)^2}{4n^4} \right]
\]
The spin of the electron does not enter into this energy shift, since \( H_1 \) does not depend on the spin.

\( H_2 \) does depend on the spin, and for our unperturbed wave functions we must take two-component wave functions, since what we want to calculate is the expectation value of

\[
H_2 = \frac{1}{2m^2c^2} \mathbf{S} \cdot \mathbf{L} \frac{1}{r} \frac{d(e\Phi)}{dr} = \frac{Ze^2}{2m^2c^2} \mathbf{S} \cdot \mathbf{L} \frac{1}{r^3}
\]

Here, again we have an example of degenerate perturbation theory.
For a given $n$ and $l$, there are $2(2l + 1)$ degenerate eigenstates of $H_0$ with the additional factor of 2 coming from the two spin states.

Thus the calculation of the energy shift involves a diagonalization of a submatrix, as in

$$
\Sigma_i \alpha_i \left\langle \phi_n^{(j)} \right| \lambda H_1 \left| \phi_n^{(i)} \right\rangle = \lambda E_n^{(1)} \alpha_j \text{ equation we can save a great deal of labor by noting that}
$$

$$
S + L = J \quad \text{implies that} \quad S^2 + 2S.L + L^2 = J^2 \quad \text{that is}
$$

$$
J^2 = L^2 + S^2 + 2L_z S_z + L_+ S_- + L_- S_+ \\
L.S = \frac{1}{2} \left( J^2 - L^2 - S^2 \right)
$$
Thus if we combine the degenerate eigenfunctions into linear combinations that are eigenfunctions of $J^2$ (they already are eigenfunctions of $J_z = L_z + S_z$), then these linear combinations will diagonalize $H_2$.

The appropriate linear combinations can be obtained as follows:

$$\Psi_{l+\frac{1}{2},m+\frac{1}{2}} = \sqrt{\frac{l + m + 1}{2l + 1}} Y_{lm} \chi_+ + \sqrt{\frac{l-m}{2l + 1}} Y_{lm+1} \chi_-$$

$$\Psi_{l-\frac{1}{2},m+\frac{1}{2}} = \sqrt{\frac{l-m}{2l+1}} Y_{lm} \chi_+ - \sqrt{\frac{l+m+1}{2l+1}} Y_{lm+1} \chi_-$$

Why?
Let us consider the linear combination

\[ \Psi_{j,m+\frac{1}{2}} = \alpha Y_{l,m} \chi_+ + \beta Y_{l,m+1} \chi_- \]

\[ l = l, m_l = m \]
\[ s = \frac{1}{2}, m_s = \frac{1}{2} \]
\[ j = l + s = l + \frac{1}{2} \]
\[ m_{tot} = m_l + m_s = m + \frac{1}{2} \]

\[ \Psi_{j,m+\frac{1}{2}} \]

\[ l = l, m_l = m + 1 \]
\[ s = \frac{1}{2}, m_s = -\frac{1}{2} \]
\[ j = l + s = l + \frac{1}{2} \]
\[ m_{tot} = m_l + m_s = m + \frac{1}{2} - \frac{1}{2} = m + \frac{1}{2} \]

\[ \Psi_{j,m+\frac{1}{2}} \]
It is, by construction, an eigenfunction of $J_z$ with eigenvalue $(m+1/2)\hbar$:

$$J_z \Psi_{j,m+\frac{1}{2}} = \left( m + \frac{1}{2} \right) \hbar \Psi_{j,m+\frac{1}{2}}$$

$$J_z \Psi_{j,m+\frac{1}{2}} = (L_z + S_z) \Psi_{j,m+\frac{1}{2}}$$

$$J_z \Psi_{j,m+\frac{1}{2}} = L_z \Psi_{j,m+\frac{1}{2}} + S_z \Psi_{j,m+\frac{1}{2}}$$

$$L_z \Psi_{j,m+\frac{1}{2}} = \alpha L_z Y_{lm} \chi_+ + \beta L_z Y_{lm+1} \chi_-$$
\[ L_z \Psi_{j,m+\frac{1}{2}} = \alpha \chi + L_z Y_{lm} + \beta \chi - L_z Y_{lm+1} \]

\[ L_z \Psi_{j,m+\frac{1}{2}} = \alpha m \hbar Y_{lm} \chi + \beta (m + 1) \hbar \chi - Y_{lm+1} \]

\[ S_z \Psi_{j,m+\frac{1}{2}} = \alpha Y_{lm} S_z \chi + \beta Y_{lm+1} S_z \chi - \]

\[ S_z \Psi_{j,m+\frac{1}{2}} = \alpha Y_{lm} (1/2 \hbar) \chi + \beta Y_{lm+1} (-1/2 \hbar) \chi - \]

\[ (L_z + S_z) \Psi_{j,m+\frac{1}{2}} = \alpha (m + 1/2) \hbar Y_{lm} \chi + \beta (m + 1 - 1/2) \hbar \chi - Y_{lm+1} \]

\[ J_z \Psi_{j,m+\frac{1}{2}} = (m + 1/2) \hbar \{ \alpha Y_{lm} \chi + \beta \hbar \chi - Y_{lm+1} \} = (m + 1/2) \hbar \Psi_{j,m+\frac{1}{2}} \]
We now determine $\alpha$ and $\beta$ such that it is also an eigenstate of $J^2$.

\[
L_+ Y_{lm} = \hbar \sqrt{l(l+1) - m(m+1)} Y_{l,m+1} \\
= \hbar \sqrt{(l+m+1)(l-m)} Y_{l,m+1}
\]

\[
L_+ Y_{lm} = \hbar \sqrt{l(l+1) - m(m-1)} Y_{l,m-1} \\
= \hbar \sqrt{(l-m+1)(l+m)} Y_{l,m-1}
\]

\[
S_+ \chi_+ = S_- \chi_- = 0
\]

\[
S_{\pm} \chi_{\mp} = \hbar \chi_{\pm}
\]
\[
\Psi_{j,m+\frac{1}{2}} = \alpha Y_{lm} \chi_+ + \beta Y_{lm+1} \chi_-
\]

\[
J^2 = L^2 + S^2 + 2L_z S_z + L_+ S_- + L_- S_+
\]

\[
J^2 \Psi_{j,m+\frac{1}{2}} = \alpha \hbar^2 \left\{ l(l+1) Y_{lm} \chi_+ + \frac{3}{4} Y_{lm} \chi_+ + 2m(\frac{1}{2}) Y_{lm} \chi_+ + \sqrt{(l+m+1)(l-m)} Y_{lm+1} \chi_- \right\}
\]

\[
+ \beta \hbar^2 \left\{ l(l+1) Y_{lm+1} \chi_- + \frac{3}{4} Y_{lm+1} \chi_- + 2(m+1)(\frac{1}{2}) Y_{lm+1} \chi_- + \sqrt{(l-m)(l+m+1)} Y_{lm} \chi_+ \right\}
\]

This will be of the form:

\[
\hbar^2 j(j+1) \Psi_{j,m+\frac{1}{2}} = \hbar^2 j(j+1) \left( \alpha Y_{lm} \chi_+ + \beta Y_{lm+1} \chi_- \right)
\]

Provided that:
\[\alpha \left[ l(l+1) + \frac{3}{4} + m \right] + \beta \sqrt{(l-m)(l+m+1)} = \alpha j(j+1)\]

\[\beta \left[ l(l+1) + \frac{3}{4} - m - 1 \right] + \alpha \sqrt{(l+m+1)(l-m)} = \beta j(j+1)\]

\[\beta \sqrt{(l-m)(l+m+1)} = \alpha \left[ j(j+1) - l(l+1) - \frac{3}{4} - m \right]\]

\[\alpha \sqrt{(l+m+1)(l-m)} = \beta \left[ j(j+1) - l(l+1) - \frac{3}{4} + m + 1 \right]\]
\[ \beta \sqrt{(l-m)(l+m+1)} = \alpha \left[ j(j+1) - l(l+1) - \frac{3}{4} - m \right] \]

\[ \alpha \sqrt{(l+m+1)(l-m)} = \beta \left[ j(j+1) - l(l+1) - \frac{3}{4} + m + 1 \right] \]

\[ \frac{\sqrt{(l-m)(l+m+1)}}{j(j+1) - l(l+1) - \frac{3}{4} + m + 1} = \frac{j(j+1) - l(l+1) - \frac{3}{4} - m}{\sqrt{(l+m+1)(l-m)}} \]

\[ (l+m+1)(l-m) = \left[ j(j+1) - l(l+1) - \frac{3}{4} + m + 1 \right] \left[ j(j+1) - l(l+1) - \frac{3}{4} - m \right] \]

\[ j(j+1) - l(l+1) - \frac{3}{4} = x \]
\((l + m + 1)(l - m) = [x + m + 1][x - m]\)

\((l + m + 1)(l - m) = x^2 + x - m^2 - m\)

\(x^2 + x - m^2 - m - (l + m + 1)(l - m) = 0\)

\(x^2 + x - m^2 - m - (l^2 - m^2 + l - m) = 0\)

\(x^2 + x - l^2 - l = 0\)

\[x = \frac{-1 \pm \sqrt{1 + 4l^2 + 4l}}{2}\]

\[x = \frac{-1 \pm \sqrt{(2l + 1)^2}}{2} = \begin{cases} -l - 1 \\ l \end{cases}\]
\[ j(j+1) - l(l+1) - \frac{3}{4} = \begin{cases} -l - 1 \\ l \end{cases} \]

\[ j = \begin{cases} l - 1/2 \\ l + 1/2 \end{cases} \]

\[ \beta \sqrt{(l - m)(l + m + 1)} = \alpha \left[ j(j+1) - l(l+1) - \frac{3}{4} - m \right] \]

\[ \frac{\alpha}{\beta} = \sqrt{(l - m)(l + m + 1)} \left( j(j+1) - l(l+1) - \frac{3}{4} - m \right)_{j = l + \frac{1}{2}} = \sqrt{\frac{l + m + 1}{l - m}} \]

\[ \Psi_{j,m + \frac{1}{2}} = \alpha Y_{lm} \chi_+ + \beta Y_{lm + 1} \chi_- = \beta \left( \frac{\alpha}{\beta} Y_{lm} \chi_+ + Y_{lm + 1} \chi_- \right) \]
\[ \Psi_{l+\frac{1}{2},m+\frac{1}{2}} = \beta \left( \sqrt{\frac{l+m+1}{l-m}} Y_{lm} \chi_+ + Y_{lm+1} \chi_- \right) \]

\[ \left\langle \Psi_{j,m+\frac{1}{2}} \middle| \Psi_{j,m+\frac{1}{2}} \right\rangle = 1 \]

\[ \beta^2 \left( \frac{l+m+1}{l-m} + 1 \right) = 1 \]

\[ \beta = \sqrt{\frac{l-m}{2l+1}} \]

\[ \frac{\alpha}{\beta} = \sqrt{\frac{l+m+1}{l-m}} \]

\[ \alpha = \sqrt{\frac{l+m+1}{2l+1}} \]

\[ \Psi_{l+\frac{1}{2},m+\frac{1}{2}} = \sqrt{\frac{l+m+1}{2l+1}} Y_{lm} \chi_+ + \sqrt{\frac{l-m}{2l+1}} Y_{lm+1} \chi_- \]
We can guess that the \( j=l-1/2 \) solution must have the form:

\[
\Psi_{l+\frac{1}{2},m+\frac{1}{2}} = \sqrt{\frac{l + m + \frac{1}{2}}{2l + 1}} Y_{lm} \chi_+ + \sqrt{\frac{l-m}{2l + 1}} Y_{lm+1} \chi_-
\]

In order to be orthogonal to the \( j=l+1/2 \) solution.
with these linear combinations we have

\[ \text{S.L} \Psi \quad j=\frac{l}{2}, m_j=m+\frac{1}{2} = \frac{1}{2} \left( J^2 - L^2 - S^2 \right) \Psi \quad j=\frac{l}{2}, m_j=m+\frac{1}{2} \]

\[ = \frac{1}{2} \hbar^2 \left[ (l+1/2)(l+1/2+1) - l(l+1) - 1/2(1/2+1) \right] \Psi \quad j=\frac{l}{2}, m_j=m+\frac{1}{2} \]

\[ \text{S.L} \Psi \quad j=\frac{l}{2}, m_j=m+\frac{1}{2} = \frac{1}{2} \hbar^2 l \Psi \quad j=\frac{l}{2}, m_j=m+\frac{1}{2} \]

\[ \text{S.L} \Psi \quad j=\frac{l-1}{2}, m_j=m+\frac{1}{2} = \frac{1}{2} \hbar^2 \left[ (l-1/2)(l-1/2+1) - l(l+1) - 3/4 \right] \Psi \quad j=\frac{l-1}{2}, m_j=m+\frac{1}{2} \]

\[ \text{S.L} \Psi \quad j=\frac{l-1}{2}, m_j=m+\frac{1}{2} = -\frac{1}{2} \hbar^2 (l + 1) \Psi \quad j=\frac{l}{2}, m_j=m+\frac{1}{2} \]
For a given $l$ value there are \( \left[ 2 \left( l + \frac{1}{2} \right) + 1 \right] + \left[ 2 \left( l - \frac{1}{2} \right) + 1 \right] = 2(2l + 1) \) states.

If we call the linear combination $\phi_{jmjl}$, then

\[
\langle \phi_{jmjl} | H_2 | \phi_{jmjl} \rangle = \frac{Ze^2}{2m^2c^2} \frac{\hbar^2}{2} \left\{ \begin{array}{c} l \\ -l - 1 \end{array} \right\} \langle 1 \rangle_{nl} \frac{S.L\frac{1}{r^3}}{Z^3 e^2} \frac{Ze^2}{2m^2c^2} \frac{\hbar^2}{2} \left\{ \begin{array}{c} l \\ -l - 1 \end{array} \right\} a_0^3 n^3 l (l + 1/2)(l + 1) \]
\[ \Delta E = \frac{Z^4 e^2 \hbar^2}{4m^2 c^2 a_0^3} n^3 l(l + 1/2)(l + 1) \]

\[ \alpha = \frac{e^2}{hc} \]

\[ a_0 = \frac{1}{\alpha mc} \]
We must of course combine the effect of $H_1$ and $H_2$. When this is done, we obtain after some algebra

$$\Delta E = \frac{Z^4 \alpha^4 mc^2}{4} \frac{\left\{ \begin{array}{c} l \\ -l - 1 \end{array} \right\}}{n^3 l (l + 1/2)(l + 1)}$$

$$\Delta E = -\frac{1}{2} mc^2 (Z \alpha)^4 \frac{1}{n^3} \left[ \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right]$$

How?
\[ \Delta E = -\frac{1}{2}mc^2 \left( \frac{(Z\alpha)^2}{n^3(l+1/2)} - \frac{3(Z\alpha)^2}{4n^4} \right) + \frac{Z^4\alpha^4mc^2}{4n^3l(l+1/2)(l+1)} \left\{ \frac{l}{-l-1} \right\} \]

\[ \Delta E = -\frac{1}{2}mc^2 \left( \frac{(Z\alpha)^2}{n^3} \right)^2 \left\{ \frac{1}{(l+1/2)} - \frac{3}{4n} \right\} - \frac{1}{2} \frac{Z^4\alpha^4mc^2}{l(l+1/2)(l+1)} \left\{ \frac{l}{-l-1} \right\} \]

\[ \Delta E = -\frac{1}{2}mc^2 \left( \frac{(Z\alpha)^2}{n^3} \right)^2 \frac{l(l+1/2)-1/2}{l(l+1/2)(l+1)} \left\{ \frac{l}{-l-1} \right\} - \frac{3}{4n} \]
$$\Delta E = -\frac{1}{2}mc^2 \frac{(Z\alpha)^2}{n^3} \left\{ \frac{l(l+1/2)-1/2l}{l(l+1/2)(l+1)} - \frac{3}{4n} \right\}$$
\[ \Delta E = -\frac{1}{2}mc^2 \left( \frac{(Z\alpha)^2}{n^3} \right) \left\{ \frac{1}{(l + 1/2)(l + 1)} \right\} \left\{ \frac{1}{l + 1} \right. \right\} \left( \frac{l}{l(l + 1/2)(l + 1)} \right) - \frac{3}{4n} \]

The result is also correct within the relativistic Dirac equation for \( l = 0 \).

\[ \Delta E = -\frac{1}{2}mc^2 \left( \frac{(Z\alpha)^2}{n^3} \right) \left\{ \frac{1}{j + 1/2} - \frac{3}{4n} \right\}; \text{for} \left\{ \begin{array}{l} l = j-1/2 \\ l = j+1/2 \end{array} \right. \text{ or } \left\{ \begin{array}{l} j = l+1/2 \\ j = l-1/2 \end{array} \right. \]
Although the $l$ for $^2S_{1/2}$ and $^2P_{3/2}$ are different, they are degenerate, since they have identical $j$ and $n$ ($j = \frac{1}{2}$; $n = 2$).
A more careful discussion, using the relativistic Dirac equation, does not alter this result.

However, in 1974, a very delicate microwave adsorption experiment carried out by Lamb and Retherford showed that there was, indeed, a tiny splitting of the two levels.

The magnitude of the splitting, of order \( mc^2 (Z\alpha)^4 \alpha \log \alpha \), could be explained by the additional interaction of the electron with its own electromagnetic field, that is, as a self-energy effect.

These matters are outside of the scope of this course.
Let us now turn to the discussion of the behavior of hydrogenlike atoms in an external magnetic field, that is, to the anomalous Zeeman effect.

There is, of course, nothing anomalous about the effect; it is just that the Zeeman effect that could be explained classically was exhibited only by atoms in states in which the total electronic spin was zero.

For the other states, for which there was no classical explanation (since that involves spin), the Zeeman splitting pattern was different, and therefore “anomalous”.
For the unperturbed Hamiltonian we take the usual $H_0$ together with the spin-orbit term.

The reason for doing this is that the external perturbation may be small compared with the effect of what we called $H_2$. 