Full set of relativistic corrections

Start with Dirac equation, expand in a series of (α^2) powers

$(\alpha^2)^0$ — $E = mc^2$ electrons exist

$(\alpha^2)^1$ — non-relativistic Hamiltonian

$$\hat{H}^{(0)} = \frac{p^2}{2m} + \frac{ke^2}{r}$$

$(\alpha^2)^2$ — relativistic corrections

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} - \frac{ke^2}{r}}_{\hat{H}^{(0)}} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{relativistic correction}} + \underbrace{\frac{ke^2}{2}\frac{1}{m^2c^2r^3}\hat{\vec{S}}\cdot\hat{\vec{L}}}_{\text{spin-orbit interaction}} + \underbrace{\frac{\pi k e^2\hbar^2}{2m^2c^2}\delta^3(\vec{r})}_{\text{Darwin term}}$$

See textbook for a semiclassical explanation of the spin-orbit term (6.3.2)

In all previous calculations electron spin was decoupled from the perturbation, so we ignored it. Now, however, we need to remember that electron wavefunctions also contain spin quantum number: $S = 1/2$, m_s

$\psi_{nlm_l s m_s}$ $\qquad \hat{S}^2\psi = \hbar^2 S(S+1)\psi = \frac{3}{4}\hbar^2\psi$

alternative notation $|nlm_l s m_s\rangle$ $\qquad \hat{S}_z\psi = \hbar m_s\psi = \pm\frac{1}{2}\hbar\psi$

Unfortunately, spin-orbit coupling hamiltonian does not preserve the original wave functions

$\hat{H}_{SO}\,\psi_{n\ell m_\ell s m_s} \neq [\text{const}]\,\psi_{n\ell m_\ell s m_s}$

so we need to figure out what basis to use, such that the new wavefunctions are eigenfunctions of our perturbation hamiltonian

Total angular momentum: $\hat{\vec{J}} = \vec{L} + \vec{S}$

$\psi_{n\ell s j m_j}$: $\hat{J}^2 \psi_{n\ell s j m_j} = \hbar^2 j(j+1)\,\psi_{n\ell s j m_j}$

$J_z \psi_{n\ell s j m_j} = \hbar m_j\,\psi_{n\ell s j m_j}$

also $\hat{L}^2 \psi_{n\ell s j m_j} = \hbar^2 \ell(\ell+1)\,\psi_{n\ell s j m_j}$; $\hat{S}^2 \psi_{n\ell s j m_j} = \hbar^2 s(s+1)\,\psi_{n\ell s j m_j}$

$$\vec{J}^{\,2} = (\vec{L}+\vec{S})^2 = \vec{L}^2 + 2\vec{L}\cdot\vec{S} + \vec{S}^2 \Rightarrow$$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

$$\langle \psi_{n\ell s j m_j} | \vec{L}\cdot\vec{S} | \psi_{n\ell s j m_j} \rangle = \frac{\hbar^2}{2}[j(j+1) - \ell(\ell+1) - s(s+1)]$$

First-order correction in this new basis

$$V^{(1)} = \langle \psi_{n\ell s j m_j} | \hat{H}_{SO} | \psi_{n\ell s j m_j} \rangle = \frac{ke^2}{2m^2c^2} \langle \psi_{n\ell s j m_j} | \frac{\vec{L}\cdot\vec{S}}{r^3} | \psi_{n\ell s j m_j} \rangle =$$

$$= \frac{ke^2\hbar^2}{4m^2c^2}[j(j+1) - \ell(\ell+1) - s(s+1)] \left\langle \frac{1}{r^3} \right\rangle_{n\ell}$$

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)} \frac{1}{n^3a^3}$$

$$V^{(1)} = \frac{ke^2\hbar^2}{4m^2c^2} \frac{1}{n^3a^3} \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{\ell(\ell+\frac{1}{2})(\ell+1)} =$$

$$= \frac{nE_n^2}{mc^2} \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{\ell(\ell+1/2)(\ell+1)} = \frac{nE_n^2}{mc^2} \frac{j(j+1) - \ell(\ell+1) - 3/4}{\ell(\ell+1/2)(\ell+1)}$$

For $j = \ell + 1/2$: $(\ell+1/2)(\ell+3/2) - \ell(\ell+1) - 3/4 =$
$= \ell^2 + 2\ell + 3/4 - \ell^2 - \ell - 3/4 = \ell$

$$V^{(1)}_{j=\ell+1/2} = \frac{nE_n^2}{mc^2} \frac{1}{(\ell+1/2)(\ell+1)}$$

For $j = \ell - 1/2$: $(\ell-1/2)(\ell+1/2) - \ell(\ell+1) - 3/4 =$
$= \ell^2 - 1/4 - \ell^2 - \ell - 3/4 = -\ell - 1$

$$V^{(1)}_{j=\ell-1/2} = -\frac{nE_n^2}{mc^2} \frac{1}{\ell(\ell+1/2)}$$

It is interesting to note that if $\ell = 0$ (s-state) we expect that the spin-orbit correction is zero... yet, if we look at

$$V^{(1)}_{j=\ell+1/2} \overset{\ell=0}{=} \frac{2nE_n^2}{mc^2} \neq 0 \quad (?!)$$

Mathematically, it is because we had ℓ/ℓ cancellation.

However, if we are doing the calculations properly, $\langle H_{SO} \rangle = 0$ for $\ell = 0$, but then we need to account the contribution of the Darwin term:

$$\langle \psi_{\ell=0} | \frac{\pi k e^2 \hbar^2}{2m^2c^2} \delta^3(\vec{r}) | \psi_{\ell=0} \rangle = \frac{\pi k e^2 \hbar^2}{2m^2c^2} |\psi_{\ell=0}(0)|^2 = \frac{2nE_n^2}{mc^2}$$

It is clear that this term will only contribute for $\ell = 0$ states, since $|\psi_{\ell>0}(0)|^2 = 0$

Let's combine all relativistic corrections now

$$E_{n\ell s j m_j} = E_n^{(0)} + V_{rel}^{(1)} + V_{SO}^{(1)} + V_{Darwin}^{(1)} =$$

$$= E_n^{(0)} + \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{\ell+1/2}\right] + \frac{nE_n^2}{2mc^2}\left\{\begin{array}{ll} 2/(\ell+1/2)(\ell+1) & j=\ell+1/2 \\ -2/\ell(\ell+1/2) & j=\ell-1/2 \end{array}\right.$$

$$j=\ell+1/2: \quad -\frac{4n}{\ell+1/2} + \frac{2n}{(\ell+1/2)(\ell+1)} = \frac{2n}{\ell+1/2}\left(-2+\frac{1}{\ell+1}\right) = -\frac{4n}{\cancel{\ell+1/2}}\,\frac{\cancel{2\ell+1}^{\,2}}{\ell+1} =$$

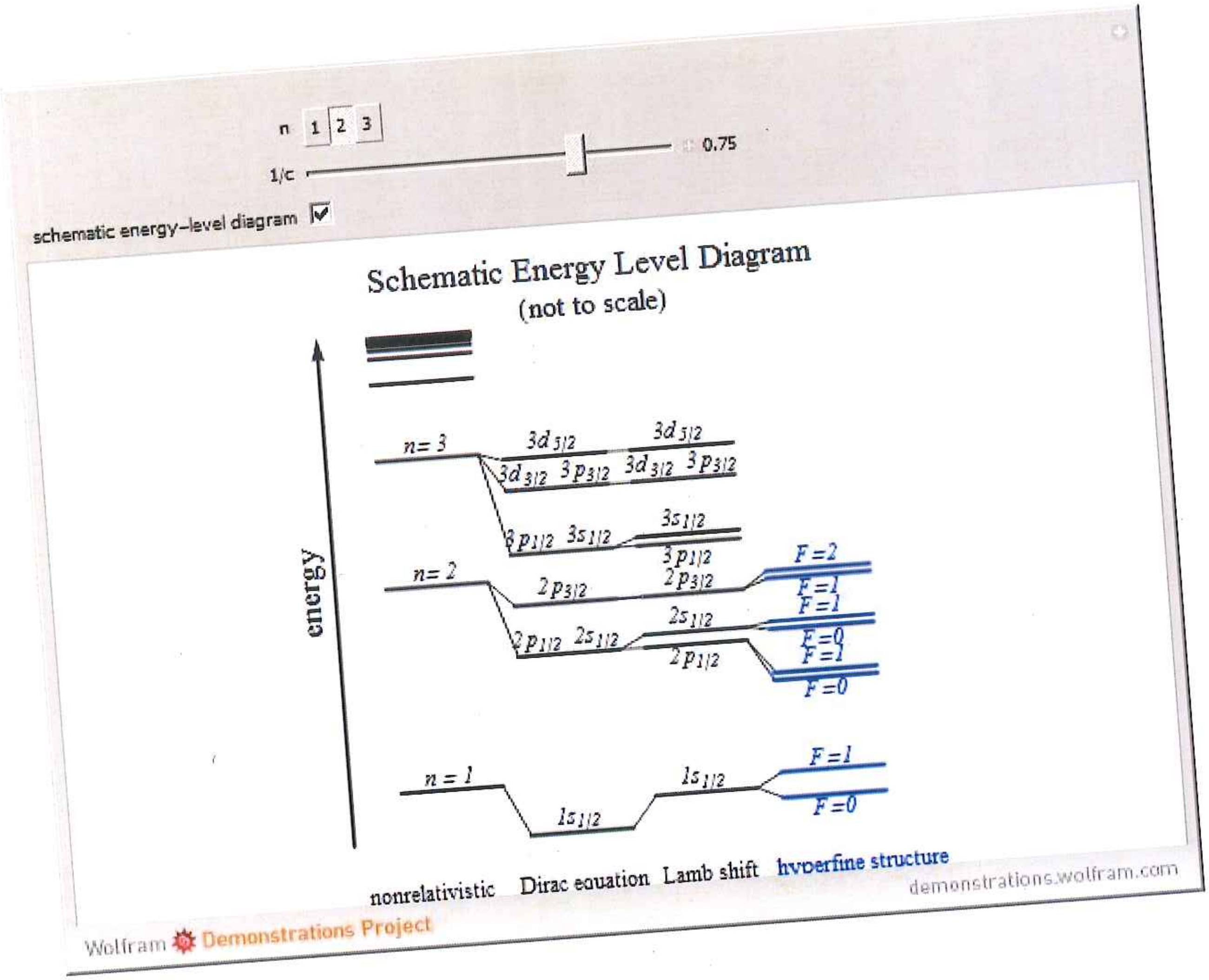
$$= -\frac{4n}{\ell+1} = -\frac{4n}{j+1/2}$$

$$j=\ell-1/2: \quad -\frac{4n}{\ell+1/2} - \frac{2n}{\ell(\ell+1/2)} = -\frac{2n}{\ell+1/2}\left(2+\frac{1}{\ell}\right) = -\frac{4n}{\cancel{\ell+1/2}}\,\frac{\cancel{2\ell+1}^{\,2}}{\ell} =$$

$$= -\frac{4n}{\ell} = -\frac{4n}{j+1/2}$$

$$E_{n\ell s j m_j} = E_n^{(0)} + \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+1/2}\right]$$

Total angular momentum degeneracy is lifted, but states with different ℓ, but same j ($\ell=0, j=1/2$ and $\ell=1, j=1/2$) remain degenerate.
(One needs QED to lift this degeneracy).


n 1 2 3
1/c
0.75
schematic energy–level diagram
Schematic Energy Level Diagram
(not to scale)
energy
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3d 5/2
3d 3/2 3p 3/2
3p 1/2 3s 1/2
3s 1/2
3p 1/2
n= 2
2p 3/2
2p 1/2 2s 1/2
2s 1/2
2p 1/2
F =2
F =1
F =0
n = 1
1s 1/2
nonrelativistic
Dirac equation
Lamb shift
hyperfine structure
demonstrations.wolfram.com
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The Two Component Dirac Equation

First, we can write the **two component equation that is equivalent to the Dirac equation**. Assume that the solution has the **usual time dependence** $e^{-iEt/\hbar}$. We start from the equation in ψ_A and ψ_B.

$$\begin{pmatrix} -i\hbar\frac{\partial}{\partial x_0} & -i\hbar\vec{\sigma}\cdot\vec{\nabla} \\ i\hbar\vec{\sigma}\cdot\vec{\nabla} & i\hbar\frac{\partial}{\partial x_0} \end{pmatrix}\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix} + mc\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix} = 0$$
$$\begin{pmatrix} -\frac{E}{c} & \vec{\sigma}\cdot\vec{p} \\ -\vec{\sigma}\cdot\vec{p} & \frac{E}{c} \end{pmatrix}\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix} + mc\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix} = 0$$

Turn on the EM field by making the usual substitution $\vec{p}\rightarrow\vec{p}+\frac{e}{c}\vec{A}$ and adding the scalar potential term.

$$\begin{pmatrix} -\frac{1}{c}(E+eA_0-mc^2) & \vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right) \\ -\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right) & \frac{1}{c}(E+eA_0+mc^2) \end{pmatrix}\begin{pmatrix}\psi_A\\ \psi_B\end{pmatrix} = 0$$
$$\frac{1}{c}(E+eA_0-mc^2)\psi_A = \vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\psi_B$$
$$\frac{1}{c}(E+eA_0+mc^2)\psi_B = \vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\psi_A$$

These two equations can be turned into one by eliminating ψ_B.

$$\frac{1}{c}(E+eA_0-mc^2)\psi_A = \vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\frac{c}{(E+eA_0+mc^2)}\vec{\sigma}\cdot\left(\vec{p}+\frac{e}{c}\vec{A}\right)\psi_A$$

This is the two component equation which is equivalent to the Dirac equation for energy eigenstates. The one difference from our understanding of the Dirac equation is in the **normalization**. We shall see below that the normalization difference is small for non-relativistic electron states but needs to be considered for atomic fine structure.
