Fine structure of hydrogen

Rest energy of an electron: $m_e c^2$

Rydberg energies (atomic levels): $E_R = \frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$

$$\frac{E_R}{m_e c^2} = \frac{1}{2}\,\frac{1}{c^2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = \frac{1}{2}\,\alpha^2 \quad \text{(dimentionless)}$$

Scaling factor for e-m interaction

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar} \simeq \frac{1}{137}$$

This factor is also a scaling parameter for relativistic corrections compare to the atomic levels

Rest mass: $m_e c^2$

Atomic energies: $\propto \alpha^2 m_e c^2$

Fine-structure: $\propto \alpha^4 m_e c^2$ (due to relativistic nature of an electron)

Lamb shift: $\propto \alpha^5 m_e c^2$ (due to quantum nature of e-m field)

Hyperfine structure: $\propto \alpha^4 \left(\frac{m_e}{m_p}\right) m_e c^2$

Corrections due to relativistic nature of an electron

- Relativistic correction (to the kinetic energy)
- Spin - orbit interaction

Relativistic correction

Proper definition of the kinetic energy

$$K = \gamma mc^2 - mc^2 = E - mc^2$$

$$E^2 = p^2c^2 + (mc^2)^2 \quad \Rightarrow \quad E = \sqrt{p^2c^2 + (mc^2)^2}$$

If $pc \ll mc^2$ (non-relativistic limit)

$$\sqrt{p^2c^2 + (mc^2)^2} = mc^2 \sqrt{1 + (pc)^2/(mc^2)^2} = mc^2 \sqrt{1 + \left(\frac{p}{mc}\right)^2}$$

$$\sqrt{1+x} \approx 1 + \frac{1}{2}x - \frac{1}{8}x^2$$

$$mc^2 \sqrt{1 + \left(\frac{p}{mc}\right)^2} \approx mc^2 + \frac{1}{2}\frac{p^2}{m} - \frac{1}{8}\frac{p^4}{m^3c^2}$$

Kinetic energy $K \approx \frac{1}{2}\frac{p^2}{m} - \frac{1}{8}\frac{p^4}{m^3c^2}$

More precise hamiltonian $\hat{H} = \underbrace{\frac{\hat{p}^2}{2m} - \frac{ke^2}{r}}_{\hat{H}^{(0)}} \underbrace{- \frac{1}{8}\frac{\hat{p}^4}{m^3c^2}}_{\hat{H}'}$

First order correction: $E^{(1)} = \langle \psi | \left(-\frac{\hat{p}^4}{8m^3c^2}\right) | \psi \rangle$

$$\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} - \frac{ke^2}{r} \quad \Rightarrow \quad \hat{p}^2 = 2m\left(\hat{H}^{(0)} + \frac{ke^2}{r}\right)$$

$$\hat{p}^4 = 4m^2\left(\hat{H}^{(0)} + \frac{ke^2}{r}\right)^2 = 4m^2\left\{\left(\hat{H}^{(0)}\right)^2 + \hat{H}^{(0)}\frac{ke}{r} + \frac{ke}{r}\hat{H}^{(0)} + \left(\frac{ke^2}{r}\right)^2\right\}$$

$$\langle \psi^{(0)}_{n\ell m}|\hat{p}^4|\psi^{(0)}_{n\ell m}\rangle = 4m^2\left\{\langle \psi^{(0)}_{n\ell m}|\hat{H}^{(0)}\hat{H}^{(0)}|\psi^{(0)}_{n\ell m}\rangle + \langle \psi^{(0)}_{n\ell m}|\hat{H}^{(0)}\frac{ke^2}{r}|\psi^{(0)}_{n\ell m}\rangle + \right.$$

$$\left. - \langle \psi^{(0)}_{n\ell m}|\frac{ke^2}{r}\hat{H}^{(0)}|\psi^{(0)}_{n\ell m}\rangle + \langle \psi_{n\ell m}|\left(\frac{ke^2}{r}\right)^2|\psi_{n\ell m}\rangle\right\}$$

$$\hat{H}^{(0)}|\psi^{(0)}_{n\ell m}\rangle = E^{(0)}_n|\psi^{(0)}_{n\ell m}\rangle \qquad \langle \psi^{(0)}_{n\ell m}|\hat{H}^{(0)} = E^{(0)}_n\langle \psi^{(0)}_{n\ell m}|$$

$$\langle \psi^{(0)}_{n\ell m}|\left(\hat{H}^{(0)}\right)^2|\psi^{(0)}_{n\ell m}\rangle = E^{(0)2}_n$$

$$\langle \psi^{(0)}_{n\ell m}|\frac{ke^2}{r}\hat{H}^{(0)}|\psi^{(0)}_{n\ell m}\rangle = E^{(0)}_n\langle \psi^{(0)}_{n\ell m}|\frac{ke^2}{r}|\psi^{(0)}_{n\ell m}\rangle$$

$$\langle \psi^{(0)}_n|\hat{H}^{(0)}\frac{ke^2}{r}|\psi^{(0)}_n\rangle = E^{(0)}_n\langle \psi^{(0)}_{n\ell m}|\frac{ke^2}{r}|\psi^{(0)}_{n\ell m}\rangle$$

$\langle \psi^{(0)}_{n\ell m}|\left(\frac{ke^2}{r}\right)^2|\psi^{(0)}_{n\ell m}\rangle$ ← need to calculate

$\langle \psi^{(0)}_{n\ell m}|\frac{ke^2}{r}|\psi^{(0)}_{n\ell m}\rangle = -\langle U\rangle_n$ average potential energy

For the Coulumb potential $\langle U\rangle_n = 2E^{(0)}_n$

$$\langle \psi^{(0)}_{n\ell m}|\left(\frac{ke^2}{r}\right)^2|\psi^{(0)}_{n\ell m}\rangle = \frac{k^2e^4}{\hbar^3a^2(\ell+1/2)} = \frac{4n}{\ell+1/2}\left(E^{(0)}_n\right)^2$$

Putting it all together

$$\langle \psi^{(0)}_{n\ell m}|\hat{p}^4|\psi^{(0)}_{n\ell m}\rangle = 4m^2\left\{\left(E^{(0)}_n\right)^2 - 4\left(E^{(0)}_n\right)^2 + \frac{4n}{\ell+1/2}\left(E^{(0)}_n\right)^2\right\} =$$

$$= -4m^2\left(E^{(0)}_n\right)^2\left\{3 - \frac{4n}{\ell+1/2}\right\}$$

$$E^{(1)}_{n\ell m} = -\frac{\langle \psi_{n\ell m}|\hat{p}^4|\psi_{n\ell m}\rangle}{8m^3c^2} = \frac{\left(E^{(0)}_n\right)^2}{2mc^2}\left\{3 - \frac{4n}{\ell+1/2}\right\}$$

Thus, the ~~kinetic~~ relativistic correction to the kinetic energy predicts lifting the l-degeneracy, but not m-degeneracy (which is not so surprising, considering that p^4 is isotropic, and does not have any preffered direction)

We can also check that

$$E^{(1)}_{nlm} \sim \frac{(E^{(0)}_n)^2}{mc^2} \propto \frac{(\alpha^2 mc^2)^2}{mc^2} \propto \alpha^4 mc^2$$

$$\text{or} \quad E^{(1)}_{nlm} \propto \alpha^2 E^{(0)}_n$$

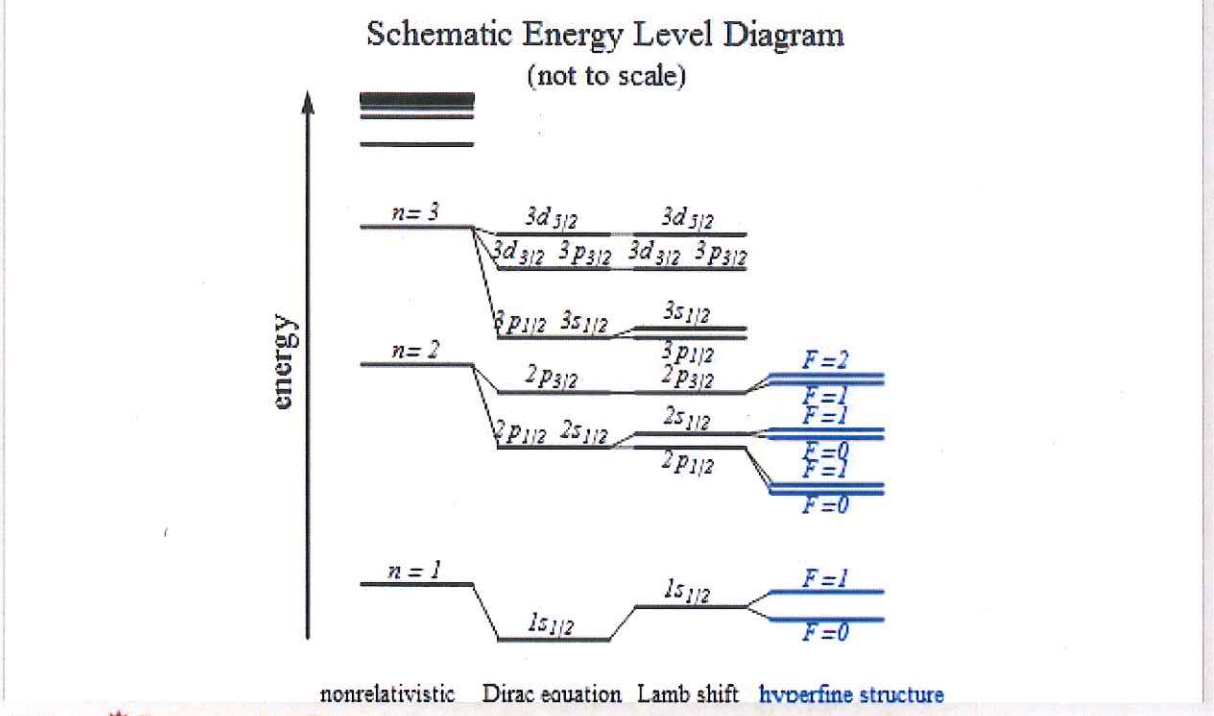
(Hence the name "fine structure constant")

α^2 is the relative

n 1 2 3

1/c 0.75

schematic energy–level diagram ☑



nonrelativistic Dirac equation Lamb shift hyperfine structure

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 $\vec{p} \to \vec{p} + \frac{e}{c}\vec{A}$ 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.
