# Learning Outcomes

You'll be able to:

- Describe the structure of hydrogen in the absence of fine or hyperfine structure
- Characterise the relative splittings in hydrogen
- Identify sources of fine and hyperfine structure
- Apply degenerate perturbation theory to calculate energy splittings in the fine and hyperfine structure of hydrogen
- Define good quantum numbers for hydrogen wavefunctions in presence of fine and hyperfine structure
- Describe the Zeeman effect
- Identify weak, intermediate and strong field regimes of the Zeeman effect
- Apply perturbation theory to hydrogen to calculate the energy splitting at first order in the weak and strong field regimes.

# The hydrogen atom (again)

We've now a number of examples of perturbation theory, but they're all been rather unrealistic – so let's look at the classic realistic application of quantum mechanics: the hydrogen atom.

As a reminder, the basic structure (i.e. to first approximation) of the hydrogen atom is captured by the Bohr Hamiltonian

$$H_{Bohr} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Note we are now in 3D! In general the time-independent Schrödinger equation takes the form

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\bar{r})\right]\psi(\bar{r}) = E\,\psi(\bar{r})$$

but in the presence of a spherical potential we can use separation of variables to write

$$\psi(\bar{r}) = \psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

Here

- $Y_\ell^m(\theta,\phi) = \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\,e^{im\phi}\,P_\ell^m(\cos\theta)$

  ↑ spherical harmonics, eq. 4.32

  ↑ associated Legendre function, eq 4.27/4.28 of G+S

- For hydrogen $V(\vec{r}) = V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

$\Rightarrow$ radial Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2 u}{\partial r^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

$u(r) \equiv rR(r)$

Solutions are

$$\psi_{n\ell m}(r,\vartheta,\phi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}}\, e^{-r/na}\left(\frac{2r}{na}\right)^{\ell}\left[L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na}\right)\right] Y^m_\ell(\vartheta,\phi)$$

Bohr radius: $a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \simeq 0.5\times10^{-10}\,m$

associated Laguerre polynomial eq. 4.87/4.88

spherical harmonics eq 4.27/4.28

principal quantum number $n$

- $n$ determines energy level
- $\ell, m$ determine orbital angular momentum

$$E_n = -\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2} \equiv \frac{E_1}{n^2} \qquad n = 1, 2, 3, \ldots$$

ground state energy

$$E_1 = -\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \simeq -13.6\,eV$$

N.B. ground state wavefunction is

$$\psi_{100}(r,\vartheta,\phi) = \frac{1}{\sqrt{\pi a^3}}\, e^{-r/a}$$

spherically symmetric

This characterises the basic structure of hydrogen atoms, but you will not be surprised to learn there's quite a lot more to it than that.

There are a number of corrections to this basic structure, and to characterise their relative importance, it is useful to introduce the fine structure constant

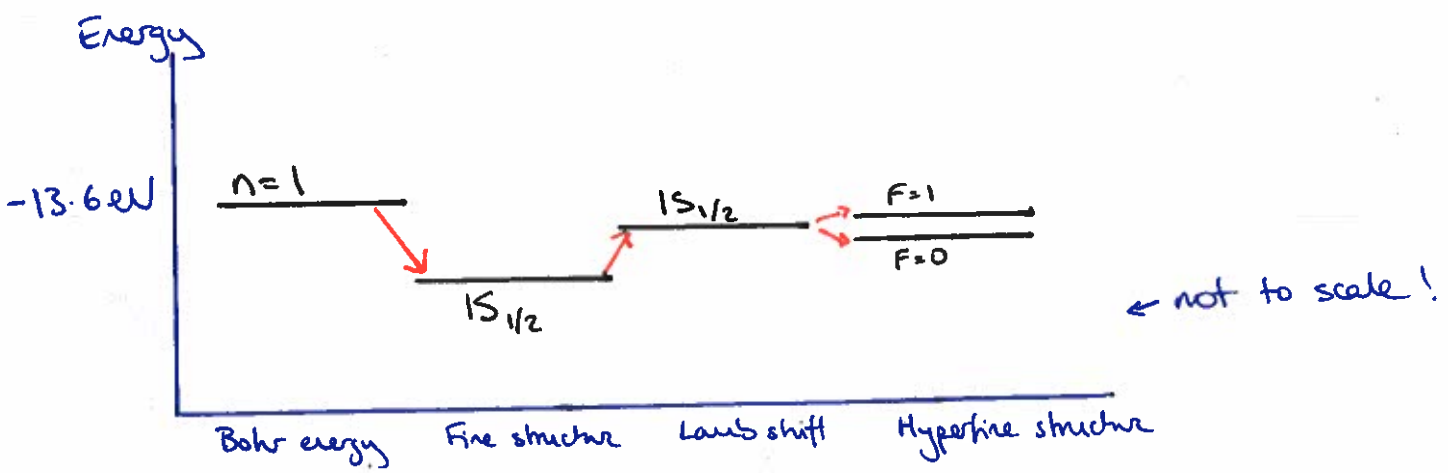
$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} \simeq \frac{1}{137}$$

The various corrections are:

| | Order | Ground state effect |
|---|---|---|
| Bohr energies | $\alpha^2 mc^2$ | $\sim -13.6$ eV |
| Proton motion | $\alpha^2 \mu c^2$ | $\sim 10^{-3}$ eV |
| Fine structure | $\alpha^4 mc^2$ | $\sim 10^{-4}$ eV |
| Lamb shift | $\alpha^5 mc^2$ | $\sim 10^{-5}$ eV |
| Hyperfine structure | $\frac{m_e}{m_p}\alpha^5 mc^2$ | $\sim 10^{-6}$ eV |

Proton motion - affects all energy levels, so does not appear in plots showing relative splittings and fine/hyperfine structure

↑ see problem 5.1/5.2 of G+S




← not to scale!

## Fine structure

- relativistic mass correction ← electron is not entirely nonrelativistic
- spin-orbit coupling ← interaction between electron spin and magnetic field due to orbiting proton!
- "Darwin term"
  - ↑ affects only s-orbitals
  - ↑ correction due to non point-like nature of the electron (think energy uncertainty principle)

## Lamb shift

- radiative corrections (quantum fluctuations)
- requires quantum field theory for full explanation

Explanation of the $2S_{1/2}$ and $2P_{1/2}$ energy splitting, observed in 1947 by Lamb and Retherford, by Bethe was one of foundations of quantum electrodynamics, perhaps the most successful physical theory of all time.

## Hyperfine structure

- spin-spin coupling ← interaction between electron spin and proton spin, arising from the magnetic dipole of the proton

Let's look at the first correction, due to relativity.

For the usual (nonrelativistic) Hamiltonian that appears in the time-independent Schrödinger equation, the kinetic energy is

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m} \xrightarrow{\vec{p} \to -i\hbar\vec{\nabla}} -\frac{\hbar^2}{2m}\nabla^2$$

nonrelativistic

↑ G+S call this "classical", but usually I consider that to mean "non-quantum", not "pre-20th century".

The relativistic kinetic energy is, however,

$$T = mc^2\left(\frac{1}{\sqrt{1 - v^2/c^2}} - 1\right)$$

total relativistic energy; rest energy $= mc^2$

difference is energy attributable to motion.

and the relativistic momentum is

$$p = \frac{mv}{\sqrt{1 - v^2/c^2}}$$

Rearranging this (← and adding $m^2c^4$) gives

$$p^2c^2 + m^2c^4 = \frac{m^2v^2c^2}{1 - v^2/c^2} + m^2c^4 = \frac{m^2v^2c^2 + m^2c^4(1 - v^2/c^2)}{1 - v^2/c^2}$$

$$= \frac{m^2c^4}{1 - v^2/c^2} = (T + mc^2)^2$$

Thus

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2$$

The nonrelativistic limit is $p \ll mc$ (i.e. $v \ll c$)

$$\Rightarrow T = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} - mc^2$$

$$= mc^2\left[\sqrt{1 + \frac{p^2}{m^2c^2}} - 1\right]$$

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

$$= \frac{p^2}{2m} - \frac{(p^2)^2}{8m^3c^2} + \cdots$$

↑ usual nonrelativistic kinetic energy

↖ first relativistic correction to the nonrelativistic kinetic energy

Therefore the perturbing Hamiltonian for the relativistic correction is:

$$H_r' = -\frac{(p^2)^2}{8m^3c^2}.$$

The first-order correction to the energy levels in perturbation theory is:

$$E_r^1 = -\langle\varphi|\frac{(p^2)^2}{8m^3c^2}|\varphi\rangle$$

$$= -\frac{1}{8m^3c^2}\langle p^2\varphi|p^2\varphi\rangle$$

Q: Why is nondegenerate perturbation theory acceptable? $\varphi_{1,0,0}$ are the "good states".

To calculate this expression we use a trick. From the Schrödinger equation for the unperturbed states, we have

$$p^2\varphi = 2m(E - V)\varphi$$

And therefore

$$E_r^1 = -\frac{1}{2mc^2}\langle (E-V)^2 \rangle$$

$$= -\frac{1}{2mc^2}\left[E^2 - 2E\langle V\rangle + \langle V^2\rangle\right]$$

For hydrogen

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

$$\Rightarrow E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right]$$

Clearly we need $\langle 1/r\rangle$ and $\langle 1/r^2\rangle$ for hydrogen.

These are worked out in Problems 7.15 and 7.42:

$$\left\langle\frac{1}{r}\right\rangle = \frac{1}{n^2 a}$$

($a$ ← Bohr radius)

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

$$E_r^1 = -\frac{1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{an^2} + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{(\ell+1/2)n^3a^2}\right]$$

But the Bohr radius is $a = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$ (Eq. 4.72) and $E_n = -\frac{me}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{n^2}$ (Eq. 4.70)

PTO

$$\Rightarrow E_r^1 = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{\ell+1/2} - 3\right].$$

We note that

- some degeneracy has been lifted (different $l$ lead to different energy levels), but there is still the $(2l+1)$-fold degeneracy associated with $m$, because this is associated with spherical symmetry, which is not broken by $H_r'$.

> Warning! The following is very hardwary at certain points!

Now let's turn to the spin-orbit coupling

From the point-of-view of the electron, the proton orbits the the electron, which generates a magnetic field $\bar{B}$. The electron has a magnetic moment $\bar{\mu}$ and the interaction between a magnetic moment and a magnetic field is

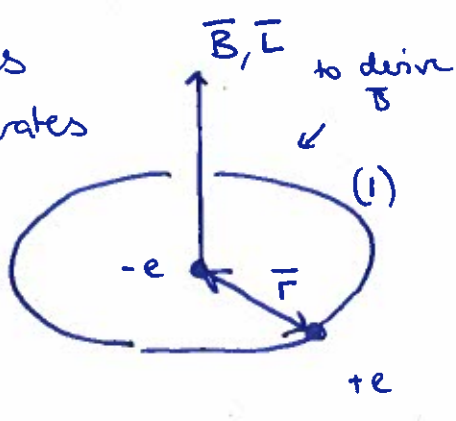
$$H_B = -\bar{\mu}\cdot\bar{B}$$

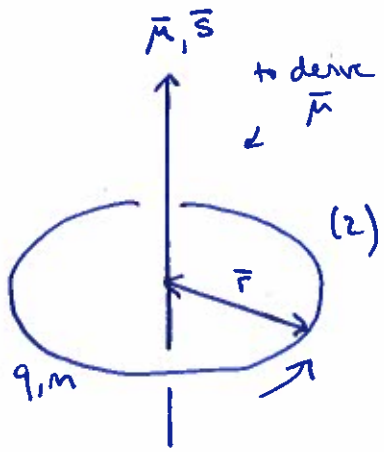
↖ But we need the specific form of $\bar{\mu}$ for the electron and $\bar{B}$ due to the proton.

(1)

We can represent the proton as a continuous current loop, which generates a magnetic field

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r}\frac{e}{T}$$




$e$ = charge of proton
$T$ = period of orbit
} effective current is $I = e/T$

To relate this to the more usual quantum quantities, we note that the orbital angular momentum of the electron is

$$L = rmv = \frac{2\pi m_e r^2}{T}$$

$$\Rightarrow B = \frac{\mu_0}{2r}\frac{eL}{2\pi m_e r^2} = \frac{1}{2r}\cdot\frac{1}{\epsilon_0 c^2}\cdot\frac{e}{2\pi m_e r^2}L$$

($c = \frac{1}{\sqrt{\epsilon_0\mu_0}}$)

Since $\bar{B}$ and $\bar{L}$ point in the same direction, we can write

$$\bar{B} = \frac{1}{4\pi\epsilon_0}\frac{e}{mc^2r^3}\bar{L}$$

Now we need the magnetic moment of the electron, which we obtain (approximately) from (2).

For charge $q$ smeared out in a ring of radius $r$, rotating with period $T$, the <u>magnetic dipole moment</u> is

$$\mu = \frac{q\pi r^2}{T}$$

(defined as current $\frac{q}{T}$ × area $\pi r^2$)

If the ring has mass $m$, its <u>angular momentum</u> is

$$S = \frac{2\pi m r^2}{T}$$

(defined as moment of inertia $mr^2$ × angular velocity $\frac{2\pi}{T}$)

$$\Rightarrow \frac{\mu}{S} = \frac{q}{2m}$$

Now, $\bar{\mu}$ and $\bar{S}$ point in opposite directions if $q$ is negative.

$$\Rightarrow \quad \bar{\mu}^{NR} = -\frac{|q|}{2m}\bar{S}$$ ← wrong!

However, this turns out to be wrong. The correct answer is

$$\bar{\mu}_e^e = -\frac{|q_e|}{m_e}\bar{S} = -\frac{e}{m_e}\bar{S}$$ ← right!

Why, you ask? Because relativity.

↑ Unfortunately to fully explain this, you need relativistic quantum mechanics and the Dirac equation. And even this isn't exactly correct, because of QED corrections

Now we can put $\bar{B}$ and $\bar{\mu}_e$ together to give

$$H'_{SO} = \frac{e^2}{8\pi\varepsilon_0}\frac{1}{m^2c^2r^3}\bar{S}\cdot\bar{L}$$

↑ You may notice that $\bar{\mu}_e \cdot \bar{B}$ has a numerical factor equal to $4\pi\varepsilon_0$ here, not the $8\pi\varepsilon_0$ as written. That is because this hardwary "derivation" ignored the fact that the electron is accelerating (i.e. in a noninertial reference frame). This leads to Thomas precession, which gives an extra factor of $\frac{1}{2}$ in $H'$.

↑ In fact, the extra factor of 2 in $\bar{\mu}_e$ cancels the factor of $\frac{1}{2}$ from Thomas precession! So a naive nonrelativistic guess would have worked.

This spin-orbit Hamiltonian is our perturbing Hamiltonian, so now we need to calculate the shift in the energy levels.

To do this we need $\left\langle \frac{\bar{L}\cdot\bar{S}}{r^3} \right\rangle$ and in fact we can calculate $\langle \bar{L}\cdot\bar{S} \rangle$ and $\left\langle \frac{1}{r^3} \right\rangle$ separately.

To determine $\langle \bar{L} \cdot \bar{S} \rangle$ we note that

$$[H'_{so}, \bar{L}] \neq 0$$
$$[H'_{so}, \bar{S}] \neq 0$$

} spin and orbital angular momentum no longer separately conserved

See problem 7.19

But

$$[H'_{so}, L^2] = [H'_{so}, S^2] = [H'_{so}, \bar{J}] = 0$$

$\bar{J} = \bar{L} + \bar{S}$

So the "good states" are not eigenstates of $L_z$ and $S_z$, but the eigenstates of $L^2, S^2, J^2, J_z$.

Since

$$J^2 = (\bar{L} + \bar{S}) \cdot (\bar{L} + \bar{S}) = L^2 + S^2 + 2\bar{L} \cdot \bar{S}$$

$$\Rightarrow \bar{L} \cdot \bar{S} = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$$

$s = \frac{1}{2}$ for an electron and a proton!

$$\Rightarrow \text{eigenvalues of } \bar{L} \cdot \bar{S} \text{ are } \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]$$

And

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

See problem 7.43

Putting this together

The $\ell = 0$ case is special and $= 0$, but on physical grounds $E'^{0}_{so} = 0$ for $\ell = 0$.

$$E'^{1}_{so} = \langle H'_{so} \rangle = \frac{e^2}{8\pi\varepsilon_0} \frac{1}{m^2c^2} \frac{\hbar^2}{2} \frac{j(j+1) - \ell(\ell+1) - 3/4}{\ell(\ell + 1/2)(\ell + 1)n^3 a^3}$$

P.T.O.

or

$$E'^{1}_{so} = \frac{E_n^2}{mc^2} \frac{n\left(j(j+1) - \ell(\ell+1) - 3/4\right)}{\ell(\ell + 1/2)(\ell + 1)}$$

The sum of these two terms is

$$E^1_{FS} = E^1_r + E^1_{so}$$

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

see problem 7.20

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

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

$$= \frac{E_1}{n^4}\cdot\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right)$$

$$= \frac{E_1}{n^4}\,\frac{1}{4}\left(\frac{e^2}{4\pi\hbar\epsilon_0 c}\right)^2\left(3 - \frac{4n}{j+1/2}\right)$$

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

$$\boxed{E^1_{FS} = \frac{E_1}{n^2}\,\frac{\alpha^2}{n}\left(\frac{3}{4n} - \frac{1}{j+1/2}\right)}$$

When we include the Bohr energy level, this gives us the complete energy structure of the hydrogen atom, including the fine structure.

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

Comments

- fine structure breaks degeneracy in $\ell$ — so states with the same $n$, but different $\ell$, have different energies.
- fine structure preserves degeneracy in $j$.
- good quantum numbers are now: $\{n, \ell, s, j, m_j\}$ ↑ not $m_\ell$ or $m_s$!
- what about the Darwin term?
  - this is given by $H'_{\text{Darwin}} = \frac{\pi\hbar^2}{2m_e^2c^2}\frac{e^2}{4\pi\epsilon_0}\delta^{(3)}(\vec{r})$
  - affects only $\ell = 0$ states
  - generates energy shift $E'_{\text{Darwin}} = \frac{2nE_n^2}{m_ec^2} = \frac{E_1}{n^4}\cdot n\alpha^2$
  - exactly compensates for issues with spin-orbit coupling for $\ell = 0$ states
- In fact, this whole derivation has been kind of hardwavy. A correct treatment requires the Dirac equation ↑ reconcile relativistic quantum mechanics and it gives

You do not need to know this ↘

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

← see problem 7.22

Expanding this at first order gives (somewhat miraculously) exactly the result we put together earlier.

Let's now briefly look at the hyperfine structure of hydrogen.

As we know, the electron has a magnetic dipole moment

$$\bar{\mu}_e = -\frac{g_e e}{2m_e}\bar{S}_e \qquad g_e \simeq 2.00$$ Section 7.5

Not surprisingly – because the proton is a charged spin ½ particle – so does the proton

$$\bar{\mu}_p = \frac{g_p e}{2m_p}\bar{S}_p$$

> Q. Predict $\bar{\mu}_p$ given your knowledge of $\bar{\mu}_e$. Do we expect $|\bar{\mu}_p| \ll |\bar{\mu}_e|$ or $|\bar{\mu}_p| \gg |\bar{\mu}_e|$?

The magnetic field due to a dipole is

$$\bar{B} = \frac{\mu_0}{4\pi r^3}\left[3(\bar{\mu}\cdot\hat{r})\hat{r} - \bar{\mu}\right] + \frac{2}{3}\mu_0\bar{\mu}\,\delta^3(\bar{r})$$

This magnetic field generates another perturbation in the hydrogen Hamiltonian

$$H'_{HF} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e}\frac{3(\bar{S}_p\cdot\hat{r})(\bar{S}_e\cdot\hat{r}) - \bar{S}_p\cdot\bar{S}_e}{r^3} + \frac{\mu_0 g_p e^2}{3m_p m_e}\bar{S}_p\cdot\bar{S}_e\,\delta^3(\bar{r})$$

Some comments:

- $\bar{\mu}_p$ has opposite sign to $\bar{\mu}_e$, because charge of proton is $+e$, not $-e$.
- $|\bar{\mu}_p| \ll |\bar{\mu}_e|$, because $\frac{1}{m_p} \ll \frac{1}{m_e}$.
- $g_p \simeq 5.59$. The proton is made of three quarks, so "classically" one might expect $3 \times 2 = 6$, but the internal structure of the proton is governed by quantum chromodynamics, the theory of the strong nuclear force, which is highly nontrivial.

This leads to the first-order correction to the energy

$$E'_{HF} = \frac{\mu_0 g_p e^2}{8\pi m_p m_e}\left\langle\frac{3(\bar{S}_p\cdot\hat{r})(\bar{S}_e\cdot\hat{r}) - \bar{S}_p\cdot\bar{S}_e}{r^3}\right\rangle + \frac{\mu_0 g_p e^2}{3m_p m_e}\langle\bar{S}_p\cdot\bar{S}_e\rangle|\psi(0)|^2$$

Rather than treating this in general, let's consider what effect this has on the ground state.

If $\ell = 0$, then the wavefunction is spherically symmetric and the first term vanishes (see Problem 7.31).

Moreover, for the ground state

$$|\psi_{100}(0)|^2 = \frac{1}{\pi a^3} \Rightarrow E^1_{HF}\Big|_{GS} = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a^3} \langle \vec{S}_p \cdot \vec{S}_e \rangle$$

↑ this is the "spin-spin coupling"

In the presence of coupled spins, the individual spins are no longer good quantum numbers – but the total spin $\vec{S} = \vec{S}_p + \vec{S}_e$ is a good quantum number.

Thus

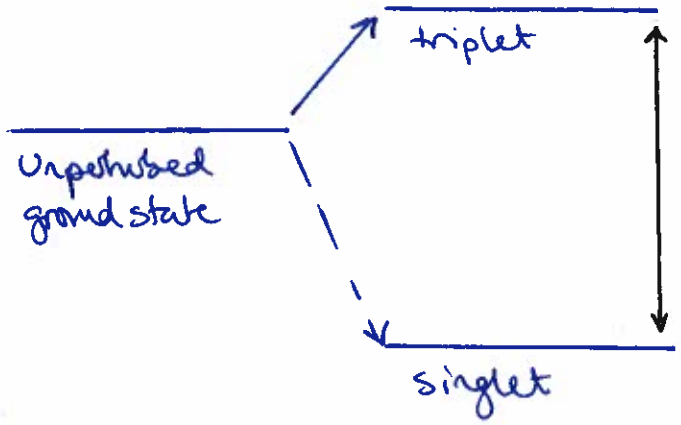
$$\vec{S}_p \cdot \vec{S}_e = \frac{1}{2}\left(S^2 - S_e^2 - S_p^2\right)$$

$S^2$: $s=1$ for triplet $\Rightarrow S^2 = 2\hbar^2$; $s=0$ for singlet $\Rightarrow S^2 = 0$

$S_e^2 = S_p^2 = \frac{3\hbar^2}{4}$

Putting this together we get

$$E^1_{HF}\Big|_{GS} = \frac{g_p \hbar^4}{3 m_p m_e^2 c^2 a^4} \times \begin{cases} 1 & \text{triplet} \\ -3 & \text{singlet} \end{cases} \Rightarrow \text{spin degeneracy is lifted!}$$




$$\Delta E = \frac{4 g_p \hbar^4}{3 m_p m_e^2 c^2 a^4} \simeq 5.9 \times 10^{-6}\ \text{eV}$$

↳ photon emitted in transition has

$$\nu = \frac{\Delta E}{\hbar} = 1420\ \text{MHz}$$

$$\lambda = c/\nu = 21\ \text{cm}$$ ← famous cosmological [illegible]

# Zeeman effect

So far we've only considered the hydrogen atom in isolation, in the absence of any external fields. But we know that the electron (and the proton) has a magnetic dipole moment, so we naturally expect it to respond to an external magnetic field. The resulting energy shifts are known as the Zeeman effect.

That is, linear in $|\bar{B}|$. You will study the quadratic case in homework.

There is an analogous effect, the Stark effect, for an external electric field. You will study this in a homework.

The linear Zeeman effect has perturbing Hamiltonian

$$H_z' = -(\bar{\mu}_l + \bar{\mu}_s)\cdot\bar{B}_{ext} = \frac{e}{2m}(\bar{L} + 2\bar{S})\cdot\bar{B}_{ext}$$

$$\bar{\mu}_l = -\frac{e}{2m}\bar{L}$$ associated with orbital motion

$$\bar{\mu}_s = -\frac{e}{m}\bar{S}$$ associated with spin

The nature of this Zeeman effect depends on the relative strengths of the internal magnetic field relative to the external magnetic field

$$\bar{B}_{int} = \frac{1}{4\pi\varepsilon_0}\frac{e}{mc^2r^3}\bar{L}$$

There are three cases

1. Weak-field Zeeman effect

$|\bar{B}_{ext}| \ll |\bar{B}_{int}|$ $\Rightarrow$ fine structure dominates

$H'_z$ is the perturbation

↑ to $H_{Bohr} + H'_{FS}$

2. Intermediate-field Zeeman effect

$|\bar{B}_{ext}| \simeq |\bar{B}_{int}|$ $\Rightarrow$ neither dominates

treat $H'_{FS} + H'_z$ as perturbation

(to Bohr Hamiltonian)

3. Strong-field Zeeman effect

$|\bar{B}_{ext}| >> |\bar{B}_{int}|$ $\Rightarrow$ Zeeman effect dominates

treat $H'_{FS}$ as a perturbation

↑ to $H_{Bohr} + H'_z$

Q: Estimate $|\bar{B}_{int}|$ to characterise the strong- and weak-field regimes quantitatively. [Problem 7.23]

P.T.O.

## Weak-field effect

We treat $H'_z$ as a perturbation to $H_{Bohr} + H'_{FS}$

still some degeneracy

↗ assuming $\bar{B}_{ext} = B_z \hat{z}$

unperturbed states $|n\, l\, j\, m_j\rangle$

unperturbed energies $E_{nj}$

Since $[H'_z, J_z] = [H'_z, L^2] = 0$

and the degenerates are uniquely labelled by $l$ and $m_j$, we can use $|n\, l\, j\, m_j\rangle$ as the "good states" and apply nondegenerate perturbation theory.

Thus the first-order correction to the energy, due to the Zeeman effect, is

$$E_z^{(1)} = \langle n\, l\, j\, m_j | H_z' | n\, l\, j\, m_j \rangle$$
$$= \frac{e}{2m} B_{ext}\, \hat{k} \cdot \langle \bar{L} + 2\bar{S} \rangle$$
$$= \frac{e}{2m} B_{ext}\, \hat{k} \cdot \langle \bar{J} + \bar{S} \rangle$$

To calculate this, we note that

- $\bar{J} = \bar{L} + \bar{S}$ is a constant
- $\bar{L}, \bar{S}$ precess rapidly around $\bar{J}$
- $\bar{S}_{AVE} = \left(\frac{\bar{S} \cdot \bar{J}}{J^2}\right) \bar{J}$
  ↑ time average
- $\bar{L} = \bar{J} - \bar{S} \Rightarrow L^2 = J^2 + S^2 - 2\bar{J} \cdot \bar{S}$
  $\Rightarrow \bar{J} \cdot \bar{S} = \frac{1}{2}\left(J^2 + S^2 - L^2\right)$
  $= \frac{\hbar^2}{2}\left(j(j+1) + s(s+1) - l(l+1)\right)$

We now replace $\bar{J} = \bar{L} + \bar{S} \rightarrow \bar{L} + \bar{S}_{AVE}$

$$E_z^{(1)} = \frac{e}{2m} B_{ext}\, \hat{k} \cdot \langle \bar{J} + \bar{S}_{AVE} \rangle$$
$$= \frac{e}{2m} B_{ext}\, \hat{k} \cdot \langle \bar{J} + \frac{\bar{S} \cdot \bar{J}}{J^2} \bar{J} \rangle$$
$$= \frac{e}{2m} B_{ext}\, \hat{k} \cdot \left[1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}\right] \langle \bar{J} \rangle$$
$$= \frac{e}{2m} B_{ext} \underbrace{\left[1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}\right]}_{g_J = \text{Landé g-factor}} \hbar M_j$$
$$= \mu_B g_J B_{ext} M_j$$

$\mu_B = \frac{e\hbar}{2m} \simeq 5.8 \times 10^{-5} \frac{eV}{T}$ Bohr magneton

## Strong-field effect

Here the unperturbed Hamiltonian is $H_{Bohr} + H'_z$ and the corresponding unperturbed energies are

($H'_z = \frac{e}{2m} B_{ext} (L_z + 2S_z)$)

$$E_{n\ell m_\ell m_s} = \frac{E_1}{n^2} + \mu_B B_{ext} (m_\ell + 2m_s)$$

The unperturbed states $|n\ell m_\ell m_s\rangle$ are degenerate, but happen to be "good states", because $[H'_{FS}, L^2] = [H'_{FS}, J_z] = 0$

($L^2$: breaks degeneracy in $\ell$; $J_z$: resolves degeneracy in states with $m_\ell + 2m_s = m_j + m_s$)

The perturbing Hamiltonian is $H'_{FS}$ and so

$$E'_{FS} = \langle n\ell m_\ell m_s | H'_r + H'_{so} | n\ell m_\ell m_s \rangle$$

($H'_r$: same as before; $H'_{so}$: need $\langle \vec{S}\cdot\vec{L} \rangle = \underbrace{\langle S_x\rangle\langle L_x\rangle + \langle S_y\rangle\langle L_y\rangle}_{=0} + \langle S_z\rangle\langle L_z\rangle = \hbar^2 m_\ell m_s$)

Thus

$$E'_{FS} = -\frac{E_1}{n^2}\frac{\alpha^2}{n^2}\left[\frac{3}{4} - \frac{n(\ell(\ell+1) - m_\ell m_s)}{\ell(\ell+\frac{1}{2})(\ell+1)}\right]$$

↑ if $\ell = 0$ then correct value is 0 see problem 7.28

N.B. Total energy is

$$E_{n\ell m_\ell m_s} + E'_{FS}$$

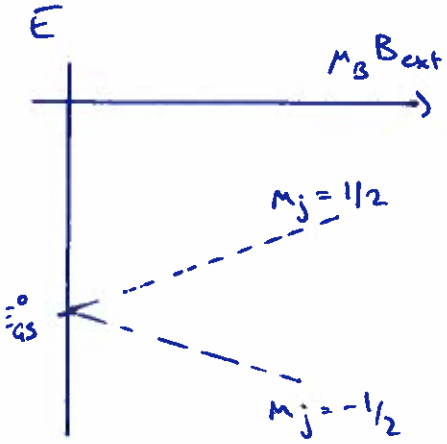
Thus the weak-field Zeeman effect breaks degeneracy in $m$, because $H'_z$ picks a special direction ($B_{ext}$) and therefore breaks spherical symmetry (which gives rise to degeneracy in $m$).

In the presence of the external magnetic field, the total energy is the sum of the fine structure and the Zeeman effect contribution.

$$E_{nj} = \frac{E_1}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right] + \mu_B g_j B_{ext} m_j$$

e.g the ground state

$n=1,\ \ell=0,\ j=1/2 \Rightarrow g_j = 2,\ m_j = \pm\frac{1}{2}$ $\Big\}$ $E_{1\,1/2} = E_1\left(1 + \frac{\alpha^2}{4}\right) \pm \mu_B B_{ext}$




## Intermediate-field effect

This requires degenerate perturbation theory, since we don't initially know what the good states are. The example for $n=2$ is worked out in pages 309-310, and problem 7.30 guides you through the $n=3$ case.