Fine Structure of Hydrogen using perturbation theory.

$$H^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

Hierarchy of corrections to the Bohr energies of hydrogen.

No perturbations $\Rightarrow$ Bohr energy: $\sim m_e c^2 \alpha^2$

1. Fine Structure: $\Delta E \sim \alpha^4 m_e c^2$

2. Lamb Shift: $\Delta E \sim \alpha^5 m_e c^2$

3. Hyperfine Splitting: $\Delta E \sim \left(\frac{m_e}{m_p}\right) \alpha^4 m_e c^2$

where $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137.036}$

Fine structure: is due to 2 distinct mechanisms

1.) Relativistic corrections
2.) Spin-Orbit Coupling $\vec{S}\cdot\vec{L}$

1. Relativistic Corrections: $E = T + m_0 c^2 = \sqrt{p^2c^2 + m_e^2 c^4}$

$$T = -\frac{\hbar^2}{2m}\nabla^2 \quad \Rightarrow \quad T = \sqrt{p^2c^2 + m_e^2c^4} - m_e c^2$$

$$T = m_e c^2\left[\sqrt{1 + \left(\frac{p_e}{m_e c}\right)^2} - 1\right]$$

Fine Structure of Hydrogen (cont'd)

$$T = m_e c^2 \left[1 + \frac{1}{2}\left(\frac{p_e}{m_e c}\right)^2 - \frac{1}{8}\left(\frac{p_e}{m_e c}\right)^4 + \cdots \quad - 1 \right]$$

So, $$T = \left(\frac{p_e^2}{2 m_e^2 c^2} - \frac{p_e^4}{8 m_e^4 c^4} + \cdots \right) m_e c^2$$

So, the lowest order relativistic correction is: $H_r = ?$

$$H_r' = - \frac{p_e^4}{8 m_e^3 c^2}$$

The correction to E° is given by 1st order perturbation theory.

$$E_r^1 = \langle H_r' \rangle = -\frac{1}{8 m_e^3 c^2} \langle \psi | p^4 | \psi \rangle = -\frac{1}{8 m_e^3 c^2} \langle p^2\psi | p^2 \psi \rangle$$

However, $p^2 \psi \to -\hbar^2 \nabla^2 \psi = 2m(E - V)\psi$

So, $$E_r^1 = -\frac{1}{2mc^2} \langle (E-V)^2 \rangle = -\frac{1}{2 m_e c^2} \left[E^2 - 2E\langle V \rangle + \langle V^2 \rangle \right]$$

For the hydrogen atom, we use $V(r) = \dfrac{-e^2}{4\pi\varepsilon_0 r}$

$$\langle V \rangle = \frac{-e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle \quad \text{and} \quad \langle V^2 \rangle = \left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle$$

It can be shown that:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a_0} \quad \text{and} \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(\ell + \frac{1}{2}) n^3 a_0^2}$$

$$E_r^1 = \frac{-1}{2mc^2}\left[E_n^2 + 2E_n\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{n^2 a_0} + \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{(\ell+\frac{1}{2})n^3 a_0^2}\right]$$

Make the following substitutions:

$$\left(\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right)\hbar c \equiv \alpha \hbar c \qquad a_0 \equiv \frac{\hbar}{m\alpha c} \qquad E_n = -\frac{1}{2} mc^2 \frac{\alpha^2}{n^2}$$

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

The relativistic correction $\sim \dfrac{E_n}{mc^2} = \dfrac{13.6\ \text{eV}}{511{,}000\ \text{eV}} \cong 2\times 10^{-5}$

Spin-Orbit Coupling

Electron's point of view, the orbiting proton creates a magnetic field at the e^-.

$H' = -\vec{\mu}\cdot\vec{B}$

$\vec{B}$ = mag. field due to proton

$\vec{\mu}$ = mag. dipole moment of the e^-

a.) Magnetic Field of the proton:

$B = \dfrac{\mu_0 I}{2r}$ (Biot-Savart Law)

$\underset{\uparrow\ \text{current}}{I} = \dfrac{e}{T}$ $\qquad$ $L = \underset{\uparrow\ \text{mom. of inertia}}{I}\omega = mr^2\left(\dfrac{2\pi}{T}\right)$

$$\frac{1}{T} = \frac{L}{mr^2 2\pi} \qquad B = \frac{\mu_0}{2r}\left(\frac{eL}{2\pi m r^2}\right) \qquad \vec{B} = \frac{\mu_0}{4\pi}\frac{e\vec{L}}{mr^3}$$

$$\boxed{\vec{B} = \frac{1}{4\pi\varepsilon_0}\frac{e\vec{L}}{mc^2 r^3}}$$

b.) Magnetic Dipole Moment of the Electron

$\mu = IA = \dfrac{q}{T}(\pi r^2)$ $\qquad$ S = spin ang. mom. $= I\omega = mr^2 \dfrac{2\pi}{T}$

Spin-Orbit Coupling

μ/S = gyromagnetic ratio $\qquad \frac{\mu}{S} = \frac{q}{2m} g_s$ ← g-factor

$$\vec{\mu} = \frac{q}{2m} g_s \vec{S} \qquad g_s = 2 \text{ for the } e^- \text{ so...} \qquad \boxed{\vec{\mu}_e = \frac{-e}{m} \vec{S}}$$

H' becomes:

$$H' = -\vec{\mu} \cdot \vec{B} = \frac{e}{m} \frac{e}{4\pi\varepsilon_0} \frac{1}{mc^2 r^3} \vec{S} \cdot \vec{L}$$

Another factor $(\frac{1}{2})$ is introduced due to Thomas Precession.

H' becomes:

$$\boxed{H' = \left(\frac{e^2}{8\pi\varepsilon_0}\right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}}$$

Spin-Orbit Interaction

H' no longer commutes with $\vec{L}$ and $\vec{S}$

$$[\vec{L} \cdot \vec{S}, \vec{L}] = i\hbar(\vec{L} \times \vec{S}) \qquad [\vec{L} \cdot \vec{S}, \vec{S}] = i\hbar(\vec{S} \times \vec{L})$$

$$[\vec{L} \cdot \vec{S}, \vec{J}] = 0 \qquad [\vec{L} \cdot \vec{S}, L^2] = 0 \qquad [\vec{L} \cdot \vec{S}, S^2] = 0$$

$$[\vec{L} \cdot \vec{S}, J^2] = 0$$

So, $\vec{L}$ and $\vec{S}$, the orbital and spin angular momentum are no longer separately conserved. $\vec{J} = \vec{L} + \vec{S}$ is conserved. The eigenstates of L_z and S_z are not "good" states to use in perturbation theory, but the eigenstates of L^2, S^2, J^2, and J_z are "good" states.

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

$$J^2 = L^2 + S^2 + 2\vec{S} \cdot \vec{L} \qquad \vec{S} \cdot \vec{L} = \frac{J^2 - L^2 - S^2}{2}$$

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

In our case $s = \frac{1}{2}$, and $\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1) n^3 a_0^3}$

Spin-Orbit Coupling

So, the 1st order correction to the energy due to spin-orbit coupling is:

$$E^1_{so} = \langle H'_{so} \rangle = \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2c^2} \frac{\left(\frac{\hbar^2}{2}\right)\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)}{\ell(\ell+\frac{1}{2})(\ell+1)\, n^3 a_0^3}$$

Again using $E_n = -\frac{1}{2} mc^2 \frac{\alpha^2}{n^2}$ $\quad a_0 = \frac{\hbar}{m\alpha c}$ and $\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c}$

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

$$E^1_{fs} = \underbrace{E^1_r}_{\text{relativistic}} + \underbrace{E^1_{so}}_{\text{spin-orbit}} \Rightarrow \quad E^1_{fs} = \frac{(E_n)^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right)$$

$$E_{nj} = \underbrace{E_n^{(0)}}_{\text{ground state}} + E_{fs}^{(1)} \Rightarrow \quad \boxed{E_{nj} = -\frac{13.6\text{ eV}}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right]}$$

Ground State + Fine Structure

m_ℓ and m_s are no longer "good" quantum numbers.
The "good" quantum numbers are n, ℓ, s, j, m_j

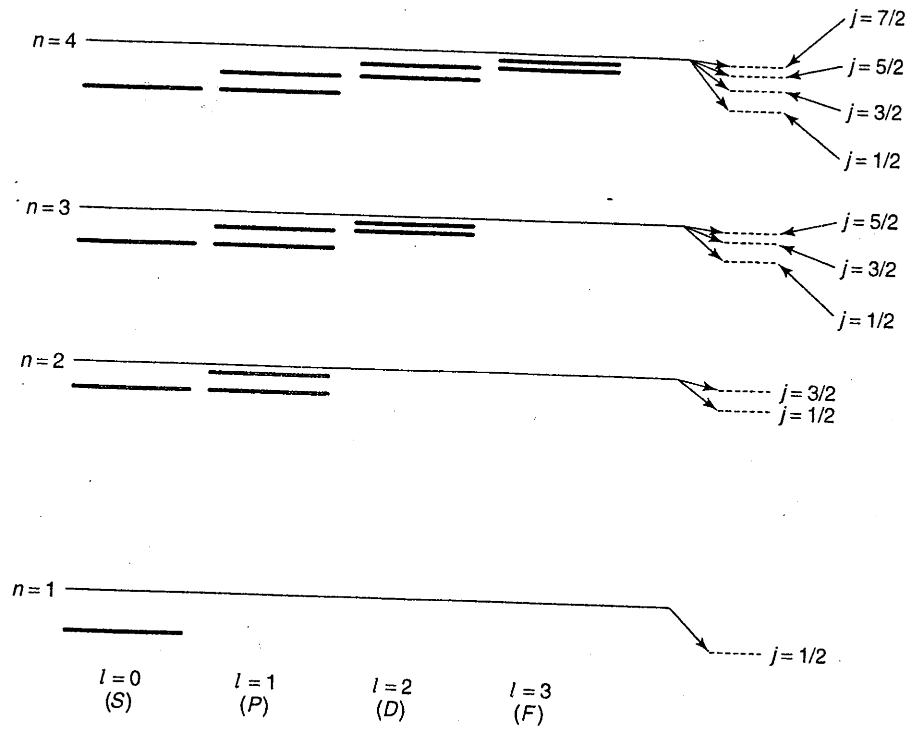


FIGURE 6.9: Energy levels of hydrogen, including fine structure (not to scale).

Zeeman Effect

The perturbation is

$$H_z' = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{ext}$$

where $\vec{\mu}_s = -\frac{e}{2m} g_s \vec{S}$ & $\vec{\mu}_l = \frac{-e}{2m} g_l \vec{L}$

g_s: g-factor $= 2.0023\ldots$ g_l: g-factor $= 1$

$$H_z' = \frac{e}{2m} (\vec{L} + 2\vec{S}) \cdot \vec{B}_{ext}$$

If $B_{ext} \ll B_{internal}$, then $\vec{S}\cdot\vec{L}$ (fine structure) dominates and H_z' can be treated as a perturbation.

See Problem 6.20 ~ 12 Tesla

Weak-Field Zeeman Effect $B_{ext} \ll B_{int}$

$\frac{\mu_0}{4\pi} \frac{e(\alpha c)}{a_0^2}$

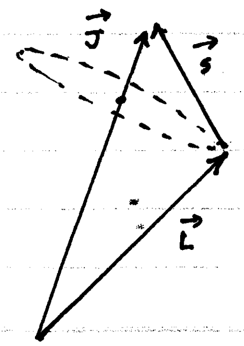
Good quantum numbers: n, l, j, and m_j
because in $\vec{S}\cdot\vec{L}$ coupling, $\vec{L}$ and $\vec{S}$ are not separately conserved.

$\frac{8\ m/s)}{2} \frac{1}{137}$

1st order perturbation theory:

$$H \quad E_z' = \langle n\,l\,j\,m_j | H_z' | n\,l\,j\,m_j \rangle = \frac{e}{2m} \vec{B}_{ext} \cdot \langle \vec{L} + 2\vec{S} \rangle$$

$$\vec{L} + 2\vec{S} = \vec{J} + \vec{S}$$



$$\vec{S}_{Ave} = (\vec{S}\cdot\hat{J})\hat{J} = \frac{\vec{S}\cdot\vec{J}}{J^2}\vec{J}$$

Zeeman Effect

$$\vec{L} = \vec{J} - \vec{S} \qquad L^2 = J^2 + S^2 - 2\vec{J}\cdot\vec{S}$$

So, $$\vec{S}\cdot\vec{J} = \frac{1}{2}\left(J^2 + S^2 - L^2\right)$$

$$\vec{S}\cdot\vec{J} = \frac{\hbar^2}{2}\left(j(j+1) + s(s+1) - \ell(\ell+1)\right)$$

It follows that:

$$\langle \vec{L} + 2\vec{S} \rangle = \left\langle \left(1 + \frac{S\cdot\vec{J}}{J^2}\right)\vec{J} \right\rangle = \underbrace{\left[1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}\right]}_{g_J \,=\, \text{Landé g-factor}} \langle J \rangle$$

$$\langle L + 2S \rangle = g_J \langle J \rangle$$

Choosing the z-axis to be aligned with $\vec{B}_{ext}$, we have:

$$E_z' = \frac{e}{2m}\vec{B}_{ext}\cdot\langle \vec{L} + 2\vec{S} \rangle = \frac{e}{2m}\vec{B}_{ext}\cdot\langle \vec{J} \rangle g_J$$

$$E_z' = \frac{e}{2m} g_J B_{ext} \langle J_z \rangle = \frac{e}{2m} g_J B_{ext} (m_J \hbar)$$

$$E_z' = \left(\frac{e\hbar}{2m}\right) g_J B_{ext} m_J = \mu_B g_J B_{ext} m_J$$

$$\boxed{E_z' = \mu_B g_J B_{ext} m_J}$$ where $\mu_B = \frac{e\hbar}{2m_e}$ Bohr magneton

$$\boxed{\mu_B = 5.788 \times 10^{-5} \frac{eV}{T}}$$

Zeeman Effect

Example: (from the book) Ground State of hydrogen

$n=1 \quad l=0 \quad j=\frac{1}{2}$

$$g_J = 1 + \frac{\frac{1}{2}\left(\frac{3}{2}\right) - 0 + 3/4}{2\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)} \Rightarrow g_J = 1 + \frac{\frac{6}{4}}{\frac{6}{4}} = 2$$

Since $j=\frac{1}{2}$, m_J can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

Combining this with f.s. we obtained earlier

$$E_{n_{1\,1/2}} = \frac{-13.6\text{ eV}}{1^2}\left[1 + \frac{\alpha^2}{1^2}\left(\frac{1}{\frac{1}{2}+\frac{1}{2}} - \frac{3}{4}\right)\right] = -13.6\text{eV}\left[1 + \frac{\alpha^2}{4}\right]$$

We obtain: $E_{TOTAL} = E_{1,1/2} \pm \mu_B B_{ext}$ $\quad g_J = 2$

$$\boxed{E_{TOTAL} = -13.6\text{ eV}\left(1 + \frac{\alpha^2}{4}\right) \pm \mu_B B_{ext}}$$

Hydrogen $n=1$, $l=0$
$m_J = +\frac{1}{2}$ or $-\frac{1}{2}$
fine structure + Zeeman effect

Correction Terms:

1.) $-13.6\text{eV}\,\frac{\alpha^2}{4} = \underline{\underline{-1.81 \times 10^{-4}\text{ eV}}}$

2.) $+\mu_B B_{ext} = 5.788 \times 10^{-5}\,\frac{\text{eV}}{\text{T}} \times 1\text{ tesla} = \underline{\underline{5.788 \times 10^{-5}\text{ eV}}}$

Question: Weak field with respect to what?

Biot-Savart Law

$$B_{internal} = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2a_0}\frac{e}{T} = \frac{\mu_0}{2a_0}\frac{ev}{2\pi a_0} = \frac{\mu_0}{4\pi}\frac{e(\alpha c)}{a_0^2}$$

$$B_{internal} = \frac{4\pi \times 10^{-7}\left[\frac{T \cdot M}{A}\right]}{4\pi} \frac{1.602 \times 10^{-19}\, C \; (3 \times 10^{8}\, m/s)}{(0.0529 \times 10^{-9}\, m)^2} \frac{1}{137}$$

$$\boxed{B_{internal} = 12.54 \text{ tesla}}$$