# Physic 492 - Quantum II

## Lecture 23: Spin-Orbit Coupling and Fine Structure Splitting

So far, in looking at the energy spectrum of atoms we have included only electrostatic effects (Coulomb interaction) with modifications due to the exchange density of identical electrons. The relative motion of the electron has a characteristic velocity $v$, leading to magnetic effects. The magnetic forces are generally much smaller. Given $\vec{E}$ and $\vec{B}$ fields of the same strength (c.g.s. units)

$$\vec{F}_{mag} = q\frac{\vec{v}}{c}\times\vec{B} \qquad \vec{F}_{elec} = q\vec{E}$$

Thus $|\vec{F}_{mag}| << |\vec{F}_{elec}|$ when $v << c$

Only for relativistic velocities are the forces comparable.

Atomic units: Energy $\frac{e^2}{a_0}$, time $= \frac{\hbar}{E_c} = \frac{\hbar a_0}{e^2} = t_{char}$

$$\Rightarrow \frac{v_{characteristic}}{c} = \frac{a_0}{t_{char}c} = \frac{e^2}{\hbar c} \equiv \alpha = \frac{1}{137}$$

$\alpha = \frac{v_{\text{charge}}}{c} = \frac{e^2}{\hbar c} = \frac{1}{137}$ is known as the

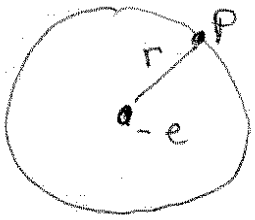
"fine structure constant" since it determines

fine structure is the emission lines of hydrogen spectrum, as we will see below. It is also the fundamental "coupling constant" in quantum electrodynamics (QED).

We thus see that the electron is "mildly relativistic". A complete relativistic equation is the Dirac eq (and QED more generally). We will content ourselves here with relativistic perturbations to the Schrödinger equation.

Magnetic interaction energy

Consider the hydrogen atom. In the frame of the electron, the proton is circling it (Next Page)




The proton thus creates a current loop which produces a magnetic field at the position of $-e$. The interaction energy is thus

$$\hat{H}_{int} = -\hat{\vec{\mu}} \cdot \vec{B}_{@electron}$$

where $\hat{\vec{\mu}} = g_s \mu_B \frac{\hat{\vec{S}}}{\hbar} = -2\frac{\mu_B}{\hbar}\hat{\vec{S}}$ is the intrinsic magnetic moment of the electron due to its spin.

The current produced by proton $I = \frac{e\omega}{2\pi} = \frac{ev}{2\pi r}$

$$= \frac{emvr}{2\pi r^2 m} = \frac{eL}{2\pi r^2 m}$$

where $L$ is the angular momentum of relative motion between electron and proton.

$$\Rightarrow \vec{B} = \frac{2\pi}{c}\frac{I}{r}\vec{e}_n = \frac{e\vec{L}}{cr^3 m} = \frac{1}{r^3}\underbrace{\frac{e\hbar}{mc}}_{=2\mu_B}\frac{\vec{L}}{\hbar}$$

($\vec{e}_n$: normal to loop)

$$\Rightarrow \hat{H}_{int} = 4\frac{\mu_B^2}{r^3}\hat{\vec{l}}\cdot\hat{\vec{S}} \qquad \left(\text{where } \hat{\vec{l}} = \frac{\hat{\vec{L}}}{\hbar},\ \hat{\vec{S}} = \frac{\hat{\vec{S}}}{\hbar}\right)$$

This Hamiltonian couples the relative motion of the electron with the proton to its spin. It is known as spin-orbit coupling (sometimes L-S coupling for jargon).

Note: An alternative way to derive this expression is to recall that an electric field in one inertial frame produces a magnetic field in a co-moving frame. This method is discussed in Liboff.

Now, we have fudged this because the electron orbit is not an inertial frame. The effect of moving to a rotating frame has a subtle effect on the intrinsic magnetic moment, effective reducing the interaction by a factor of 2. This is known as thomas precession

(see Eisberg + Resnick, Modern Physics)

$$\Rightarrow \quad \hat{H}_{int} = -\frac{1}{2}\vec{\mu}\cdot\vec{B}$$

The spin-orbit Hamiltonian is then

$$\hat{H}^{SO}_{int} = \frac{2\mu_B^2}{r^3}\,\hat{\vec{l}}\cdot\hat{\vec{s}} = \frac{2\mu_B^2}{a_0^3}\,\frac{1}{\bar{r}^3}\,\hat{\vec{l}}\cdot\hat{\vec{s}}$$

in characteristic units:

Aside $\quad \frac{\mu_B^2}{a_0^3} = \left(\frac{e^2}{a_0}\right)\left(\frac{\mu_B}{e a_0}\right)^2$

($e^2/a_0$: Hartree; $\mu_B$: magnetic dipole; $e a_0$: electric dipole)

$$\mu_B = \frac{e\hbar}{2mc} \qquad a_0 = \frac{\hbar^2}{me^2}$$

$$\Rightarrow \frac{\mu_B}{e a_0} = \frac{1}{2}\,\frac{e^2}{\hbar c} = \frac{1}{2}\,\alpha$$

($\alpha$: Fine-structure constant)

$$\therefore \hat{H}^{SO}_{int} = \underbrace{\frac{1}{2}\frac{e^2}{a_0}}_{R}\,\alpha^2\,\frac{1}{\bar{r}^3}\,\hat{\vec{l}}\cdot\hat{\vec{s}}$$

$$R = 13.6\ eV$$

Perturbation since $\alpha^2 \ll 1$

Let us consider the effect of spin–orbit coupling on the energy levels of hydrogen.

- ground state: $n=1 \quad \ell=0$ (s-state)

$$\Rightarrow \langle 1s| \hat{H}^{so}_{int} |1s\rangle = 0 \qquad (\text{since } \ell=0)$$

$\Rightarrow$ No first order shift

- First excited state $n=2$, (p-state and s-state) $\otimes$ (spin)
  (3 deg)

Must use degenerate perturbation theory

$\Rightarrow$ diagonalize $\hat{H}^{s\text{-}o}_{int}$ in 8-dim subspace

However we already did this in P.S. #7.

The eigenstates of $\hat{\ell}\cdot\hat{s}$ are the states of total electron angular momentum $\hat{j} = \hat{\ell} + \hat{s}$.

This is the "coupled representation"

$$|j\, m_j;\, \ell, s\rangle = \sum C_{m_\ell, m_s} \, |\ell\, m_\ell\rangle\, |s\, m_s\rangle$$

Note, $\ell$ remains a "good quantum number"

Thus spin orbit does not mix $s$ ($\ell=0$) and $p$ ($\ell=1$) symmetry.

The eigenvalues follow simply by noting,

$$\hat{j}^2 = \hat{l}^2 + \hat{s}^2 + 2\hat{\vec{l}}\cdot\hat{\vec{s}} \Rightarrow \hat{\vec{l}}\cdot\hat{\vec{s}} = \frac{\hat{j}^2 - \hat{l}^2 - \hat{s}^2}{2}$$

$$\Rightarrow \hat{l}\cdot\hat{s}\,|\,j\,m_j;\,l\,s\rangle = \frac{j(j+1) - l(l+1) - \underbrace{s(s+1)}_{\frac{3}{4}}}{2}$$

Finally, we need to include the radial wave function.

The first order shift due to spin-orbit is thus

$$\Delta E^{(1)}_{nj\ell} = \langle n j \ell |\, \hat{H}^{s\text{-}o}\,|\, n j \ell\rangle$$

$$= \frac{e^2}{2a_0}\,\alpha^2 \underbrace{\langle n\ell |\, \frac{1}{r^3}\,|\, n\ell\rangle}_{\parallel}\; \frac{j(j+1) - l(l+1) - \frac{3}{4}}{2}$$

$$\int_0^\infty dr\; \frac{1}{r^3}\left(u_{n\ell}(r)\right)^2$$

↑ Can do this $= \dfrac{1}{n^3\, l(l+\frac{1}{2})(l+1)}$

(Next Page)

The first order shifts for $n = 2$

$l = 0 \Rightarrow j = \frac{1}{2}$ only

$l = 1 \Rightarrow j = l + \frac{1}{2} = \frac{3}{2}$ or $j = l - \frac{1}{2} = \frac{1}{2}$

$\Rightarrow$ Perturbation to 2p state due to spin orbit

$$\Delta E_{n=2,\ l=1,\ j=3/2} = \frac{1}{96} \frac{e^2}{a_0} \alpha^2$$

$$\Delta E_{n=2,\ l=1,\ j=1/2} = -\frac{1}{48} \frac{e^2}{a_0} \alpha^2$$

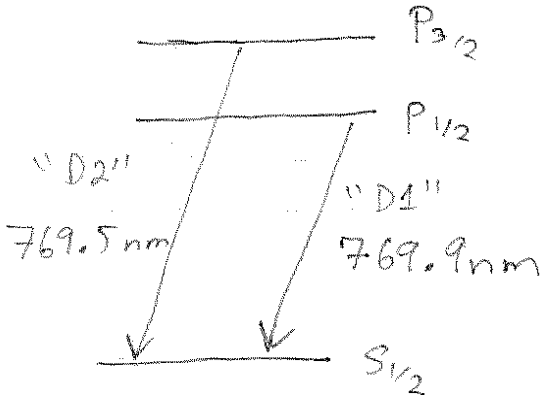
$$\Delta E_{n=2,\ l=0,\ j=1/2} = 0$$


Spin-orbit splitting

Spectroscopic notation

$L_J$

The spin-orbit coupling gives rise to the famous "Sodium doublet" in the spectrum of Na




First excited state.

Ground state

In an alkali, we have one valence electron, as in hydrogen. However, that electron no longer sees a pure Coulombic potential $\frac{1}{r}$ due to nucleus, but a mean field due to all other electrons.

$$\Rightarrow \vec{\mathcal{E}} = -\vec{\nabla}\phi = -\frac{d}{dr}\phi(r)\,\hat{e}_r$$

↖ central potential

$$\Rightarrow \vec{B} \text{ in electron frame} = -\frac{\vec{v}}{c}\times\vec{\mathcal{E}} = -\frac{\vec{p}}{mc}\times\vec{\mathcal{E}}$$

$$\Rightarrow \hat{H}_{SO} = -\tfrac{1}{2}\vec{\mu}\cdot\vec{B} = \tfrac{1}{2}\vec{\mu}\cdot\left(\frac{\vec{p}}{mc}\times\vec{\mathcal{E}}\right)$$

$$= -\tfrac{1}{2}\vec{\mu}\cdot\left(\frac{\vec{r}}{r}\times\vec{p}\right)\left(\frac{1}{mc}\frac{dV}{dr}\right)$$

$$= \frac{-1}{2mc}\,\vec{\mu}\cdot\vec{L}\left(\frac{1}{r}\frac{dV}{dr}\right) = +\frac{\mu_B}{2mc}\left(\frac{1}{r}\frac{dV}{dr}\right)\vec{L}\cdot\vec{S}$$

# Other relativistic corrections

The spin-orbit interaction is a "relativistic" correction to the dominant electrostatic interaction. For consistency we should include other relativistic effects.

Relativistic correction to kinetic energy:

$$\hat{T} = \left(\hat{p}^2 c^2 + (mc^2)^2\right)^{1/2} - mc^2$$

$$= \frac{\hat{p}^2}{2m} - \frac{\hat{p}^4}{8m^3c^2} + \cdots$$

Thus we have another perturbation

$$\hat{H}_{kin} = -\frac{\hat{p}^4}{8m^3c^2}$$

Scales $p_c = m v_c = \alpha (mc)$

$$\Rightarrow \Delta E_{kin} = \alpha^4 mc^2 = \alpha^2 \left(\frac{e^2}{\hbar c}\right)^2 mc^2 = \alpha^2 \left(\frac{me^4}{\hbar}\right)$$

$$= \alpha^2 \left(\frac{e^2}{a_0}\right)$$ (same scale as spin-orbit effect)

Perturbation to $n\ell m_\ell$ in hydrogen

$$E^{(1)}_{n\ell m_\ell} = \langle n\ell m_\ell | \hat{H}_{rel} | n\ell m_\ell \rangle = -\frac{1}{8m^3c^4} \langle n\ell m_\ell | \hat{p}^4 | n\ell m_\ell \rangle$$

Aside: $\hat{p}^4 = \left(2m \frac{\hat{p}^2}{2m}\right)^2 = \left[2m\left(E - \hat{V}_{coul}\right)\right]^2$

$$\Rightarrow \langle n\ell m_\ell | \hat{p}^4 | n\ell m_\ell \rangle = \int d^3r \, \psi^*_{n\ell m_\ell} \left(2m\left(E_n - \hat{V}_{coul}\right)\right)^2 \psi_{n\ell m_\ell}$$

$$= 4m^2 \left( E_n^2 - 2E_n \langle \hat{V} \rangle_{n\ell m_\ell} + \langle \hat{V}^2 \rangle_{n\ell m_\ell} \right)$$

$$\langle \hat{V} \rangle_{n\ell m_\ell} = -e^2 \left\langle \frac{1}{r} \right\rangle_{n\ell m_\ell} = -\frac{e^2}{a_0} \frac{1}{n^2}$$

$$\langle \hat{V} \rangle_{n\ell m_\ell} = e^4 \left\langle \frac{1}{r^2} \right\rangle_{n\ell m_\ell} = \frac{e^4}{a_0^2} \frac{2}{n^3(2\ell+1)}$$

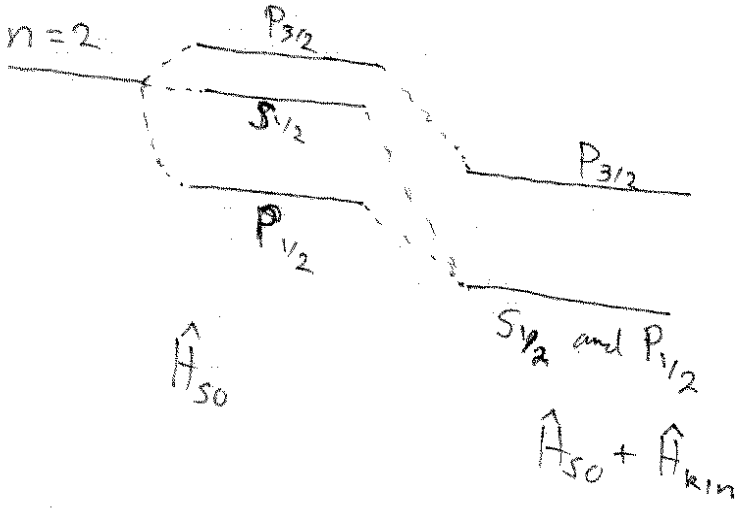
$$\Rightarrow \Delta E^{(1)}_{n\ell m_\ell} = -\alpha^2 \frac{e^2}{a_0} \left( \frac{1}{n^3(2\ell+1)} - \frac{3}{8n^4} \right)$$

Note, no coupling to spin here

For hydrogenic atoms with a pure $\frac{1}{r}$ coulomb interaction we have the "accidental degeneracy" with $l$.

Thus, both the spin-orbit and kinetic terms must be accounted for to see how the $l$-degeneracy is broken.

For this case a new degeneracy forms

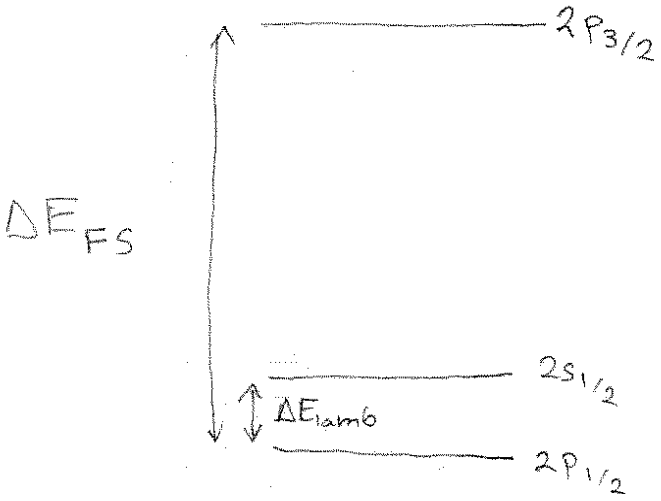



Energy level depends only on $j$ quantum number

"Exact" solution via Dirac equation:

$$\Delta E_{nj} = -\alpha^2 \frac{e^2}{a_0}\left[\frac{1}{n^3(2j+1)} - \frac{3}{8n^4}\right]$$

Finally, there is a perturbation due to the coupling of the electron to the quantum electromagnetic vacuum. This breaks the degeneracy between $2S_{1/2}$ and $2P_{1/2}$ in hydrogen. This effect is known as the Lamb-Shift




Fine-Structure splitting $\frac{\Delta E_{FS}}{h} \simeq 11$ GHz

Lamb Shift $\frac{\Delta E_{Lamb}}{h} \simeq 1$ MHz