Spin-orbit interaction (or “coupling”)  

This interaction is weaker than the Coulomb interaction and is responsible for the **fine-structure** of atomic lines.

How do we understand the spin-orbit interaction?

• The electron has a **spin** \( s \), as well as **orbital angular momentum** \( l \).

• For each angular momentum, there is an associated **magnetic moment**, \( \mu_l \) and \( \mu_s \).

• Spin-orbit = interaction between \( \mu_l \) and \( \mu_s \).

Let’s start with the definition of magnetic moment....
Magnetic moment $\mu_l$

electron orbit = current loop

the magnetic moment is defined as $\mu_l = I \cdot A$ where $I$ is the current and $A$ the area of the orbit.

$\mu_l$ is a vector perpendicular to the plane of the orbit.

Now let’s show that $\mu_l$ is linked to the orbital angular momentum:

![Diagram showing electron orbit, area A, and vectors]

**orbit period**

$$T = \frac{2\pi}{\omega} \quad \Rightarrow \quad I = \frac{-e}{T} = \frac{-e}{2\pi}$$

$$\mu_l = I \cdot A = \frac{-e}{2\pi} \pi r^2 = -\frac{1}{2} e \omega r^2$$

**orbital ang. mom.**

$$\left| \vec{l} \right| = \left| \vec{r} \times \vec{p} \right| = m_0 v r = m_0 \omega r^2$$

$$\vec{\mu}_l = -\frac{e}{2m_0} \vec{l}$$
Note that $\vec{\mu}_l$ and $\vec{l}$ point in opposite directions because the electron is negatively charged.

Let’s consider the case $|\vec{l}| = \hbar$: this is the orbital angular momentum of the ground state in Bohr’s theory, and is therefore taken as the unit of angular momentum in atoms. The modulus of the corresponding magnetic moment is known as **Bohr magneton**:

$$\mu_B = \frac{e\hbar}{2m_o}$$

Bohr magneton

It is unit of magnetic moments in atoms.
More generally, for a state with quantum numbers $l$ and $m_l$:

**Modulus** \[ |\vec{l}| = \hbar \sqrt{l(l+1)} \]

\[ |\vec{\mu}_l| = \frac{e}{2m_o} \hbar \sqrt{l(l+1)} = \mu_B \sqrt{l(l+1)} \]

**Component along z** \[ \mu_{l,z} = -\frac{e}{2m_o} l_z = -\mu_B m_l \]

\[ l_z = m_l \hbar \quad \text{with} \quad m_l = 0, \pm 1, \pm 2, \ldots, \pm l \quad \text{magnetic quantum number} \]

We also can apply these definitions to the electron spin....
**Electron spin**

- An intrinsic property like charge or mass.
- Its existence proven by **Stern-Gerlach experiment** (see later), and justified by **Dirac’s relativistic quantum theory**.
- It’s an intrinsic angular momentum with quantum number $s = \frac{1}{2}$

Hence we can apply the same theory that we saw for the orbital angular momentum (see Hydrogen atom- angular momentum aside).

**Modulus**

$$|\vec{s}| = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

Component along z

$$s_z = m_s\hbar$$

(with $m_s = \pm \frac{1}{2}$)
Spin magnetic moment

\[ \vec{\mu}_s = -g_s \frac{e}{2m_o} \vec{s} \]

Where \( g_s = 2.0023 \) is a numerical factor known as the \textbf{Lande factor} (or “\textbf{g factor}”). Classically it should be 1, but is 2 according to Dirac’s relativistic quantum theory.

\( g_l = 1 \) for orbital angular momentum
Next, let’s consider the **magnetic interaction** of a magnetic moment $\vec{\mu}$ with a magnetic field $\vec{B}$:

**torque** \( \tau = \vec{\mu} \times \vec{B} \)

![Diagram of magnetic interaction](image)

**Magnetic potential energy:**

\[
V_{\text{mag}} = \int_{\pi/2}^{\alpha} (\vec{\mu} \times \vec{B}) d\alpha = \int_{\pi/2}^{\alpha} \mu B \sin \alpha d\alpha = -\mu B [\cos \alpha]_{\pi/2}^\alpha =
\]

\[
= -\mu B \cos \alpha = -\vec{\mu} \cdot \vec{B}
\]

(Note that the potential energy is minimised if magnetic moment is parallel to $B$, i.e. $\alpha=0$.)
Spin-orbit interaction

From the proton's "point of view"

\[ V_{l,s} = -\vec{\mu}_s \cdot \vec{B}_l \]

Orbiting proton produces a field \( \vec{B}_l \) at the site of the electron.

From the electron's "point of view"

The spin, hence \( \vec{\mu}_s \), has two possible orientations with respect to the field: "parallel", with lower energy, and "anti-parallel" with higher energy.

\[ \text{we expect energy levels in atoms to split in two (fine structure).} \]

Note that this is not the only magnetic interaction that is taking place in an atom. The nucleus also has a spin, hence a magnetic moment. The nuclear magnetic moment interacts with the magnetic field produced by the orbiting electron. This interaction is much weaker than the spin-orbit interaction considered here, and is responsible for the hyperfine structure of the energy levels – see later.
Our goal is to determine an expression for the fine structure starting from $V_{l,s} = -\vec{\mu}_s \cdot \vec{B}_l$. Let’s start by writing the B-field in terms of the orbital angular momentum:

Biot-Savart law: \[
\vec{B}_l = \frac{Ze\mu_0}{4\pi r^3} [\vec{v} \times (-\vec{r})] = -\frac{Ze\mu_0}{4\pi r^3} [\vec{v} \times \vec{r}]
\]

The – sign here is because we are in the electron’s frame of reference, see previous slide

\[
\vec{l} = \vec{r} \times m_0 \vec{v}
\]

\[
-\vec{l} = m_0 \vec{v} \times \vec{r}
\]

\[
\vec{B}_l = \frac{Ze\mu_0}{4\pi r^3 m_0} \vec{l}
\]
\[ \vec{B}_l = \frac{1}{2} \times \frac{Ze\mu_0}{4\pi r^3 m_0} \vec{l} \]

from full relativistic calculation
(“Thomas factor”)

\[ \vec{\mu}_s = -g_s \frac{e}{2m_o} \vec{s} \approx -\frac{e}{m_o} \vec{s} \]

\( (g_s \approx 2) \)

\[ V_{l,s} = \frac{e}{m_0} (\vec{s} \cdot \vec{B}_l) = \frac{Ze^2\mu_0}{8\pi m_0^2 r^3} (\vec{s} \cdot \vec{l}) \]
We define the **spin-orbit coupling constant** $a$:

$$a = \frac{Ze^2 \mu_0 \hbar^2}{8\pi m_0 r^3} \quad \Rightarrow \quad V_{l,s} = \frac{a}{\hbar^2} \vec{l} \cdot \vec{s}$$

(With this definition $a$ has the dimension of an energy.)

The constant $a$ is measurable from spectra. We won’t do the calculation, but it can be shown that

$$a \propto \frac{Z^4}{n^3 l \left( l + \frac{1}{2} \right) (l + 1)}$$

(From expectation value)

$$\left\langle \frac{1}{r^3} \right\rangle = \int \psi^* \frac{1}{r^3} \psi \, dV$$

**Heavier atoms** → **larger spin-orbit coupling**

**Larger $n$** → **smaller spin-orbit coupling**
… let’s now consider the scalar product \( \vec{l} \cdot \vec{s} = \|\vec{l}\|\|\vec{s}\| \cos(l, s) \).

It is possible to express this in terms of the **total angular momentum**:

\[
\vec{j} = \vec{l} + \vec{s}
\]

\[
|\vec{j}|^2 = |\vec{l}|^2 + |\vec{s}|^2 + 2|\vec{l}||\vec{s}| \cos(l, s) \quad \Rightarrow \quad V_{l,s} = \frac{a}{2\hbar^2} \left( |\vec{j}|^2 - |\vec{l}|^2 - |\vec{s}|^2 \right)
\]

(These vectors are operators in quantum mechanics)
Properties of $\vec{j}$:

- It is an angular momentum, hence we can apply the results we saw in the “angular momentum aside”.

  new quantum numbers $j$ and $m_j$ such that:

  modulus\(^2\): \[ \hat{j}^2 \Psi = \hbar^2 j(j+1) \Psi \quad \text{with} \quad j = \frac{\text{integer}}{2} = \frac{1}{2}, 1, \frac{3}{2}, ... \]

  projection along z-axis: \[ \hat{j}_z \Psi = \hbar m_j \Psi \quad \text{with} \quad m_j = j, j - 1, ..., -j \]

- We have the commutation relations \[ [\hat{j}^2, \hat{l}^2] = 0 \quad , \quad [\hat{j}^2, \hat{s}^2] = 0 \]

  (which follow from $[\hat{j}_i, \hat{l}^2] = [\hat{j}_i, \hat{s}^2] = 0$ where $i = x, y, z$)

  hence we can choose a set of common eigenfunctions of $\hat{l}^2, \hat{s}^2, \hat{j}^2$, and calculate $V_{l,s}$ on these eigenfunctions….
\[ V_{l,s} = \frac{a}{2\hbar^2} (|\vec{j}|^2 - |\vec{l}|^2 - |\vec{s}|^2) = \frac{a}{2} [j(j+1) - l(l+1) - s(s+1)] \]

This is our final result for spin-orbit coupling:

But we still haven’t discussed how to calculate \( j \)....

From the theory of coupling of angular momenta, it turns out that

\[ j = |l \pm s| = |l \pm \frac{1}{2}| \]

e.g. for a \( p \) state (\( l=1 \)) \( \rightarrow j=1/2 \) \( \rightarrow j=3/2 \)
Example: fine structure of sodium atoms

- state $3s$ ($l=0$) \( j = 1/2 \) and \( V_{l,s} = 0 \)
  there is no fine structure
  (physically, there is no angular momentum, hence no “current loop” and \( B_l = 0 \))

- state $3p$ \( j = 3/2 \) and \( V_{l,s} = \frac{a}{2} \left[ \frac{3}{2} \cdot \frac{5}{2} - 2 - \frac{1}{2} \cdot \frac{3}{2} \right] = \frac{a}{2} \)
  \( j = 1/2 \) and \( V_{l,s} = \frac{a}{2} \left[ \frac{1}{2} \cdot \frac{3}{2} - 2 - \frac{1}{2} \cdot \frac{3}{2} \right] = -a \)

fine structure for $3p$
$3s \rightarrow 3p$ transition is split into a doublet (D lines: D1 and D2)

Sodium doublet viewed in a Fabry-Perot interferometer:
Nomenclature for naming energy terms:

- Principal quantum number
- Orbital angular momentum from earlier = s, p, d, f etc...
- Total angular momentum
- Spin term

\[ n^{2s+1} l_j \]

E.g. ground state of sodium is \( 3^{2} s_{1/2} \)

(The spin term is sometimes omitted, like in the previous slide, because it’s the same for all the levels.)
Let’s see how the spectral lines split due to fine-structure:

• series $3s \rightarrow np$: **pairs of lines**
  (all $p$ states are double)

• series $3p \rightarrow nd$: **triple lines**
  This is because:
  
  $d$ state ($l=2$)  
  $j=5/2$  
  $j=3/2$

and furthermore we have a new selection rule on $j$
  hence only these three transitions are allowed:

$\Delta j = \pm 1,0$
Summary for FINE STRUCTURE

- \( V_{l,s} = -\vec{\mu}_s \cdot \vec{B}_l = \frac{a}{\hbar^2} \hat{l} \cdot \vec{s} \) spin-orbit coupling

- all energy states (except s-states) are split into doublets
- split \( \propto Z^4 \) (larger split in heavy atoms)

But this is not the end with fine structure....
**Hydrogen** is a special case:

Small spin-orbit $\rightarrow$ comparable to relativistic corrections

(remember Bohr-Sommerfeld: in that model the fine structure was due to relativistic effects)

In heavier atoms, spin-orbit coupling is stronger and relativistic effects can be neglected.

For the H-atom:

$$E = E_n + E_{rel} + E_{l,s}$$

- gross structure $-\frac{Ry}{n^2}$
- fine structure $E_{FS}$
- relativistic mass change
- spin-orbit coupling

$$\frac{e^2 \mu_0}{8\pi m_0^2 r^3} (\vec{s} \cdot \vec{l})$$
Result from Dirac’s relativistic theory:

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

where the dimensionless quantity \( \alpha = \frac{e^2}{2\varepsilon_0 hc} = \frac{1}{137} \)

is the fine structure constant.

(You can verify that \( \alpha = v/c \) with \( v \) = velocity of 1st Bohr orbit.)
**Example:** let’s apply this result to the $n=2$ level of Hydrogen. Here we have an $s$ state and a $p$ state:

\[
\begin{align*}
l = 0 &\Rightarrow j = 1/2 \\
l = 1 &\Rightarrow j = 1/2, \ 3/2
\end{align*}
\]

Can calculate $E_{FS}$ for these values of $j$.

This is a further splitting that can only be explained by Quantum Electrodynamics (QED)…
Significance of Lamb shift

In QED the electromagnetic field is quantised.

A quantised field has a zero point energy (analogous to the ground state of the simple harmonic oscillator). This means that even in the case of number of photons=0 ("vacuum"), there is a fluctuating electric field.

Due to this fluctuating field the electron performs small oscillations and its charge is effectively smeared out. It can be shown that the Coulomb potential acting on the electron is different than that for a point charge. This difference causes the Lamb shift.

(Note: this fluctuating electric field is also responsible for spontaneous emission.)