

Fine structure:

- So far we discussed only the gross structure. Considering only kinetic energy, electron nuclear attraction and electron – electron repulsion.
- Smaller interaction – due to magnetic effects. At this stage – only internal magnetic fields – resulting in fine structure.

Fine structure – magnetic interaction between the orbital and spin magnetic moments

Hyperfine structure – magnetic interaction between electron and nuclear magnetic moments.

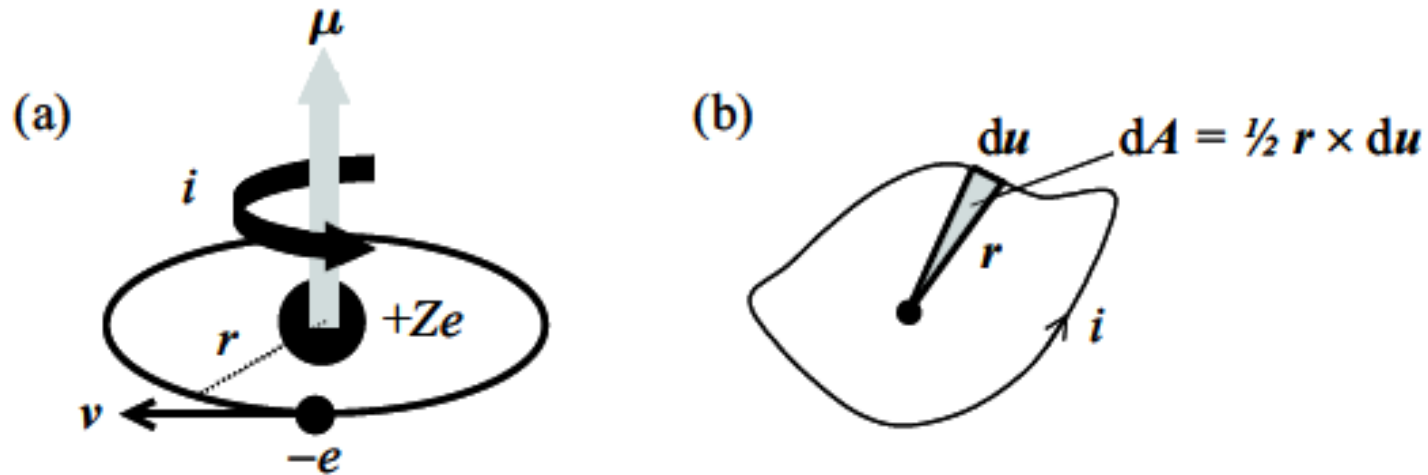
The quantum mechanical solution

- The magnitude of the orbital angular momentum is: $L = \sqrt{l(l+1)}\hbar$, l takes positive integer values up to $n-1$
- Component along a certain axis (normally z):
 $L_z = m_l \hbar$
- m takes integer values from $-l$ to l .
- As discussed already L creates a magnetic dipole μ .

$$\mu = i \times \text{Area} = -(e/T) \times (\pi r^2)$$
$$\mu = -\frac{ev}{2\pi r} \pi r^2 = -\frac{e}{2m_e} m_e v r = -\frac{e}{2m_e} L,$$

Generalization of the expression for the gyromagnetic ratio:

- We know that the orbit is not always circular:



- The magnetic dipole is given by the integral:

$$\mu = \oint i dA$$

- The incremental area is: $dA = \frac{1}{2} r \times du$ and

$$\mu = \frac{1}{2} \oint i r \times du$$

Continued:

- We write $\mathbf{l} = -e\mathbf{T}$

and get:
$$= \frac{1}{2} \oint d\mathbf{q} \mathbf{r} \times \frac{d\mathbf{u}}{dt} = \frac{1}{2} \oint d\mathbf{q} \mathbf{r} \times \mathbf{v},$$

$$= \frac{1}{2m_e} \oint d\mathbf{q} \mathbf{r} \times \mathbf{p},$$

Recall:
$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

We get:
$$\mu = \frac{1}{2m_e} \oint L d\mathbf{q} = \frac{1}{2m_e} L \oint d\mathbf{q} = \frac{1}{2m_e} L(-e)$$

$$|\mu| = \frac{e}{2m_e} \hbar \sqrt{l(l+1)} = \mu_B \sqrt{l(l+1)},$$

(This is possible because L is a constant of the motion). $e/2m_e$ – The gyromagnetic ratio.

The magnitude of μ :
$$|\mu| = \frac{e}{2m_e} \hbar \sqrt{l(l+1)} = \mu_B \sqrt{l(l+1)},$$

The Bohr magneton:

- The unit of magnetic dipole:

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} \text{ JT}^{-1}$$

Mostly we are interested in the z component:

$$\mu_z = -\frac{e}{2m_e} L_z = -\mu_B m_l$$

m_l the magnetic quantum number.

Spin magnetism: The deflection from the Stern Gerlach experiment:

$$\mu_z = -g_s \mu_B m_s$$

g_e the g value of the electron:

- $m_s = \pm 1/2$ is the magnetic quantum number of the spin. g_e is predicted by the Dirac eqn. to be 2.
- Quantum electrodynamics gives **2.0023192**, in agreement with experiments.
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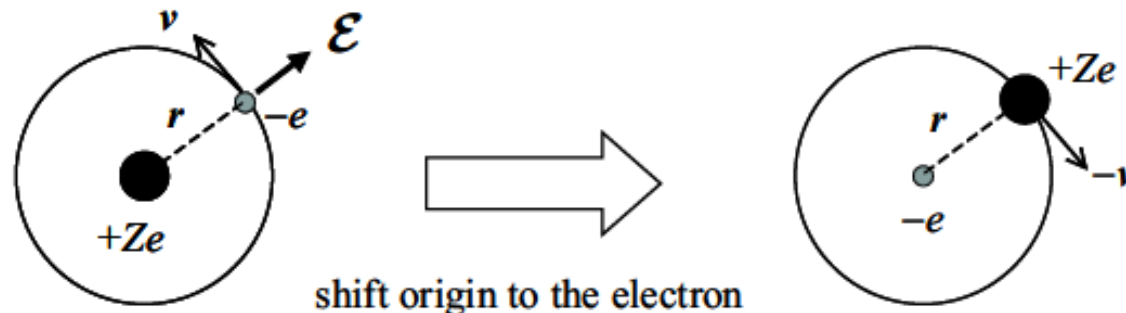
Spin orbit coupling:

- Actually – a relativistic effect (like the spin) But a more intuitive explanation –

the interaction between the magnetic field by the orbit and the magnetic moment of the spin.

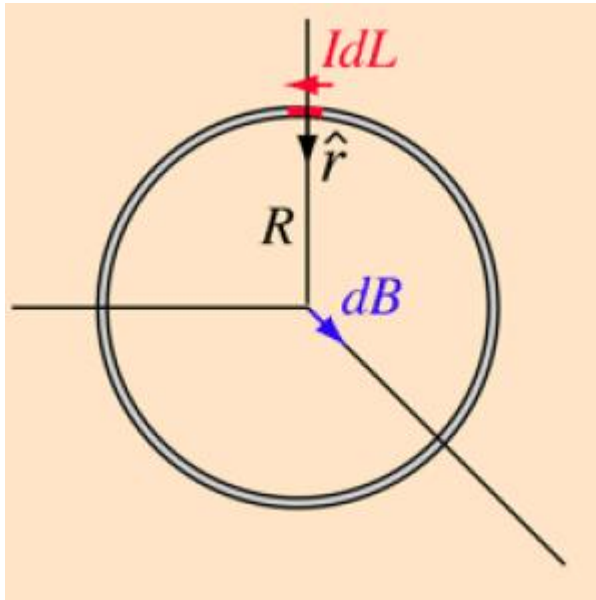
The coupling can be estimated using the Bohr model. A better result – with modern quantum mechanics.

We assume a static electron and a nucleus rotating around it.



Spin-orbit coupling in the Bohr model

Current loop calculated by Biot Savart law



$$dB = \frac{\mu_0 Id\vec{L} \times \hat{r}}{4\pi R^2} = \frac{\mu_0 IdL \sin\theta}{4\pi R^2}$$

$$B = \frac{\mu_0 I}{4\pi R^2} \oint dL = \frac{\mu_0 I}{4\pi R^2} 2\pi R = \frac{\mu_0 I}{2R}$$

$$\mu_0 = 4\pi \times 10^{-7} T \cdot m / A$$

In the direction perpendicular to the loop (z)

$$B_z = \frac{\mu_0 i}{2r}$$

Cont.

- I given by charge Ze divided by orbital period:

$$T = 2\pi r/v.$$

We get.
$$B_z = \frac{\mu_0 Z e v_n}{4\pi r_n^2}$$

Recall: according to the Bohr model:

$$r_n = \frac{n^2}{Z} \frac{m_e}{m} a_0 \quad v_n = \alpha \frac{Z}{n} c.$$

- Where the Bohr radius and the fine structure constant are:

$$a_0 = \frac{h^2 \epsilon_0}{\pi m_e e^2} \quad \alpha = \frac{e^2}{2\epsilon_0 h c}$$

The field induced by the nucleus

$$B_z = \frac{\mu_0 Z e v_n}{4\pi r_n^2} = \left(\frac{Z^4}{n^5} \right) \frac{\mu_0 \alpha c e}{4\pi a_0^2}$$

- Where: $\alpha = e^2 / 2\epsilon_0 h c \approx 1/137$
- For hydrogen with $Z=n=1$, $B_z = 12$ T.
- The interaction of the electron with this field:

$$\Delta E_{so} = -\mu_{spin} \cdot B_{orbital} :$$

- Calculating the z component:

$$\Delta E_{so} = g_s \mu_B m_s B_z = \pm \mu_B B_z$$

- (Using $g_s = 2$ and $m_s = \pm 1/2$).

Using

- The equations

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} \text{ JT}^{-1}.$$

- We get $|\Delta E_{\text{so}}| = \left(\frac{Z^4}{n^5}\right) \frac{\mu_0 \alpha c e^2 \hbar}{8\pi m_e a_0^2} \equiv \alpha^2 \frac{Z^2}{n^3} |E_n|$.

- Where we used:

- $E_n = -\frac{mZ^2e^4}{8\epsilon_0^2h^2n^2}$.

The energy is expressed in terms of Rydberg energy

$$E_n = -\frac{R'}{n^2}$$

- We get for $n=1$ (hydrogen).

$$|\Delta E_{so}| = \alpha^2 R_H = 13.6 \text{ eV} / 137^2 = 0.7 \text{ meV} \equiv 6 \text{ cm}^{-1}$$

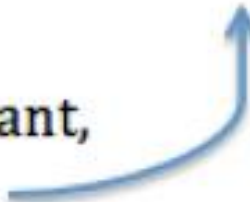
- Yet (for a given n) it grows as Z^2 .

Speed of light and electric and magnetic fields:

- Imagine two charged wires that are moving at speed v at the same direction:
- There is electrostatic repulsion between them:

$$F_E = k * \frac{2\lambda^2}{d}$$

Coulomb's Constant,
equal to $\frac{1}{4\pi\epsilon_0}$




- λ is the charge density

The magnetic attraction

- If the two wires are moving with speed v :

Electric current,
equal to I from
above eq.

A blue line representing a wire starts from the left, curves downwards and to the right, then forms a small rectangular loop. The text 'Electric current, equal to I from above eq.' is positioned to the left of the wire.
$$F_B = \frac{(\lambda v)^2 * \mu_0}{2\pi d}$$

- The velocity that these forces are balanced:

$$F_B = \frac{(\lambda v)^2 * \mu_0}{2\pi d} = \frac{2\lambda^2}{4\pi\epsilon_0 * d} = F_E$$

cont.

- Is
$$\frac{\lambda^2 * v^2 * \mu_0}{2\pi d} = \frac{\lambda^2}{2\pi d * \epsilon_0}$$

We get
$$v^2 * \mu_0 = \frac{1}{\epsilon_0}$$

and
$$v = \sqrt{\frac{1}{\mu_0 * \epsilon_0}} \quad c = \frac{1}{\sqrt{\mu_0 \epsilon_0}}$$

In the speed of light – a stable wavepacket.

Spin-orbit coupling beyond the Bohr model

- A nucleus moving around the electron at velocity v results in a magnetic field given by the Biot Savart eqn.

$$B = \frac{\mu_0}{4\pi} \oint_{\text{loop}} i \frac{d\mathbf{u} \times \mathbf{r}}{r^3}$$

- $d\mathbf{u}$ – the orbital path element.
- For simplicity – constant r .

$$\oint i d\mathbf{u} = \oint \frac{dq}{dt} d\mathbf{u} = Ze \frac{d\mathbf{u}}{dt} = Ze(-\mathbf{v}).$$

Cont.

- We get: $B = -\frac{\mu_0 Ze}{4\pi r^3} v \times r = \frac{\mu_0 Ze}{4\pi r^3} r \times v.$

- Coulombs law: The electric field:

$$\mathcal{E} = \frac{Ze}{4\pi\epsilon_0 r^2} \hat{r} = \frac{Ze}{4\pi\epsilon_0 r^3} r$$

- Hat symbol – unit vector.

- We get: $B = \mu_0\epsilon_0 \mathcal{E} \times v.$

- From Maxwells eqn. $\mu_0\epsilon_0 = 1/c^2.$

- We get: $B = \frac{1}{c^2} \mathcal{E} \times v$

- Similar result – non circular orbits and non coulombic interactions in larger atoms.

The spin orbit interaction:

- The interaction is given by:

$$\Delta E_{so} = -\mu_{spin} \cdot B_{orbital};$$

- We had:

$$\mu_{spin} = -g_s \frac{|e| \hbar}{2m_e} s = -g_s \frac{\mu_B}{\hbar} s$$

- Substitution: $\Delta E_{so} = \frac{g_s \mu_B}{\hbar c^2} s \cdot (\mathcal{E} \times v)$.
- In a central potential (V function of r only).

$$\mathcal{E} = \frac{1}{e} \frac{1}{r} \frac{dV}{dr}$$

- Substituting:

$$v = p/m_e$$

Cont.

- We get:
$$\Delta E_{\text{so}} = \frac{g_s \mu_B}{\hbar c^2 m_e} \left(\frac{1}{r} \frac{dV}{dr} \right) \mathbf{s} \cdot (\mathbf{r} \times \mathbf{p})$$

- Recall: angular momentum – $\mathbf{r} \times \mathbf{p}$. We get:

$$\Delta E_{\text{so}} = \frac{g_s \mu_B}{\hbar c^2 m_e} \left(\frac{1}{r} \frac{dV}{dr} \right) \mathbf{s} \cdot \mathbf{l}$$

Electrons that are moving in this speed are relativistic. Including it (thomas precession) gives a factor of 2 reduction. Recall $\mu_B = e\hbar/2m_e$

The final result:

$$\Delta E_{\text{so}} = \frac{g_s}{2} \frac{1}{2c^2 m_e^2} \left(\frac{1}{r} \frac{dV}{dr} \right) \mathbf{l} \cdot \mathbf{s}$$

For a coulomb field:

$$V = -Ze^2/4\pi\epsilon_0 r$$

and $g=2$:

$$\Delta E_{so} = \frac{Ze^2}{8\pi\epsilon_0 c^2 m_e^2} \left(\frac{1}{r^3} \right) l \cdot s$$

Can be used for hydrogenic atoms:

Including e-e repulsion given a more complicated result.

Evaluation of the spin-orbit energy for hydrogen

- The magnitude of the SO coupling can be written as:

$$\Delta E_{\text{so}} = \frac{1}{2c^2 m_e^2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle \langle l \cdot s \rangle$$

- Where $g=2$ and $\langle \rangle$ are the expectation value. We calculate:

$$\left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle = \iiint \psi_{nlm}^* \left(\frac{1}{r} \frac{dV}{dr} \right) \psi_{nlm} r^2 \sin \theta dr d\theta d\phi$$

- Which is dependent on r only:

Cont.

- Only the radial part should be considered.

$$\left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle = \int_0^{\infty} |R_{nl}(r)|^2 \left(\frac{1}{r} \frac{dV}{dr} \right) r^2 dr$$

- In an coulomb field we get:

$$(dV/dr)/r \propto 1/r^3$$

- We recall the radial equation:

Recall

n	l	$R_{nl}(r)$
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1	0	$(Z/a_0)^{3/2} 2 \exp(-Zr/a_0)$
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2	0	$(Z/2a_0)^{3/2} 2 \left(1 - \frac{Zr}{2a_0}\right) \exp(-Zr/2a_0)$
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2	1	$(Z/2a_0)^{3/2} \frac{2}{\sqrt{3}} \left(\frac{Zr}{2a_0}\right) \exp(-Zr/2a_0)$
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3	0	$(Z/3a_0)^{3/2} 2 \left[1 - (2Zr/3a_0) + \frac{2}{3} \left(\frac{Zr}{3a_0}\right)^2\right] \exp(-Zr/3a_0)$
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3	1	$(Z/3a_0)^{3/2} (4\sqrt{2}/3) \left(\frac{Zr}{3a_0}\right) \left(1 - \frac{1}{2} \frac{Zr}{3a_0}\right) \exp(-Zr/3a_0)$
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3	2	$(Z/3a_0)^{3/2} (2\sqrt{2}/3\sqrt{5}) \left(\frac{Zr}{3a_0}\right)^2 \exp(-Zr/3a_0)$
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$$\int_{r=0}^{\infty} R_{nl}^* R_{nl} r^2 dr = 1.$$

According to the Bohr model:

We get: $\langle r \rangle = \frac{n^2 a_H}{Z}$

We make the (crude) conjecture:

$$\langle 1/r^3 \rangle = Z^3 / (n^6 a_H^3).$$

• In fact $\left\langle \frac{1}{r^3} \right\rangle = \frac{2Z^3}{a^3 n^3 l(l+1)(2l+1)}$

Which is close to the Bohr result when l is close to n

Recall

- We had:
$$\Delta E_{\text{so}} = \frac{1}{2c^2 m_e^2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle \langle \mathbf{l} \cdot \mathbf{s} \rangle$$

This can be written as:

$$\Delta E_{\text{so}} = C_{nl} \langle \mathbf{l} \cdot \mathbf{s} \rangle$$

- What is the meaning of the $\mathbf{l} \cdot \mathbf{s}$ term?
- We can write:

$$j^2 = (\mathbf{l} + \mathbf{s})^2 = l^2 + s^2 + 2\mathbf{l} \cdot \mathbf{s}$$

- Which means:

$$\langle \mathbf{l} \cdot \mathbf{s} \rangle = \left\langle \frac{1}{2} (j^2 - l^2 - s^2) \right\rangle = \frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)]$$

Splitting of the j states:

- For a Coulomb field:

$$\Delta E_{\text{so}} = \frac{Ze^2}{8\pi\epsilon_0 c^2 m_e^2} \left(\frac{1}{r^3} \right) l \cdot s$$

- We replace $1/r^3$ with $\langle 1/r^3 \rangle$

We have an expression of the quantum numbers:

$$A \frac{j(j+1) - l(l+1) - s(s+1)}{l\left(l + \frac{1}{2}\right)(l+1)}$$

Cont.

- Recall: $\left\langle \frac{1}{r^3} \right\rangle = \frac{2Z^3}{a^3 n^3 l(l+1)(2l+1)}$
- We get: $A = \frac{Ze^2}{8\pi\epsilon_0 c^2 m_e^2} \times \frac{Z^3}{a_0^3 n^3} \times \frac{h^2}{4\pi^2}$

$$a_0 = \frac{\hbar}{m_e c} \frac{1}{\alpha} \quad a_0^3 = \frac{h^3}{8\pi^3 m_e^3 c^3 \alpha^3}$$

We get: $\frac{Ze^2}{8\pi\epsilon_0 c^2 m_e^2} \times \frac{Z^3 8\pi^3 m_e^3 c^3 \alpha^3}{n^3 h^3} \times \frac{h^2}{4\pi^2}$

Cont

- A bit algebra:

$$\frac{Z^4 e^2 \pi^2 m_e c \alpha^3}{\epsilon_0 n^3 h^3} \times \frac{h^2}{4\pi^2} = \frac{\alpha^2 Z^2}{2n^2} \times \frac{2Z^2 e^2 \pi^2 m_e c \alpha}{\epsilon_0 n h^3} \times \frac{h^2}{4\pi^2}$$

- Taking into account: $\alpha = e^2 / 2\epsilon_0 h c \approx 1/137$

$$\frac{\alpha^2 Z^2}{2n^2} \times \frac{Z^2 e^4 \pi^2 m_e}{2\epsilon_0^2 n h^4} \frac{h^2}{4\pi^2} = \frac{\alpha^2 Z^2}{2n^2} \times \frac{Z^2 e^4 m_e}{8\epsilon_0^2 n h^2}$$

Recall:

- The gross energy:

$$E_n = -R_H Z^2 / n^2 \quad R_H = 0.99995 R_\infty hc$$

- and:

$$R_\infty hc = \frac{m_e e^4}{8\epsilon_0^2 h^2}$$

- We can write: $E_n \cdot n = \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2}$

Arriving to the final destination:

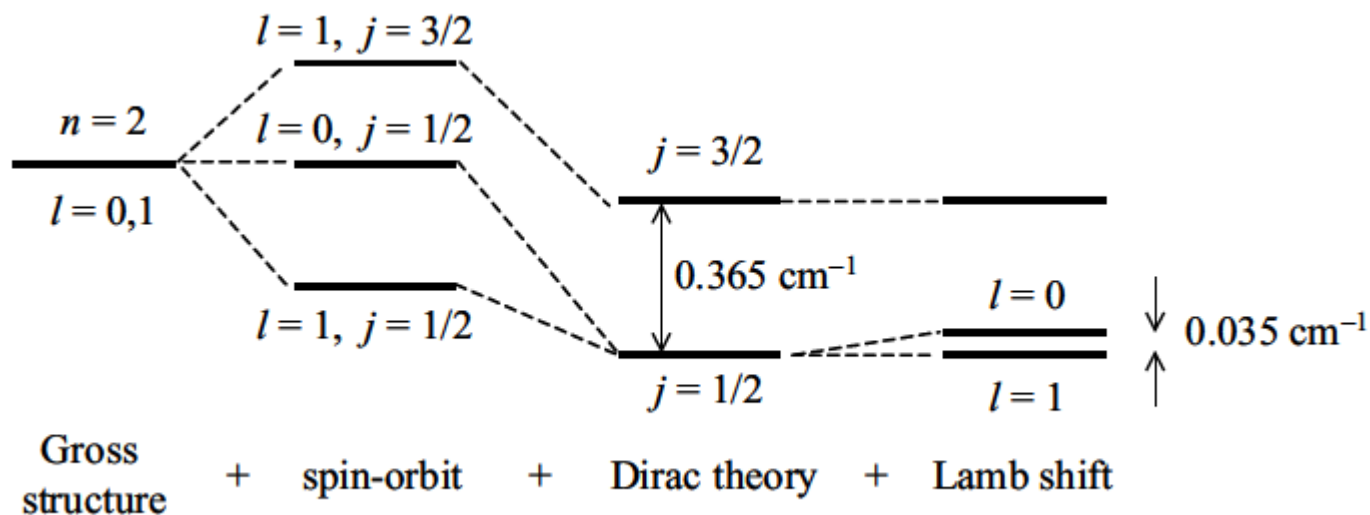
$$\Delta E_{so} = -\frac{\alpha^2 Z^2}{2n^2} E_n \frac{n}{l(l + \frac{1}{2})(l + 1)} [j(j + 1) - l(l + 1) - s(s + 1)]$$

Recall

- j takes values of $l+1/2$ and $l-1/2$ for $l > 1$.
SO coupling splits the two j states with the same value of l .

There are several relativistic corrections.

- States with the same n but different l are degenerate. Below - $n=2$ fine structure of H.



Spin-orbit coupling in alkali atoms

- Angular momentum state $|L S J\rangle$ of the atom only due to valence electron.
- In analogy with hydrogen:

$$\Delta E_{SO} \propto \langle \mathbf{L} \cdot \mathbf{S} \rangle \propto [J(J + 1) - L(L + 1) - S(S + 1)]$$

- Valence electron in s state $\Delta E_{SO} = 0$.
- $L=1, S=1/2$. $\mathbf{L} \cdot \mathbf{S} \neq 0$. J has 2 possible values

$$J = L \oplus S = L \oplus 1/2 = L \pm 1/2.$$

In a similar way to hydrogen:

$$\Delta E_{SO} = C [J(J + 1) - L(L + 1) - S(S + 1)]$$

The 2 states.

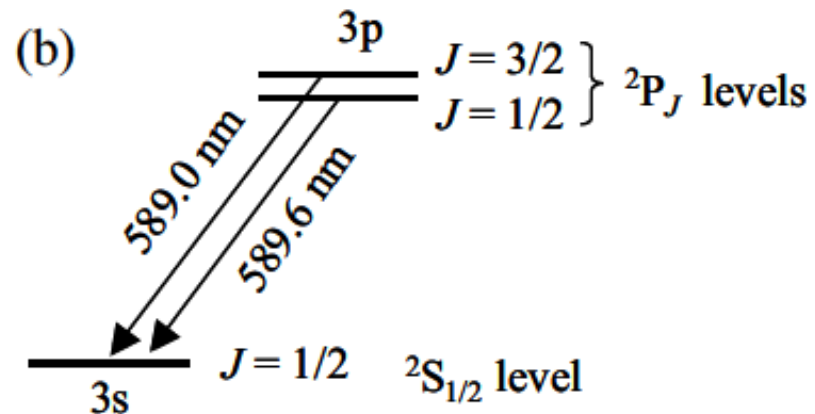
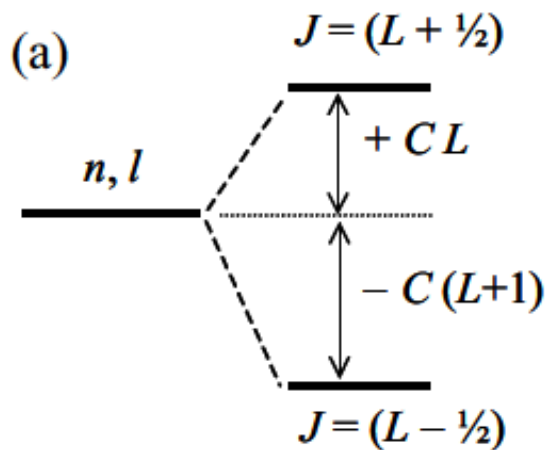
- For the $J=L+1/2$ state:

$$\Delta E_{\text{so}} = C \left[\left(L + \frac{1}{2}\right)\left(L + \frac{3}{2}\right) - L(L + 1) - \frac{1}{2} \cdot \frac{3}{2} \right] = +CL$$

- For the $J=L-1/2$ state:

$$\Delta E_{\text{so}} = C \left[\left(L - \frac{1}{2}\right)\left(L + \frac{1}{2}\right) - L(L + 1) - \frac{1}{2} \cdot \frac{3}{2} \right] = -C(L + 1)$$

The energy diagram of alkali metals and Na.



The magnitude:

- Compared with gross structure, the fine structure is smaller by $\sim \alpha^2 = 1/137^2$

Alkali atoms: One electron – with transition: $3p \rightarrow 3s$

The ground state is $^2S_{1/2}$ -no SO coupling.

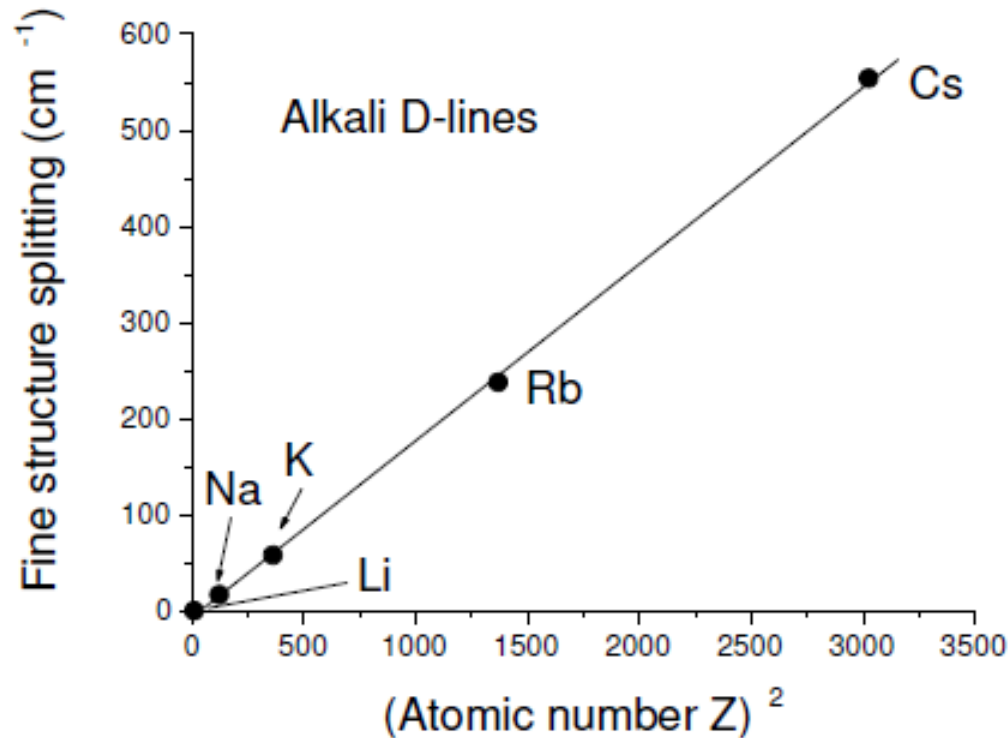
The two transitions:



Energy difference: 17cm^{-1}

As was shown already:

- The splitting should be proportional to Z^2 .



Spin-orbit coupling in many-electron atoms

- Recall: The residual non spherical electric interactions – couple the electrons to create total S and L angular momenta: These two are coupled to give:

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

- J running from $L+S$ to $|L-S|$.
- the spin-orbit coupling splits the J states of a particular LS -term into fine structure multiplets.

As before

- The spin orbit coupling takes the form:

$$\Delta E_{so} = -\mu_{spin} \cdot B_{orbital} \propto \langle \mathbf{L} \cdot \mathbf{S} \rangle$$

- Which implies:

$$\Delta E_{SO} = C_{LS} [J(J + 1) - L(L + 1) - S(S + 1)]$$

- Different J states will have a different energy even with the same L and S

Nuclear effects in atoms

- The nuclei has small but important affect: the isotope shifts and the hyperfine structure:
- Isotope shifts – mass effects- **Recall**: in the energy levels of atoms what enters is the reduced mass:

$$\frac{1}{m} = \frac{1}{m_e} + \frac{1}{m_N}$$

- A change in nuclear mass will change the energy.

Cont.

- Field effects: The electrons have a finite probability to be in the nucleus, and therefore will be sensitive to changes in charge distributions.
- Hyperfine structure: Coupling between the the electron and nucleus angular momenta:

$$\Delta E_{\text{hyperfine}} = -\mu_{\text{nucleus}} \cdot B_{\text{electron}} \propto \langle \mathbf{I} \cdot \mathbf{J} \rangle$$

The splitting is small:

- Because the dipole moment of the nucleus is 2000 times smaller than the electron.
- **Recall:** The gyro magnetic ratio inversely proportional to the mass.
- Total angular momentum:

$$F = I + J$$

- The selection rule:

$$\Delta F = 0, \pm 1,$$

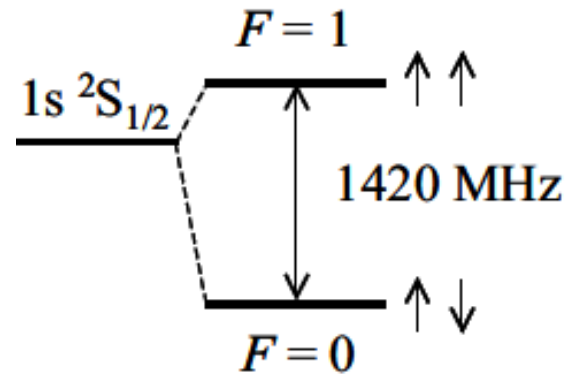
Examples of hyperfine spectrum:

- The hydrogen ground state is: $1s\ ^2S_{1/2}$ term, (J=1/2).

Hyperfine quantum number:

$$F = I \oplus J = 1/2 \oplus 1/2 = 1 \text{ or } 0.$$

Electron and nuclear spins are parallel (F=1) or antiparallel (F=0).



2 F states split by the hyperfine interaction.

- The hydrogen song. (NMR)

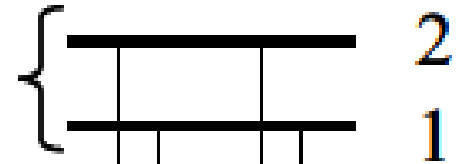
Hyperfine structure of sodium D lines.

- D lines originated from $3p \rightarrow 3s$ transitions. Two transitions split by the SO coupling.

- D₁ line: ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ F

Hyperfine splitting of

$3p \ {}^2P_{1/2}$



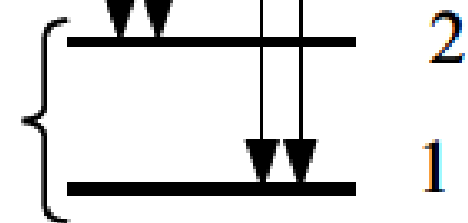
${}^2S_{1/2}$ - 1772 MHz.

of ${}^2P_{1/2}$ 190 MHz.

Two doublets with

relative frequencies:

$3s \ {}^2S_{1/2}$



(0, 190) MHz and (1772, 1962) MHz.

Cont.

- These splitting – much smaller than the spin orbit splittings of the J states: 5×10^{11} Hz.

- The higher energy D_2 line:

We get 6 hyperfine lines

with relative frequencies: $3p \ ^2P_{3/2}$

0, 34,59 MHz and

1756, 1772, 1806 MHz.

