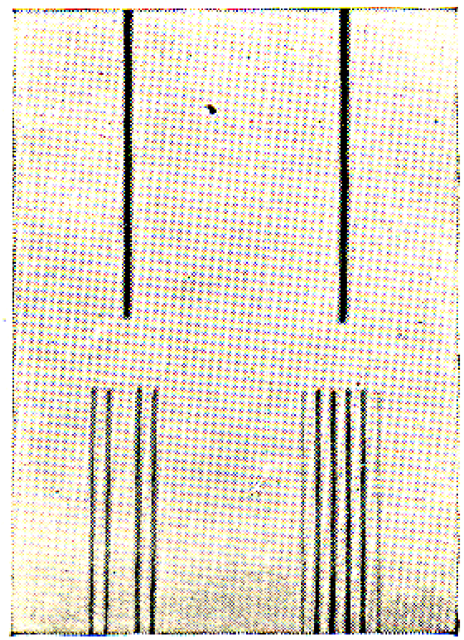
Advanced Quantum Physics

Lecture 22



David Ritchie

www.sp.phy.cam.ac.uk/~dar11/pdf

Section 5: Atoms

5.1 The real hydrogen atom

5.2 Multielectron atoms

5.3 Coupling schemes

5.4 Atomic spectra

✦ 5.5 Atoms in a uniform magnetic field

5.5 Atoms in a uniform magnetic field

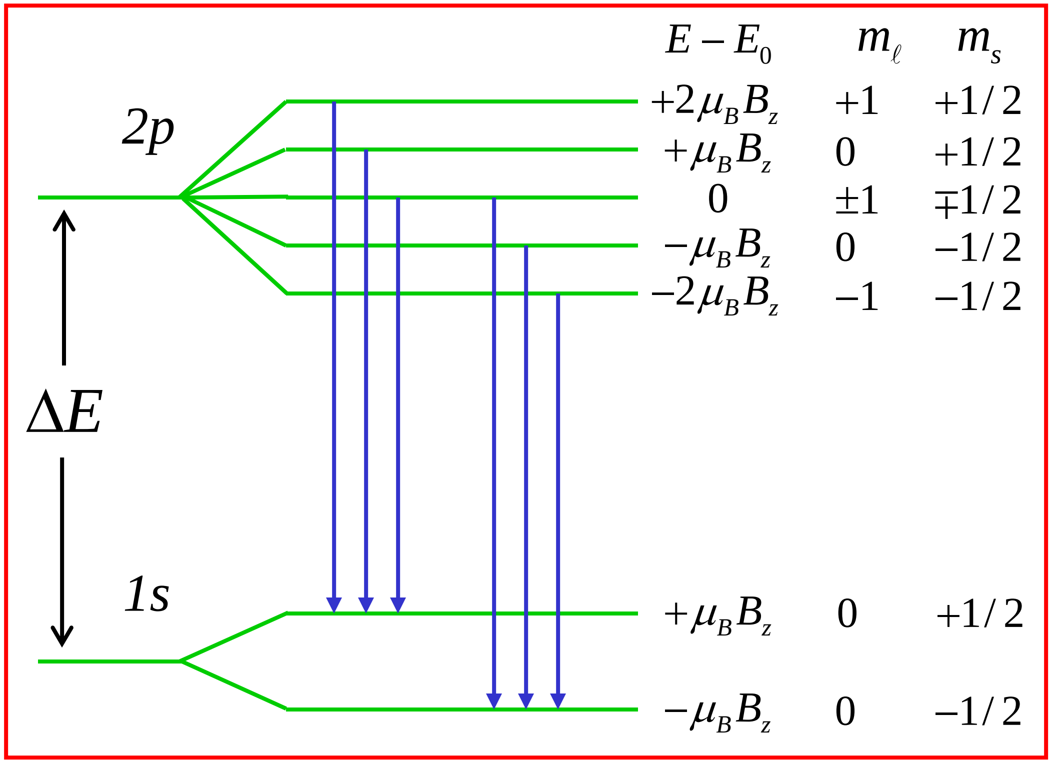
- In Lecture 12 (slide 12) we derived the energy of a single electron in an atom in an magnetic field:

$$E = E_0 + B_z \frac{e\hbar}{2m_e}(m_\ell + 2m_s) = E_0 + B_z \mu_B (m_\ell + 2m_s)$$

$g_e \approx 2$

- The deviation of these energies from E_0 is proportional to B_z and leads to the splitting of spectral lines known as the Zeeman effect.

- Example: $2\text{p} \rightarrow 1\text{s}$ transition in hydrogen, energy levels split as in diagram:



- Given the LS selection rules:

$$\Delta m_s = 0,\ \Delta m_\ell = \pm 1, 0$$

- Allowed transitions are indicated:
- Energies of allowed transitions:

$$\Delta E,\ \Delta E \pm \mu_B B_z$$

- Spectral line split into three components spaced by $\mu_B B_z$
- This is the *Normal* Zeeman effect - applies in a high B field…

Atoms in a uniform magnetic field (2)

•The *normal* Zeeman effect is *rarely* seen - because of the spin-orbit interaction.

•An estimate of the spin-orbit interaction for Hydrogen gives an energy of 10^{-4} eV - much less than energy level spacing and similar to Zeeman splitting ~ $\mu_B B = 5.8\,10^{-5} B\ \ eV$

•Heavier atoms with a greater nuclear charge have a larger spin-orbit effect and are more likely to be a problem.

•The Hamiltonian with a spin-orbit interaction is given by:

$$\hat{H} = \hat{H}_0 + \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \frac{e}{2m_e}(\hat{L}_z + 2\hat{S}_z)B_z$$

•This is not easy to diagonalise since $(\hat{L}_z + 2\hat{S}_z)$ and $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ do not commute. A simple calculation gives:

$$[\hat{L}_z + 2\hat{S}_z, \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}] = i\hbar(\hat{L}_x \hat{S}_y - \hat{L}_y \hat{S}_x)$$

•So the energy levels in a magnetic field and the spin-orbit energy cannot be specified simultaneously.

Atoms in a uniform magnetic field (3)

•We consider the two extreme cases for the Zeemen effect.

•*Strong* field. If $\mu_B B \gg \xi \mathbf{L}\cdot\mathbf{S}$ the previous analysis of *Normal* Zeeman effect is valid.

•This situation occurs if l=0 or s=0 or in strong B field, s =0 is only possible for multielectron atoms.

•The eigenstates of $\hat{H}$ are approximately those of $(\hat{L}_z + 2\hat{S}_z)$ labelled by m_l & m_s and we can treat the spin-orbit effect as a perturbation if necessary.

•*Weak* field – $\mu_B B \ll \xi \mathbf{L}\cdot\mathbf{S}$ and the effects can be calculated by perturbation theory.

•We use a set of basis eigenstates of $\mathbf{L}\cdot\mathbf{S}$ labelled by total angular momentum quantum nos. J, m_j.

•Known as the *Anomalous* Zeeman effect but is most commonly encountered!!

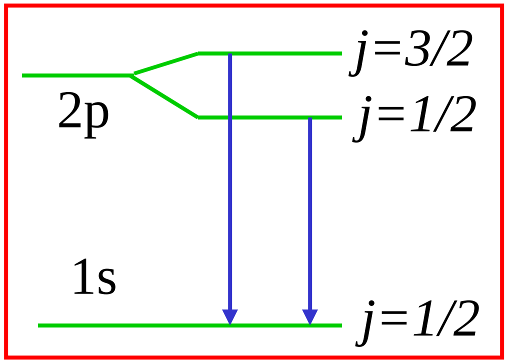
Anomalous Zeeman effect: Landé g-factor

- Consider the effect of the spin-orbit interaction:
- We determine the eigenstates of the Hamiltonian $\hat{H}_0 + \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$. Using the total angular momentum operator: $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$
- We have $\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ and so: $\xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}\xi(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)$
- Hence the eigenstates of $\hat{H}_0 + \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ are eigenstates of $\hat{\mathbf{J}}^2$, $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$ and $\hat{J}_z$ but not $\hat{L}_z$ or $\hat{S}_z$.
- For given values of quantum nos. ℓ, s the energy levels will split according to the allowed values of j: $j = \ell + s, \ell + s - 1, \cdots |\ell - s|$
- The energy shift of state j resulting from the spin-orbit interaction is:

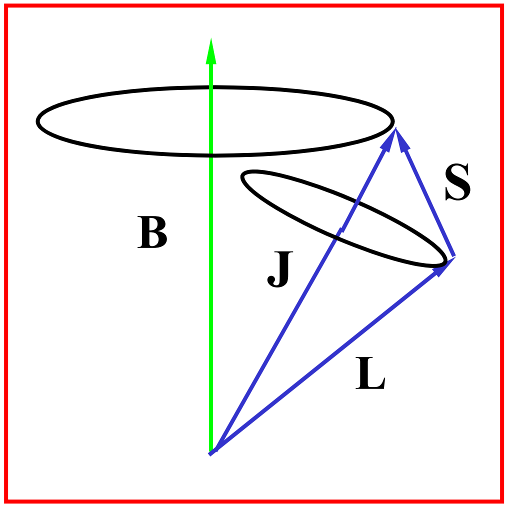
$$\Delta E_{s-o} \langle j\ell s | \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | j\ell s \rangle = \xi \frac{\hbar^2}{2}[j(j+1) - s(s+1) - \ell(\ell+1)]$$

• *Example:* $2p \rightarrow 1s$ (hydrogen)	1s: $\ell = 0$ $s = \frac{1}{2}$ $j = \frac{1}{2}$ $\langle \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle = 0$
• 1s level unaffected. • 2p level split into two by spin-orbit interaction.	2p: $\ell = 1$ $s = \frac{1}{2}$ $\begin{cases} j = \frac{1}{2} & \langle \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle = -\xi\hbar^2 \\ j = \frac{3}{2} & \langle \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle = \frac{1}{2}\xi\hbar^2 \end{cases}$

Anomalous Zeeman effect: Landé g-factor (2)



- Selection rules permit transitions from the 2p level with either $j=3/2$ or $j=1/2$ to the 1s level with $j=1/2$.
- The spectral line splits into a doublet in the absence of a magnetic field – similar to sodium 'D' lines.
- In atoms with many electrons we have a more complicated situation – but we often can combine l's and s's of individual electrons to give total L & S values and proceed as above.
- The magnetic field term acts as a perturbation – the expectation value of the magnetic moment along the field direction is:



$$\langle \hat{\mu}_z \rangle = -\langle J, m_J | \hat{L}_z + 2\hat{S}_z | J, m_J \rangle \mu_B / \hbar = -g m_J \mu_B$$

where g is the Landé g-factor.

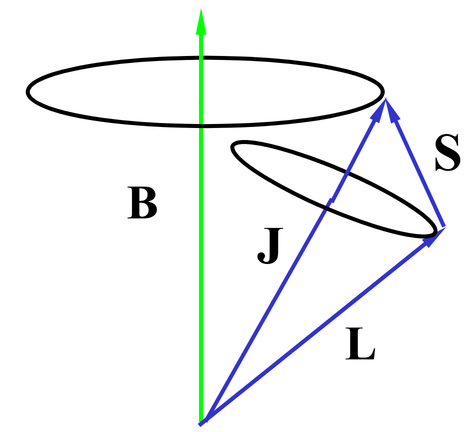
- We can compute g by a vector model, **L** and **S** precess around **J**, which precesses around B. Rapid precession of **L** and **S** around **J** means that some components of corresponding magnetic moments average to zero.

Anomalous Zeeman effect: Landé g-factor (3)

•Due to rapid precession of $\mathbf{L}$ and $\mathbf{S}$ around $\mathbf{J}$:

$$\langle \boldsymbol{\mu}_L + \boldsymbol{\mu}_S \rangle = -\left(\frac{\mathbf{L}\cdot\mathbf{J} + g_e \mathbf{S}\cdot\mathbf{J}}{|\mathbf{J}|} \right) \frac{\mathbf{J}}{|\mathbf{J}|} \frac{\mu_B}{\hbar}$$

$g_e \approx 2$ for an electron



•The z-component of this magnetic moment is:

$\langle \hat{\mu}_z \rangle = -g\mu_B m_J = -g\mu_B J_z/\hbar$ so:

$$g = \frac{\mathbf{L}\cdot\mathbf{J} + 2\mathbf{S}\cdot\mathbf{J}}{|\mathbf{J}|^2} = \frac{(\mathbf{J}-\mathbf{S})\cdot\mathbf{J} + 2\mathbf{S}\cdot\mathbf{J}}{|\mathbf{J}|^2} = 1 + \frac{\mathbf{J}\cdot\mathbf{S}}{|\mathbf{J}|^2}$$

•Now $\mathbf{J} = \mathbf{L} + \mathbf{S}$ so: $|\mathbf{L}|^2 = |\mathbf{J}-\mathbf{S}|^2 = |\mathbf{J}|^2 + |\mathbf{S}|^2 - 2\mathbf{J}\cdot\mathbf{S}$

•Since $|\mathbf{J}|^2 = J(J+1)\hbar^2$ etc, then $\mathbf{J}\cdot\mathbf{S} = \frac{1}{2}\hbar^2[J(J+1) - L(L+1) + S(S+1)]$

•Landé g-factor: $g = 1 + \frac{\mathbf{J}\cdot\mathbf{S}}{|\mathbf{J}|^2} = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)}$

$S = 0, J = L \Rightarrow g = 1$

$L = 0, J = S \Rightarrow g = 2$

As expected

•This vector model should not be taken too literally – it is essentially classical and can lead to conflicts with QM and experiment. A better way to calculate the Landé g-factor is to use Clebsch-Gorden coefficients.

Landé g-factor: Clebsch-Gordan coefficients

- We evaluate the Landé g-factor more rigorously for a specific case.
- The magnetic moment: $\langle \hat{\mu}_z \rangle = -\langle J, m_J | \hat{L}_z + 2\hat{S}_z | J, m_J \rangle \mu_B / \hbar = -g m_J \mu_B$
- The states of definite J are superpositions of different states of m_L and m_S.

$$|J, m_J\rangle = \sum_{m_L, m_S} C_{J, m_L, m_S} |L, S, m_L, m_S\rangle$$

where the coefficients C are Clebsch-Gordan coefficients.

- Having expanded the wavefunction in terms of states for which $\hat{L}_z + 2\hat{S}_z$ is well defined we have;

$$g = \sum_{m_L, m_S} |C_{J, m_L, m_S}|^2 (m_L + 2m_S)/m_J = 1 + \sum_{m_L, m_S} |C_{J, m_L, m_S}|^2 m_S/(m_L + m_S)$$

using $m_J = m_L + m_S$ and the orthonormality of the states.

- If we take the example of $S = \frac{1}{2}$ as in an alkali metal atom or hydrogen.
- There are only two possible J values for each L value: $J = L \pm \frac{1}{2}$
- When $m_L = L$ and $m_S = +\frac{1}{2}$ then $m_J = L + \frac{1}{2}$ and only $J = L + \frac{1}{2}$ is possible.
- So we have: $\left|J = L + \tfrac{1}{2}, m_J = L + \tfrac{1}{2}\right\rangle = \left|L, S = \tfrac{1}{2}, m_L = L, m_S = \tfrac{1}{2}\right\rangle$.

Landé g-factor: Clebsch-Gordan coefficients (2)

- As a consequence the only non-zero coefficient is: $C_{J,m_L,m_S} = C_{L+\frac{1}{2},L,\frac{1}{2}} = 1$
- And in this case since; $g = 1 + \sum_{m_L,m_S} |C_{J,m_L,m_S}|^2 \, m_S/(m_L + m_S)$

we have: $$g = 1 + \frac{\frac{1}{2}}{L+\frac{1}{2}} = 1 + \frac{1}{2J} \qquad (J = L + \tfrac{1}{2})\,.$$

- Now when $m_J = L - \frac{1}{2}$ we can have either $J = L + \frac{1}{2}$ or $J = L - \frac{1}{2}$.
- $\left| J = L + \tfrac{1}{2}, m_J = L - \tfrac{1}{2} \right\rangle$ is obtained by operating on $\left| J = L + \tfrac{1}{2}, m_J = L + \tfrac{1}{2} \right\rangle$ with $\hat{J}_- = \hat{L}_- + \hat{S}_-$.
- Operating with $\hat{J}_-$ on $\left| J, m_J \right\rangle$:

$$\begin{aligned}\hat{J}_- \left| J = L + \tfrac{1}{2}, m_J = L + \tfrac{1}{2} \right\rangle &= \hbar\sqrt{J(J+1) - m_J(m_J - 1)} \left| J = L + \tfrac{1}{2}, m_J - 1 \right\rangle \\ &= \hbar\sqrt{2L+1} \left| J = L + \tfrac{1}{2}, m_J = L - \tfrac{1}{2} \right\rangle\end{aligned}$$

Landé g-factor: Clebsch-Gordan coefficients (3)

- We now operate with $\hat{L}_- + \hat{S}_-$ on $\left|L, S, m_L, m_S\right\rangle$.

$$(\hat{L}_- + \hat{S}_-)\left|L, \tfrac{1}{2}, m_L = L, m_S = \tfrac{1}{2}\right\rangle = \begin{bmatrix} \hbar\sqrt{L(L+1) - m_L(m_L - 1)}\left|L, S, m_L - 1, m_S\right\rangle \\ +\hbar\sqrt{S(S+1) - m_S(m_S - 1)}\left|L, S, L, m_S - 1\right\rangle \end{bmatrix}$$

$$= \hbar\sqrt{2L}\left|L, \tfrac{1}{2}, m_L = L-1, m_S = \tfrac{1}{2}\right\rangle + \hbar\left|L, \tfrac{1}{2}, m_L = L, m_S = -\tfrac{1}{2}\right\rangle$$

- So combining the last two results:

$$\left|J = L + \tfrac{1}{2}, m_J = L - \tfrac{1}{2}\right\rangle = \begin{bmatrix} \sqrt{\frac{2L}{2L+1}}\left|L, \tfrac{1}{2}, m_L = L-1, m_S = \tfrac{1}{2}\right\rangle \\ +\sqrt{\frac{1}{2L+1}}\left|L, \tfrac{1}{2}, m_L = L, m_S = -\tfrac{1}{2}\right\rangle \end{bmatrix}.$$

- Given that; $g = 1 + \sum_{m_L, m_S} |C_{J, m_L, m_S}|^2 \, m_S/(m_L + m_S)$

then in this state;

$$g = 1 + \frac{2L}{2L+1}\left(\frac{\frac{1}{2}}{L - \frac{1}{2}}\right) + \frac{1}{2L+1}\left(\frac{-\frac{1}{2}}{L - \frac{1}{2}}\right) = 1 + \frac{1}{2J}$$

as before.

Landé g-factor: Clebsch-Gordan coefficients (4)

- The g-factor only depends on J, L and S and not on m_J.
- So the g-factor has the same value when $J = L + \frac{1}{2}$ for all values of $m_J = L + \frac{1}{2}, L - \frac{1}{2}, \ldots, -L - \frac{1}{2}$.
- Note that when $L = 0$ we get $g = 2$ - all the magnetic moment is due to spin.
- When L is large $g \to 1$ since the orbital angular momentum is dominant.
- The only other possibility when $S = \frac{1}{2}$ is $J = L - \frac{1}{2}$.
- Now $\left|J = L - \frac{1}{2}, m_J = L - \frac{1}{2}\right\rangle$ is orthogonal to $\left|J = L + \frac{1}{2}, m_J = L - \frac{1}{2}\right\rangle$ (from last slide) so it must be:

$$\left|J = L - \tfrac{1}{2}, m_J = L - \tfrac{1}{2}\right\rangle = \begin{bmatrix} \sqrt{\frac{1}{2L+1}}\left|L, \tfrac{1}{2}, m_L = L - 1, m_S = \tfrac{1}{2}\right\rangle \\ -\sqrt{\frac{2L}{2L+1}}\left|L, \tfrac{1}{2}, m_L = L, m_S = -\tfrac{1}{2}\right\rangle \end{bmatrix}$$

and we get:

$$g = 1 + \frac{1}{2L+1}\left(\frac{\frac{1}{2}}{L - \frac{1}{2}}\right) + \frac{2L}{2L+1}\left(\frac{-\frac{1}{2}}{L - \frac{1}{2}}\right) = 1 - \frac{1}{2(J+1)} \qquad (J = L - \tfrac{1}{2}).$$

Note that in this case $g < 1$ since the spin and orbital angular momenta tend to cancel.

Anomalous Zeeman splittings

•From the result $\langle \boldsymbol{\mu}_L + \boldsymbol{\mu}_S \rangle_z = g\mu_B m_J$ in perturbation theory the shift of an energy level in a weak magnetic field B_z is: $\Delta E_{J,m_J} = g\mu_B B_z m_J$

•So the previously degenerate levels with a given J and $m_J = J, J-1, \ldots, -J$ are split into $2J+1$ distinct uniformly spaced levels.

•Spectral lines due to radiative transitions are split into components with spacings proportional to field strength. *Anomolous Zeeman effect.*

•Apply to $\mathrm{p} \rightarrow \mathrm{s}$ transition, selection rule $\Delta m_J = 0, \pm 1$

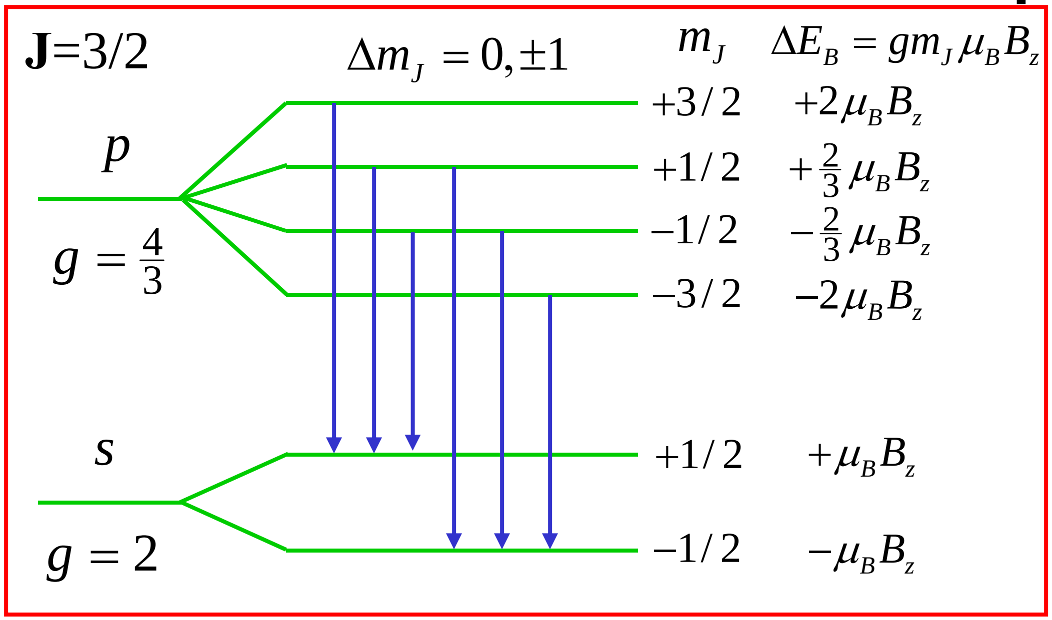
•s state has **L**=0 and **S**=1/2 , so **J**=1/2 and from Landé g-factor g=2

•p state is split into two by spin-orbit interaction

(1) **L**=1 and **S**=1/2 , **J**=1/2 and Landé g-factor g=2/3

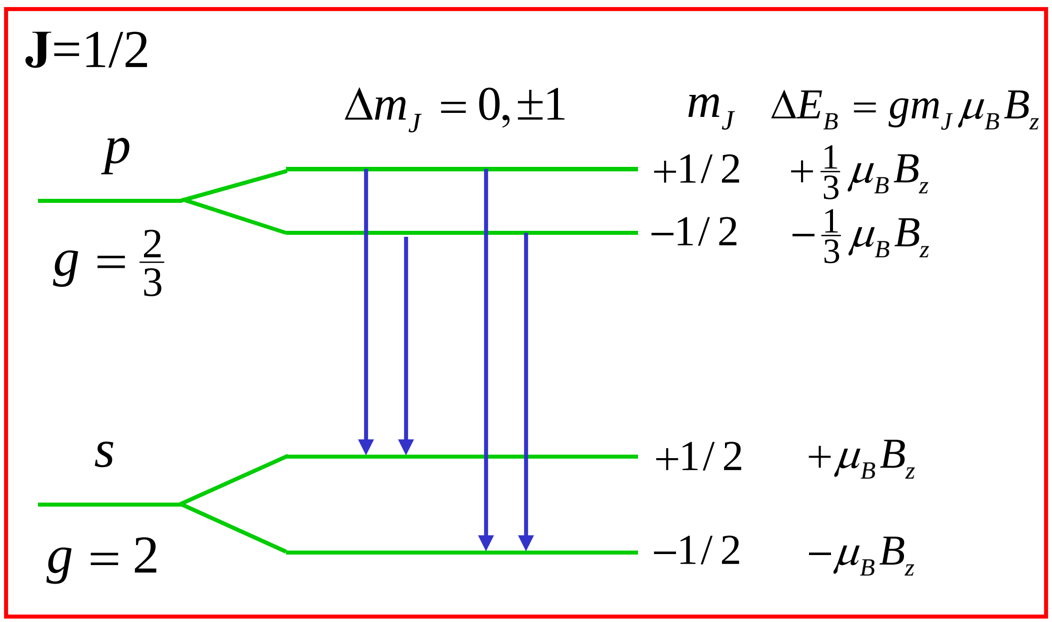
(2) **L**=1 and **S**=1/2 , **J**=3/2 and Landé g-factor g=4/3

Anomalous Zeeman splittings (2)



m_J	$\Delta(E_p - E_s)$
$+\frac{3}{2} \to +\frac{1}{2}$	$+\mu_B B_z$
$+\frac{1}{2} \to +\frac{1}{2}$	$-\frac{1}{3}\mu_B B_z$
$-\frac{1}{2} \to +\frac{1}{2}$	$-\frac{5}{3}\mu_B B_z$
$+\frac{1}{2} \to -\frac{1}{2}$	$+\frac{5}{3}\mu_B B_z$
$-\frac{1}{2} \to -\frac{1}{2}$	$+\frac{1}{3}\mu_B B_z$
$-\frac{3}{2} \to -\frac{1}{2}$	$-\mu_B B_z$

6 lines spaced by $\frac{2}{3}\mu_B B_z$

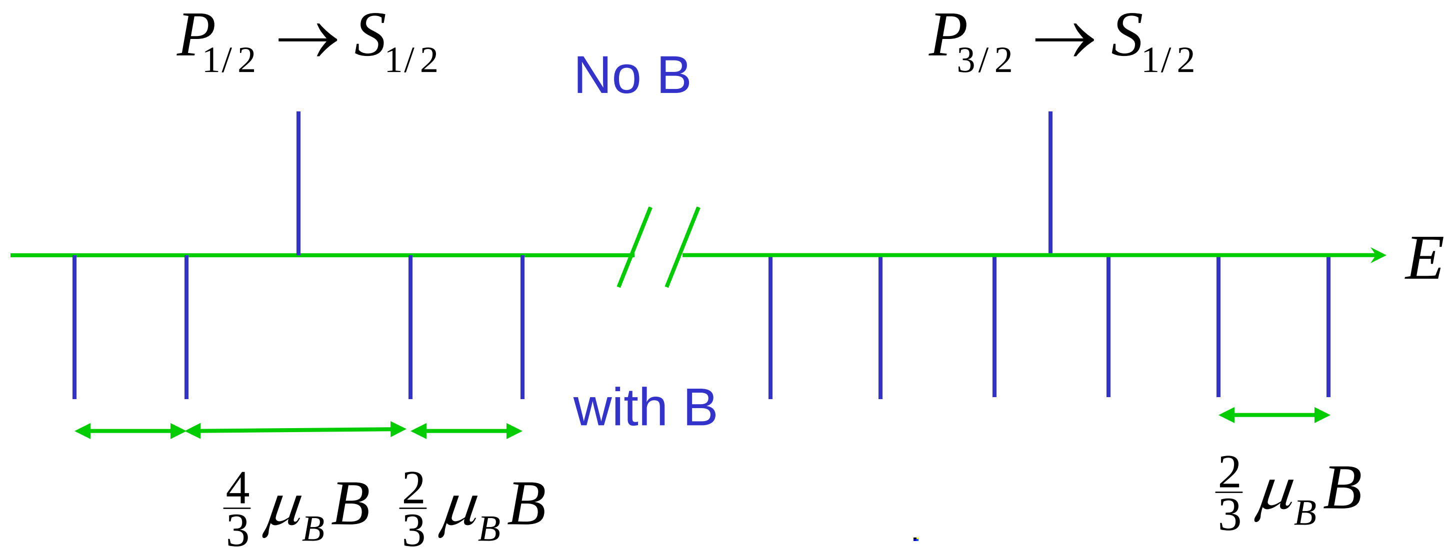


m_J	$\Delta(E_p - E_s)$
$+\frac{1}{2} \to +\frac{1}{2}$	$-\frac{2}{3}\mu_B B_z$
$-\frac{1}{2} \to +\frac{1}{2}$	$-\frac{4}{3}\mu_B B_z$
$+\frac{1}{2} \to -\frac{1}{2}$	$+\frac{4}{3}\mu_B B_z$
$-\frac{1}{2} \to -\frac{1}{2}$	$+\frac{2}{3}\mu_B B_z$

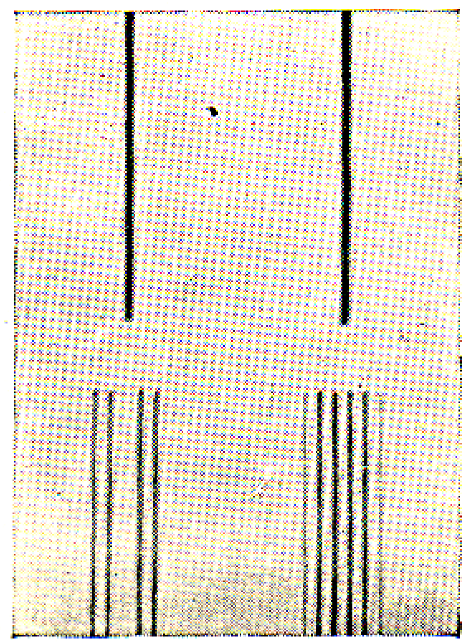
4 lines

Anomalous Zeeman splittings (3)

- Spectrum of transitions



- Zeeman effect is a powerful way of determining values of j,l,s of the levels involved in a spectral line



Anomalous Zeeman effect in Sodium

'Atomic Physics'

M Born 1944

Polarization in the Zeeman effect

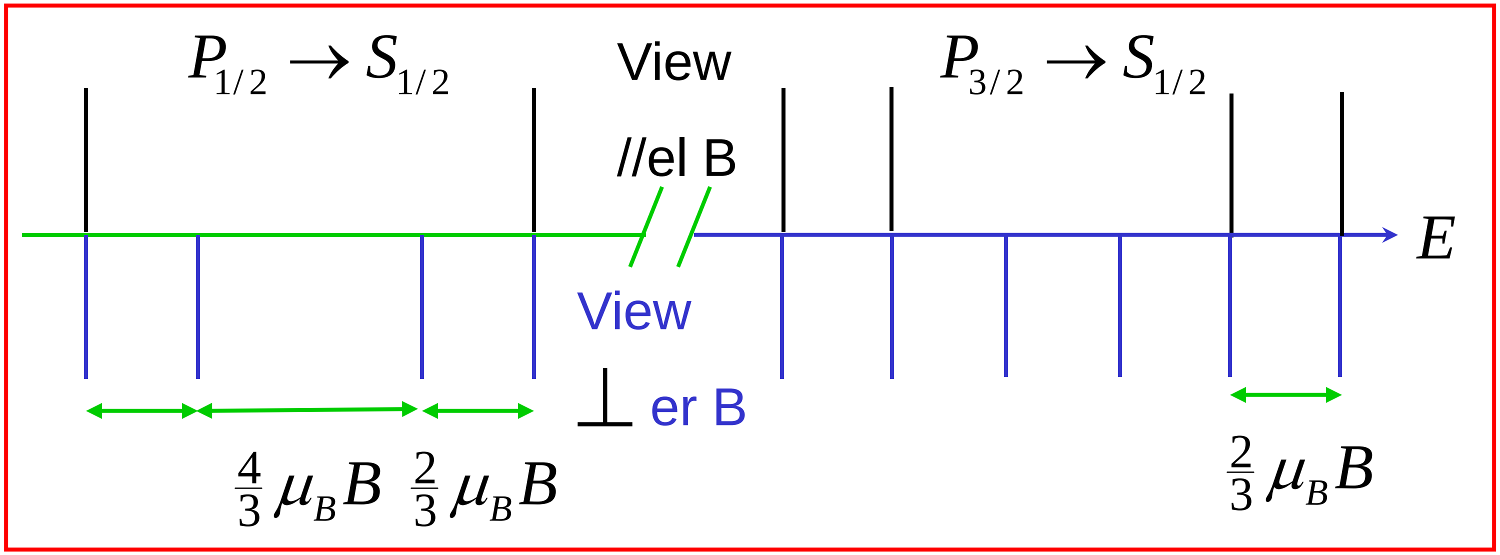
- From derivation of selection rules (slides 16.13 -16.15):

$\Delta m_J = 0$ for z-dipoles i.e. $\boldsymbol{\mathcal{E}}$ //el z $\qquad \Delta m_J = \pm 1$ For x-, y-dipoles

- Photon travelling parallel to z can only have x- or y- components of $\boldsymbol{\mathcal{E}}$.

- So view spectrum parallel to $\boldsymbol{B}$ only see $\Delta m_J = \pm 1$ transitions i.e. 4 lines for $P_{3/2} \rightarrow S_{1/2}$ and 2 lines for $P_{1/2} \rightarrow S_{1/2}$ - all circularly polarised.

- But if we view perpendicular to $\boldsymbol{B}$ – say in the x-direction can have either z- or y- components of $\boldsymbol{\mathcal{E}}$ and see lines with both $\Delta m_J = 0$ (plane polarized //el z) and $\Delta m_J = \pm 1$ (plane polarized //el y)



Lecture 22 - Summary

•Atoms in a magnetic field:

•The *normal* Zeeman effect – seen in a high magnetic field (several Tesla) where the interaction of electron orbital and spin magnetic moments with the magnetic field is larger than the spin-orbit interaction.

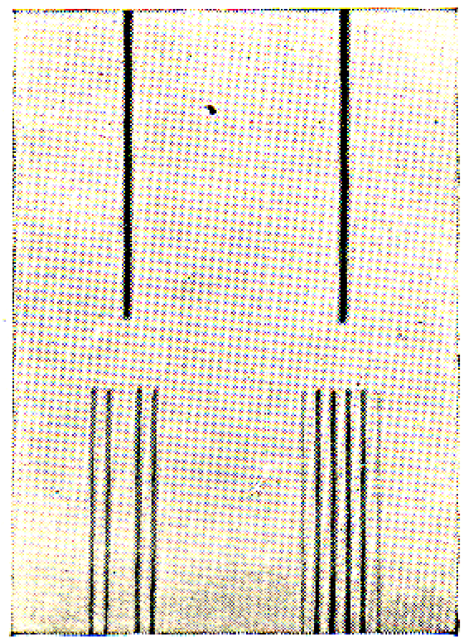
•The *anomolous* Zeeman effect - seen where the spin-orbit interaction dominates, for small magnetic fields. The spin-orbit interaction leads to a coupling of L and S, the resulting magnetic moment can be calculated using the Landé g-factor.

•The Landé g-factor can be calculated using a semi-classical vector model or more rigorously using raising and lowering operators.

•The energy level splitting and resulting transitions are calculated for a single electron atom and compared to the spectrum of sodium.

•The polarization of light emitted in a particular spectral line depends on the selection rules in operation for the corresponding transition.

Lecture 22



The End!!

(www.sp.phy.cam.ac.uk/~dar11/pdf)