The Zeeman Effect: Splitting of Spectral Lines by a Magnetic Field

Introduction

Pieter Zeeman, a Dutch physicist discovered the 'Zeeman Effect' in 1896. His discovery, led the way for a quantum explanation of spin and its relation to a particle's magnetic field. The Zeeman Effect is the splitting of a single spectral line into a group of closely spaced lines when the substance producing the single line is subjected to a uniform magnetic field. There are two types of effects, the normal and anomalous Zeeman effects. In the normal Zeeman effect, the spectral line corresponding to the original frequency of the light, in the absence of the magnetic field, appears with two other lines arranged symmetrically on either side of the original line. In the more common anomalous Zeeman effect, several lines appear, forming a complex pattern.

The normal Zeeman effect was successfully explained by H. A. Lorentz using the laws of classical physics. Lorentz was Zeeman's mentor and advisor, and they both shared the 1902 Nobel Prize for their work. The anomalous Zeeman effect was a bit more difficult to account for. It could not be explained using classical physics and had to wait for the development of quantum mechanics. The discovery of the electron's intrinsic spin led to a satisfactory explanation of the anomalous Zeeman effect. Heisenberg himself battled with the anomalous Zeeman effect as a student.

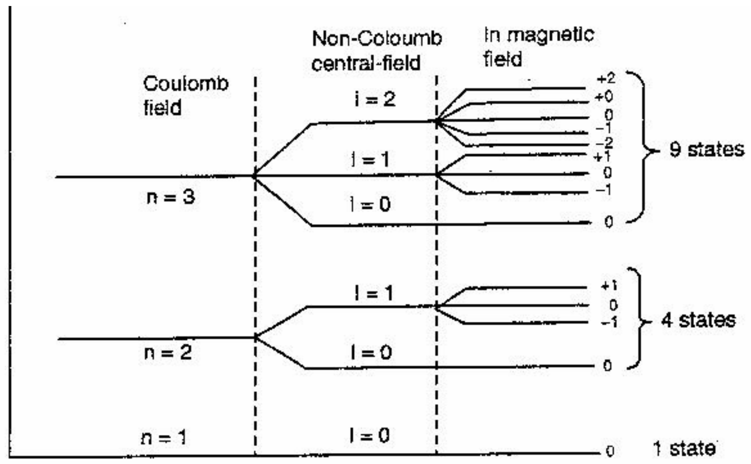


Fig. 6.12. Different eigenstates in hydrogen like atom

when a Hydrogen atom is inserted into a uniform magnetic field, the interaction term will be

$$\boldsymbol{H_m = \Delta E = -\vec{\mu}_L.\vec{B} - \vec{\mu}_S.\vec{B}}, \qquad \boldsymbol{\vec{\mu}_L = -\beta\vec{L}}, \quad \boldsymbol{\vec{\mu}_S = -\beta\vec{S}}$$

$\beta = \dfrac{e\hbar}{2m} = 9.27\times10^{-21}$ erg/G $= 9.27\times10^{-24}$ J/T is the Bohr's magneton.

If we choose $\vec{B}$ in z-direction

$$H_m = \beta B(L_z + 2S_z)$$

The total Hamiltonian of the system will be:

$$H = \frac{P^2}{2\mu} - \frac{Ze^2}{r} + \underbrace{\xi(r)\hat{\mathrm{L}}\cdot\hat{\mathrm{S}}}_{H_{LS}} + \underbrace{\beta B(\hat{\mathrm{L}}_z + 2\hat{\mathrm{S}}_z)}_{H_m}$$

$H_m >> H_{LS}$ Paschen-Back effect (Strong field). $\left|\ell m_\ell s m_s\right\rangle$ will be the reprensetative state.

$H_m << H_{LS}$ anamolus Zeemann effect. $\left|\ell s j m_j\right\rangle$ will be the reprensetative state.

In principle, we should be required to choose unperturbed set which diagonalaizes both fine structure and the magnetic energy.

A- $H_m >> H_{LS}$ Paschen-Back effect (Strong field): For strong magnetic field H_m is a dominant perturbation, so the zero-order wave function diagonalize H_m is the uncoupled function $\left|\ell m_\ell s m_s\right\rangle$

1- If we ignore the electron's spin, one finds

$$\begin{aligned}\left\langle H_m\right\rangle &= \beta B\left\langle \ell' m'_\ell s' m'_s \left| L_z \right| \ell m_\ell s m_s\right\rangle \\ &= \beta B m_\ell \delta_{\ell\ell'} \delta_{m_\ell m'_\ell} \delta_{ss'} \delta_{m_s m'_s}\end{aligned},$$

and if we put the H-atom in a magnetic field, the spliting, and the transitions, in the level will be as follows:

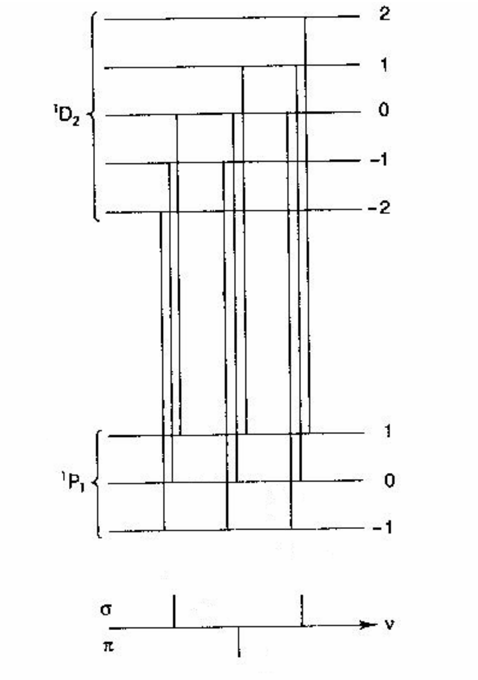
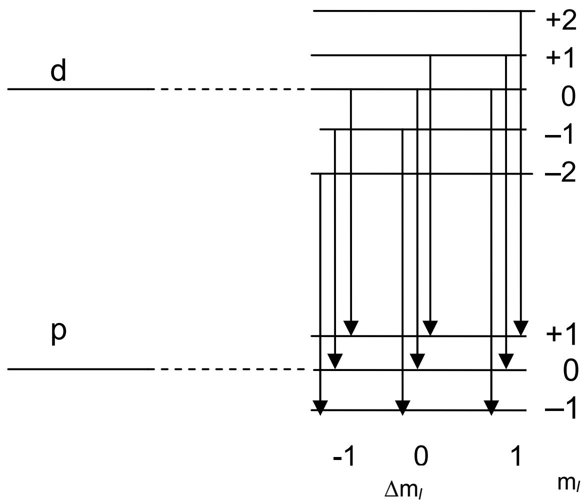


Fig. The normal Zeeman effect for the transitions $^1D_2 \to {}^1P_1$.



1- The π lines ($\Delta m_\ell = 0$) are plane polarized with the direction of polarization parallel to the field.
2- The $\sigma_\pm$ lines ($\Delta m_\ell = \pm 1$) are circularly polarized when observed parallel to the field, and linearly polarized (perpendicular to the field) when observed at right angles to the field.

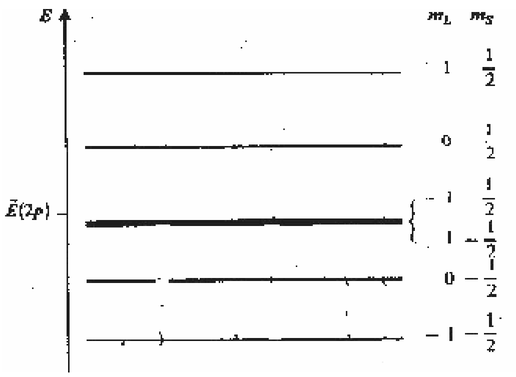
2- Including the spin, one finds

$$\langle H_m \rangle = \beta B \left\langle \ell' m'_\ell s' m'_s \right| \left(\hat{L}_z + 2\hat{S}_z \right) \left| \ell m_\ell s m_s \right\rangle$$
$$= \beta B \left(m_\ell + 2m_s \right) \delta_{\ell\ell'} \delta_{m_\ell m'_\ell} \delta_{ss'} \delta_{m_s m'_s}$$

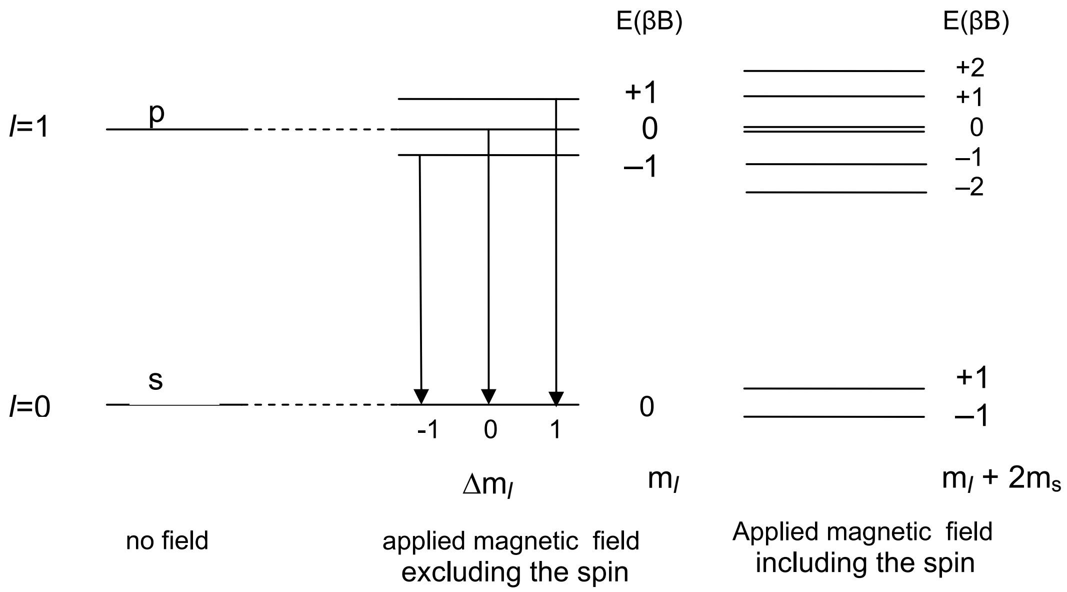
and the electron in s- and p-state will split into the following:

State	m_ℓ	m_s	$\beta B\left(m_\ell + 2m_s\right)$	ω
s	0	1/2	1	1
	0	-1/2	-1	1

State	m_ℓ	m_s	$\beta B\left(m_\ell + 2m_s\right)$	ω
p	1	1/2	2	1
	0	1/2	1	1
	(1,-1)	(-1/2,1/2)	0	2
	0	-1/2	-1	1
	-1	-1/2	-2	1



A comparison between the splitting of s- and p-energy levels under the action of a strong magnetic field. The separation of successive levels is μB



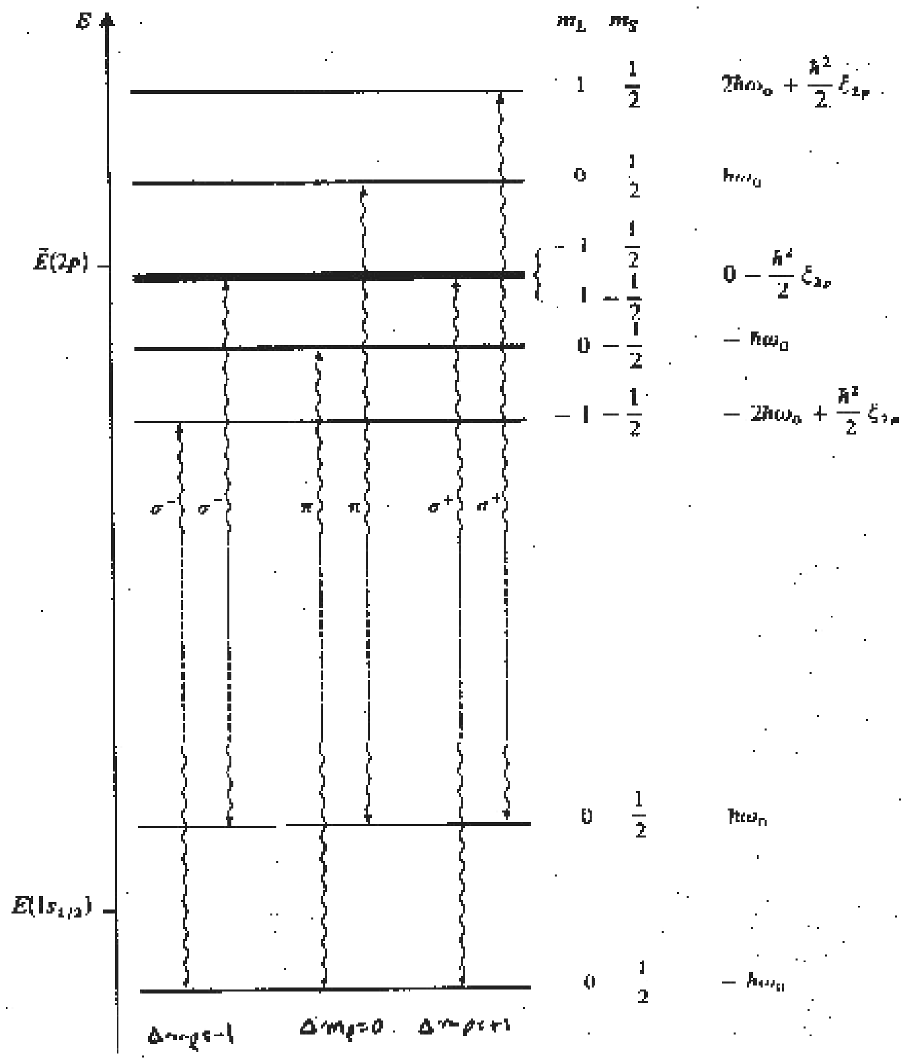
Home work: Try for the d-state

State	m_l	m_s	$2m_s$	$\beta B\left(m_\ell+2m_S\right)$	ω
d	2	1/2	1	3	1
	1	1/2	1	2	1
	(2,0)	(-1/2,1/2)	1	1	2
	(1,-1)	(-1/2,1/2)	(-1,1)	0	2
	(0,-2)	(-1/2,1/2)	-1	-1	2
	-1	-1/2	-1	-2	1
	-2	-1/2	-1	-3	1

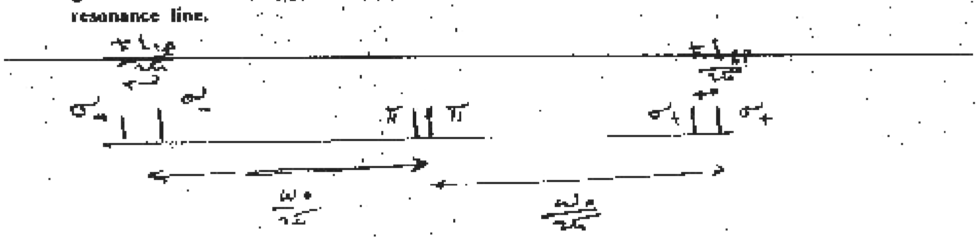
In the uncoupling representation $|m_l,m_S\rangle$, **use** $\hat{L}.\hat{S}=\hat{L}_z\hat{S}_z+\frac{1}{2}\left(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+\right)$ **for 2p-electron**

$$
\left(\hat{L}.\hat{S}\right)=\frac{\hbar^2}{2}
\begin{array}{c c}
 & \begin{array}{cccccc} |1,\tfrac{1}{2}\rangle & |1,-\tfrac{1}{2}\rangle & |0,\tfrac{1}{2}\rangle & |0,-\tfrac{1}{2}\rangle & |-1,\tfrac{1}{2}\rangle & |-1,-\tfrac{1}{2}\rangle \end{array} \\
\begin{array}{c} \langle 1,\tfrac{1}{2}| \\ \langle 1,-\tfrac{1}{2}| \\ \langle 0,\tfrac{1}{2}| \\ \langle 0,-\tfrac{1}{2}| \\ \langle -1,\tfrac{1}{2}| \\ \langle -1,-\tfrac{1}{2}| \end{array} &
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & \sqrt{2} & 0 & 0 & 0 \\
0 & \sqrt{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \sqrt{2} & 0 \\
0 & 0 & 0 & \sqrt{2} & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
\end{array}
$$

The transition will be as follows:



The disposition, in a strong field (decoupled fine structure), of the Zeeman sublevels arising from the 1s and 2p levels. On the right-hand side of the figure are indicated the values of the quantum numbers m_L and m_S associated with each Zeeman sublevel, as well as the corresponding energy, given relative to $E(1s_{1/2})$ or $\bar{E}(2p)$. The vertical arrows indicate the Zeeman components of the resonance line.



H.W. What about the term $\xi(r)\hat{\mathrm{L}}\cdot\hat{\mathrm{S}}$ in the uncoupled representation $\left|L,s,j,m_j\right\rangle$?

For coupling states $\left|j,m_j\right\rangle$, use $\hat{L}.\hat{S}=\frac{1}{2}\left\{\hat{J}^2-\hat{L}^2-\hat{S}^2\right\}$ for 2p-electron

$$\left(\hat{L}.\hat{S}\right)=\frac{\hbar^2}{2}\begin{array}{c|cccccc} & \left|\frac{3}{2},\frac{3}{2}\right\rangle' & \left|\frac{3}{2},\frac{1}{2}\right\rangle' & \left|\frac{3}{2},-\frac{1}{2}\right\rangle' & \left|\frac{3}{2},-\frac{3}{2}\right\rangle' & \left|\frac{1}{2},-\frac{1}{2}\right\rangle' & \left|\frac{1}{2},\frac{1}{2}\right\rangle' \\ \hline {}'\left\langle\frac{3}{2},\frac{3}{2}\right| & 1 & 0 & 0 & 0 & 0 & 0 \\ {}'\left\langle\frac{3}{2},\frac{1}{2}\right| & 0 & 1 & 0 & 0 & 0 & 0 \\ {}'\left\langle\frac{3}{2},-\frac{1}{2}\right| & 0 & 0 & 1 & 0 & 0 & 0 \\ {}'\left\langle\frac{3}{2},-\frac{3}{2}\right| & 0 & 0 & 0 & 1 & 0 & 0 \\ {}'\left\langle\frac{1}{2},-\frac{1}{2}\right| & 0 & 0 & 0 & 0 & -2 & 0 \\ {}'\left\langle\frac{1}{2},\frac{1}{2}\right| & 0 & 0 & 0 & 0 & 0 & -2 \end{array}$$

What about the term $a\vec{L}\cdot\vec{S}$ in the coupled representation $\left|L,s,j,m_j\right\rangle$?
We have to use the expression:

$$\vec{\hat{L}}.\vec{\hat{S}}\left|L,s,j,m_j\right\rangle=\tfrac{1}{2}\left(\hat{J}^2-\hat{L}^2-\hat{S}^2\right)\left|l,s,j,m_j\right\rangle$$
$$=\frac{\hbar^2}{2}\left[j(j+1)-l(l+1)-s(s+1)\right]\left|l,s,j,m_j\right\rangle$$
$$\left\langle\vec{\hat{L}}.\vec{\hat{S}}\right\rangle=\left\langle l,s,j,m_j\right|\vec{\hat{L}}.\vec{\hat{S}}\left|l,s,j,m_j\right\rangle=\frac{\hbar^2}{2}\left[j(j+1)-l(l+1)-\frac{3}{4}\right]$$

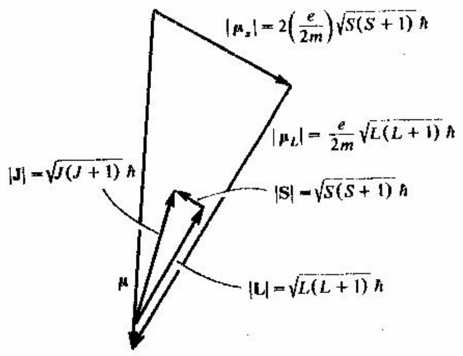
For the uncoupled representation $\left|m_l,m_S\right\rangle$ calculate the matrix element of $\left(\hat{L}.\hat{S}\right)$, use

$$\hat{L}.\hat{S}=\hat{L}_z\hat{S}_z+\frac{1}{2}\left(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+\right)$$

Knowing that

$$\boldsymbol{\mu}_L = -\left(\frac{e}{2m}\right)\mathbf{L} \quad \text{and} \quad \boldsymbol{\mu}_S = -2\left(\frac{e}{2m}\right)\mathbf{S}$$

show in a vector diagram that $\boldsymbol{\mu}$ and $\mathbf{J}$ are not parallel.

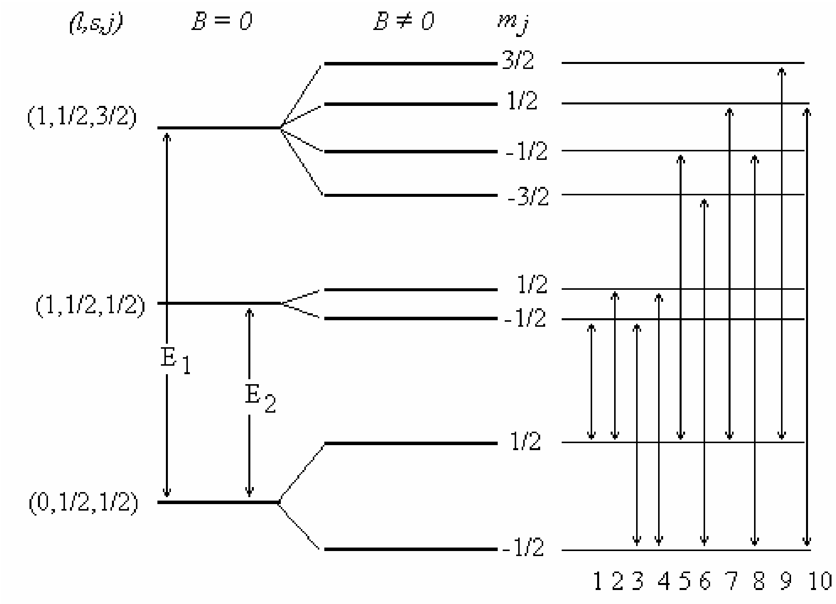


The vector relations $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and $\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S$ are shown in Fig. 24-6. Because

$$\frac{|\boldsymbol{\mu}_S|}{|\mathbf{S}|} = 2\,\frac{|\boldsymbol{\mu}_L|}{|\mathbf{L}|}$$

the two triangles are not similar, and $\boldsymbol{\mu}$ and $\mathbf{J}$ are not parallel.

In a magnetic field **B**, such that $\mu_B B$ is less than the spin-orbit energy, j and m_j are good quantum numbers and the energies of the states split as shown in the Table 4 and in Fig 7 below:



Thus, the so-called "anomalous" Zeeman effect is what would normally be expected for an electron having half-integral spin in a weak magnetic field.

The "normal" or classical Zeeman effect cannot occur for a single electron in a weak magnetic field because of the spin in the perturbed term. However, in atoms in which the spins are paired so that the total spin is zero, the g-value for all spectroscopic states is the classical value and only three spectral lines are observed.

2-

2- Weak magnetic field $H_m << H_{LS}$ anamolus Zeemann effect **.** The state which diagonalize the term $\vec{L}\vec{S}$ is $\left|\ell sjm_j\right\rangle$ will be the reprensetative state. The shift in energy due to the external magnetic field will be:

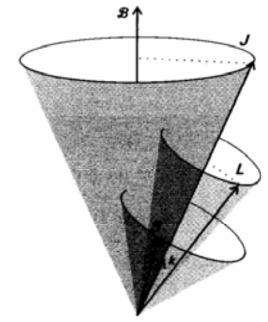


Fig. 7.23 The vector diagram used to calculate the Landé g-factor.

$$H_m = \beta(\vec{L}+2\vec{S})\cdot\vec{B} = \beta g_J\left(\vec{J}\cdot\vec{B}\right) = \beta g_J m_J B, \quad \beta = \frac{e\hbar}{2m} = 5.788\times10^{-5}\ \frac{\text{eV}}{\text{T}}$$

Where g_J is called the Lande g-Factor**.**

Lande g_J factor

There are three pressional motions:

1- $\vec{S}$ about $\vec{J}$,
2- $\vec{L}$ about $\vec{J}$, and
3- $\vec{J}$ about $\vec{B}$

The effective magnetic moment can be found by projecting $\vec{L}$ onto $\vec{J}$ and then $\vec{J}$ on to $\vec{B}$, and then doing the same for $\vec{S}$. The precession averages to zero all the components perpendicular to this motion (this classical averaging is equivalent to ignoring all off-diagonal components in a quantum mechanical calculation). If we used $\vec{J} = \left|\vec{J}\right|\hat{\text{k}}$, $\hat{\text{k}}$ is a unit vector along $\vec{J}$, it follows that the only surviving terms are:

$$\vec{L}\cdot\vec{B} \to \left(\vec{L}\cdot\hat{\text{k}}\right)\left(\hat{\text{k}}\cdot\vec{B}\right) = \frac{\left(\vec{L}\cdot\vec{J}\right)\left(\vec{J}\cdot\vec{B}\right)}{\left|\vec{J}\right|^2}, \qquad \vec{S}\cdot B \to \left(\vec{S}\cdot\hat{\text{k}}\right)\left(\hat{\text{k}}\cdot\vec{B}\right) = \frac{\left(\vec{S}\cdot\vec{J}\right)\left(\vec{J}\cdot\vec{B}\right)}{\left|\vec{J}\right|^2}$$

Because $\vec{J} = \vec{L}+\vec{S}$, it follows that (Use: $\vec{J}-\vec{L} = \vec{S}$ and $\vec{J}-\vec{S} = \vec{L}$):

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

If these quantities are now inserted into $H_m = \beta(\vec{L}+2\vec{S})\cdot\vec{B}$ and the quantum mechanical expressions for magnitudes replace the classical values (so that $\vec{J}^2$ is replaced by $J(J+1)\hbar^2$, etc.), we find

$$H_m = \beta(\vec{L}+2\vec{S})\cdot\vec{B} = \beta\left\{1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right\}\left(\vec{J}\cdot\vec{B}\right) = \beta g_J\left(\vec{J}\cdot\vec{B}\right) = \beta g_J B_z \vec{J}_z$$

We defined the **Lande g_J factor** as

$$g_J = 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

As $S=0$, $g_J=1$ we have $J=L$ and $M_J=\pm1$. In this case, the magnetic moment is independent of L, and so all singlet terms are split to the same extent. This uniform splitting results in the normal Zeeman effect. When $S\neq0$, the value of g_J depends on the values of L and S, and so different terms are split to different extents. The selection rule $\Delta M_J = 0,\pm1$ continues to limit the transitions, but the lines no longer coincide and form three neat groups.
Notes that:

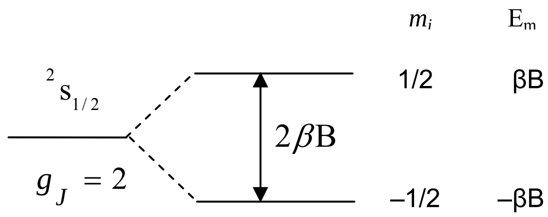
$$g_{J,\max} = 1+\frac{\left(L+S\right)(L+S+1)+S(S+1)-L(L+1)}{2\left(L+S\right)(L+S+1)} = 1+\frac{S}{S+1}, \qquad J_{\max} = L+S$$

$$g_{J,\min} = 1 + \frac{(L-S)(L-S+1) + S(S+1) - L(L+1)}{2(L-S)(L-S+1)} = 1 - \frac{S}{L-S+1}, \qquad J_{\min} = L - S$$

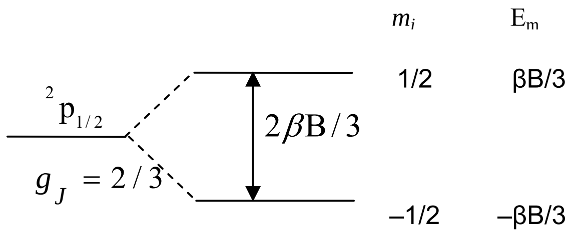
Example: Account for the form of the Zeeman effect when a magnetic field.is applied to the levels ${}^2s_{1/2}$, ${}^2p_{1/2}$, and ${}^2p_{3/2}$.

Answer:

Splitting of ${}^2s_{1/2}$ in a weak magnetic field



Splitting of ${}^2p_{1/2}$ in a weak magnetic field



Splitting of ${}^2p_{3/2}$ in a weak magnetic field

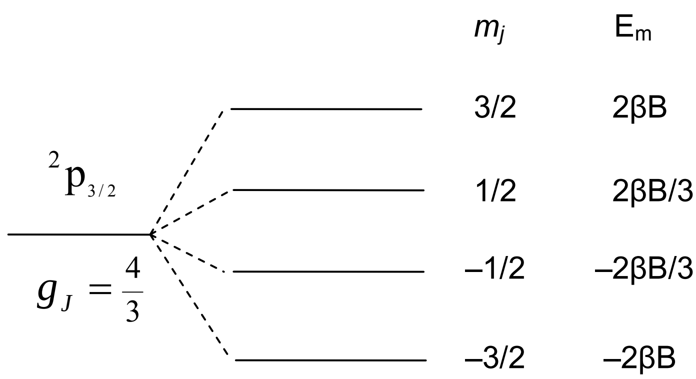


Table : Calculations of Zeeman Splittings

Orbital state	ℓ	j	m_j	g_J	$\Delta E = g_J m_J$ in units of βB
p	1	3/2	3/2	4/3	2
			1/2		2/3
			-1/2		-2/3
			-3/2		-2
		1/2	1/2	2/3	1/3
			-1/2		-1/3
s	0	1/2	1/2	2	1
			-1/2		-1

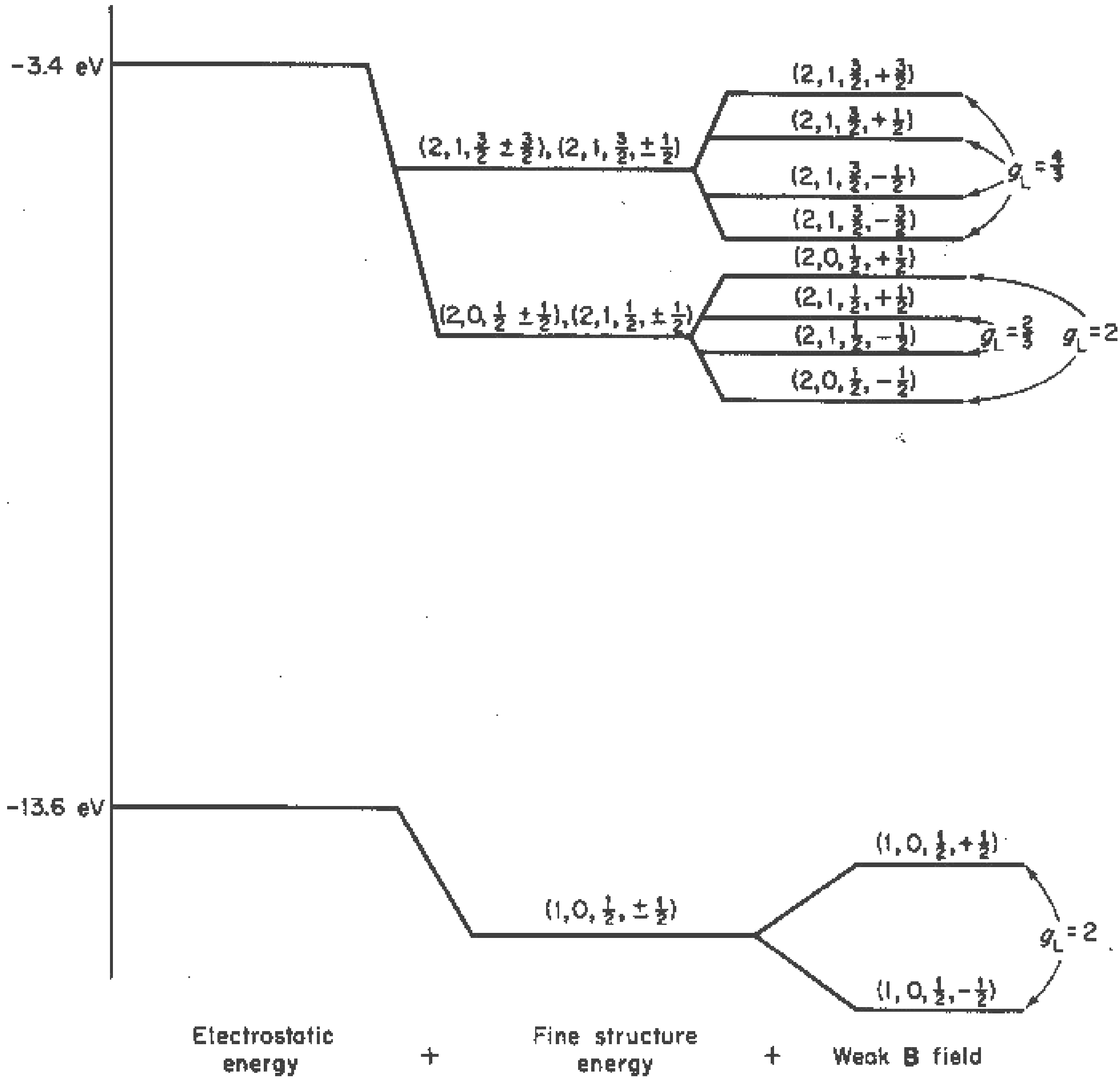


Figure 7-4 **The anomalous Zeeman effect (hydrogen). The parentheses refer to $(nljm_j)$.**

$$\left\langle E_r + E_{LS} \right\rangle = -\frac{\alpha^2 Z^4}{n^3}\left\{\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right\} \text{Ry}, \qquad \text{Ry} = 13.6 \text{ eV}, \quad \alpha = \frac{1}{137}$$

Example: Account for the form of the Zeeman effect when a magnetic field .is applied to the transition ${}^2D_{3/2} \rightarrow {}^2P_{1/2}$.

Method. Begin by calculating the Landé g-factor for each level, and then split the states by an energy that is proportional to its g-value. Proceed to apply the selection rule $\Delta M_J = 0, \pm 1$ to decide which transitions are allowed.

Answer. For the level ${}^2D_{3/2}$ we have $L = 2$, $S = \frac{1}{2}$, and $J = \frac{3}{2}$. It follows that

$g_{3/2}(2, \frac{1}{2}) = \frac{4}{5}$. For the lower level, ${}^2P_{1/2}$, we have $g_{1/2}(1, \frac{1}{2}) = \frac{2}{3}$. The splittings are

therefore of magnitude $\frac{4}{5}\beta B$ in the ${}^2D_{3/2}$ term and $\frac{2}{3}\beta B$ the ${}^2P_{1/2}$ term. The six allowed transitions are summarized in Fig. 7.24, where it is.seen that they form three doublets.

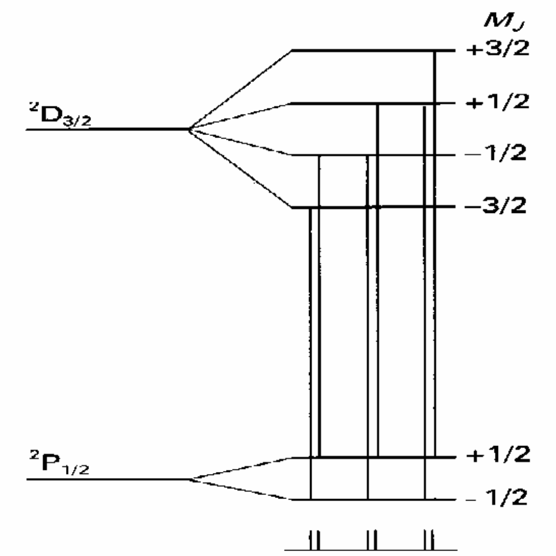
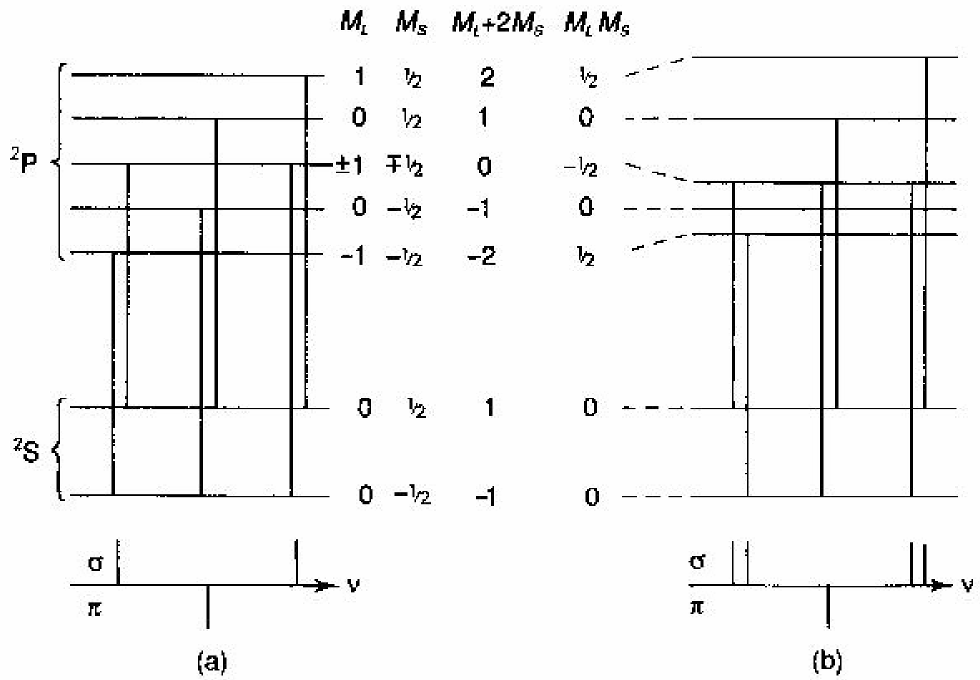


Fig. 7.24 The anomalous Zeeman effect. The splitting of energy levels with different g-values leads to a more complex pattern of lines than in the normal Zeeman effect.



Angular Momenta and Magnetic Moments (Semi - Classical Picture)

A current loop has associated with it a magnetic moment

$$\vec{\mu} = I\vec{A}$$

where I is the current and $\vec{A}$ is the vector area, $A = \pi r^2$, whose direction is perpendicular to the plane of the loop consistent with the right handed screw rule.
I = charge on electron × number of times per second electron passes a given point = ef
where f is the frequency of rotation of the electron.

Magnitude of the magnetic dipole moment

$$|\vec{\mu}| = IA = (ef)(\pi r^2)$$

Whose direction is opposite to the orbital angular momentum $\vec{L}$ because the electron has negative charge.

Now $|L| = mvr = m(2\pi r f)r = 2mf\pi r^2 = \dfrac{2m}{e}|\mu|$

Hence $\vec{\mu} = -\dfrac{e}{2m}\vec{L}$. 15

Since angular momentum is quantized we have

$$\vec{l} = m_l \hbar \hat{l}$$

In the first Bohr radius, $m_l = 1$ and so Eq.15 becomes

$$\vec{\mu}_l = \frac{-e\hbar \hat{l}}{2m} = -\mu_B \hat{l} \qquad 16$$

where μ_B is called the **Bohr magneton** and its value is given by

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

It will be observed in Eq.16 that μ_l is directed antiparallel to the orbital angular momentum.

The ratio of the magnetic moment to the orbital angular momentum is called the classical gyromagnetic ratio,

$$\gamma_l = \left|\frac{\vec{\mu}_l}{\vec{l}}\right| = \frac{e}{2m} = \frac{\mu_B}{\hbar} \qquad 17$$

The spin angular momentum also has a magnetic moment associated with it. Its gyromagnetic ratio is approximately twice the classical value for orbital moments.

ie.

$$\gamma_s = \left|\frac{\vec{\mu}_s}{\vec{s}}\right| = \frac{e}{m} \qquad 18$$

This means that spin is **twice** as effective as the orbital angular momentum in producing a magnetic moment.

Eq.17 and 18 are often combined by writing

$$\gamma = \frac{ge}{2m}$$

where the quantity g is called the ***spectroscopic splitting factor***.
For orbital angular momenta g = 1, for spin only g ≈ 2 (though experimentally g = 2.004).
For states that are mixtures of orbital and spin angular momenta, g is non-integral.

Since $s = \frac{1}{2}\hbar$

the magnetic moment due to the spin of the electron is

$$\mu_s = \gamma_s |\vec{s}| = \frac{e}{m} \cdot \frac{\hbar}{2} = \mu_B$$

Thus, the smallest unit of magnetic moment for the electron is the Bohr magneton, whether one combines orbital or spin angular momentum.

The Larmor Frequency and The Normal Zeeman Effect

(Classical Treatment)

We consider the effect of a weak magnetic field on an electron performing circular motion in a planar orbit. We assume the magnetic field is applied along the z axis and the angular momentum is oriented at an angle θ with respect to the z - axis, as shown in Fig 4 below.

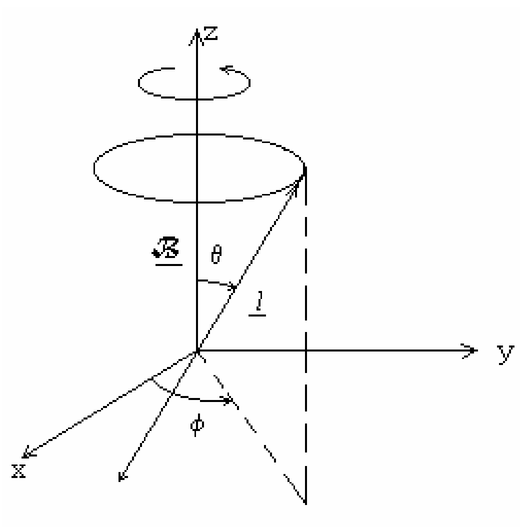


Fig 4 The Precession of The Angular Momentum Vector in A Magnetic Field

The torque on $\vec{l}$ is given by

$$\vec{\tau}_l = \vec{\mu}_l \wedge \vec{B} \qquad 19$$

this is directed into the plane of the page, in the ϕ-direction.

Now, the torque also equals the rate of change of the angular momentum, so we have

$$\vec{\tau}_l = \frac{d\vec{l}}{dt} = \vec{\mu}_l \wedge \vec{B} = \gamma_l \vec{l} \wedge \vec{B} \qquad 20$$

But

$$\left| d\vec{l} \right| = l \sin\theta d\phi$$

so that the scalar form of Eq.20 becomes

$$l \sin\theta . \frac{d\phi}{dt} = \gamma_l l B \sin\theta \qquad 21$$

We define the precessional velocity by

$$\omega_L = \frac{d\phi}{dt}$$

So that Eq.21 becomes

$$\omega_L = \gamma_l B = \frac{e}{2m} B \qquad 22$$

The angular velocity ω_L is called the ***Larmor frequency***.

Thus, the angular momentum vector precesses about the z-axis at the Larmor frequency as a result of the torque produced by the action of a magnetic field on its associated magnetic moment.

Using the Planck relation, the energy associated with the Larmor frequency is

$$\Delta E = \pm \omega_L \hbar = \pm \frac{e\hbar B}{2m} = \pm \mu_B B \qquad 23$$

where the signs refer to the sense of the rotation. It will be observed that this energy difference is the potential energy of a magnetic dipole whose moment is one Bohr magneton.

Recall that the dipolar energy is given by

$$\Delta E = -\vec{\mu}.\vec{B}$$

In Eq.23, the positive sign corresponds to antiparallel alignment while the negative sign (lower energy) indicates parallel alignment.

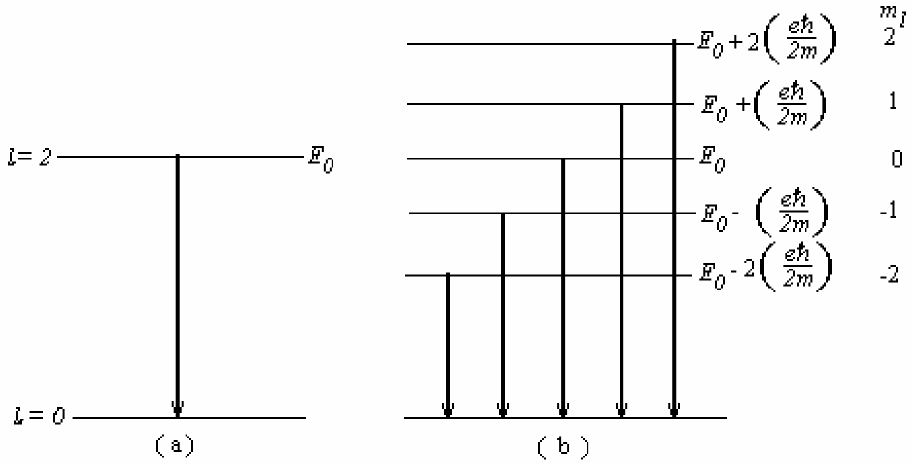
The overall effect of this energy associated with the Larmor frequency is that, if the energy of an electron having a moment μ_B is E_0 in the absence of an applied field, then it can take on one of the energies

$$E_0 \pm \mu_B B$$

in a magnetic field **B**.

Thus, in a collection of identical atomic particles of the type discussed, a magnetic field produces a triplet of levels, called a **Lorentz triplet** whose energies are $\mathbf{E_0}$, and $E_0 \pm \mu_B B$.

This phenomenon is known as the ***Normal Zeeman*** effect.


$l=2$
E_0
$l=0$
(a)
$E_0+2\left(\frac{e\hbar}{2m}\right)$
$E_0+\left(\frac{e\hbar}{2m}\right)$
E_0
$E_0-\left(\frac{e\hbar}{2m}\right)$
$E_0-2\left(\frac{e\hbar}{2m}\right)$
m_l
2
1
0
-1
-2
(b)