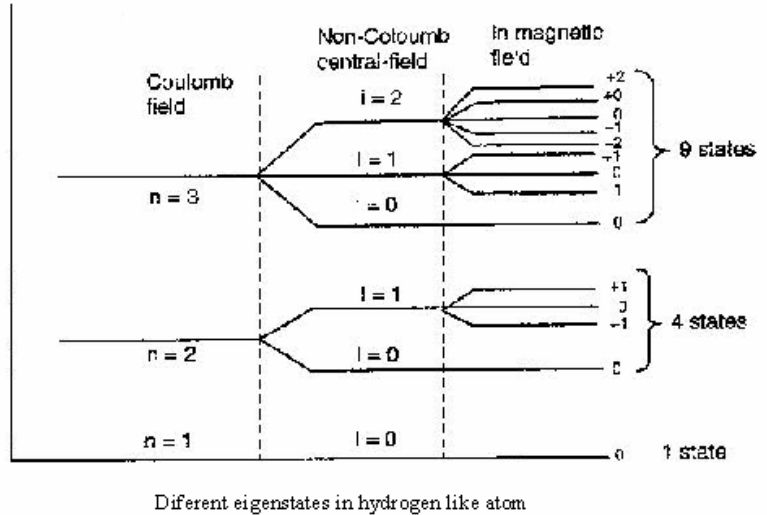


The Zeeman Effect (Chapter 17) Splitting of Spectral Lines by a Magnetic Field

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.

When a hydrogen atom is inserted into a uniform magnetic field, the interaction term will be

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

$$\beta = \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \frac{\text{eV}}{\text{T}} = 9.27 \times 10^{-21} \text{ erg/G} = 9.27 \times 10^{-24} \text{ J/T}$$

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:

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

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

$H_m \ll H_{LS}$ anomalous Zeemann effect . $|\ell s j m_j\rangle$ will be the representative state.

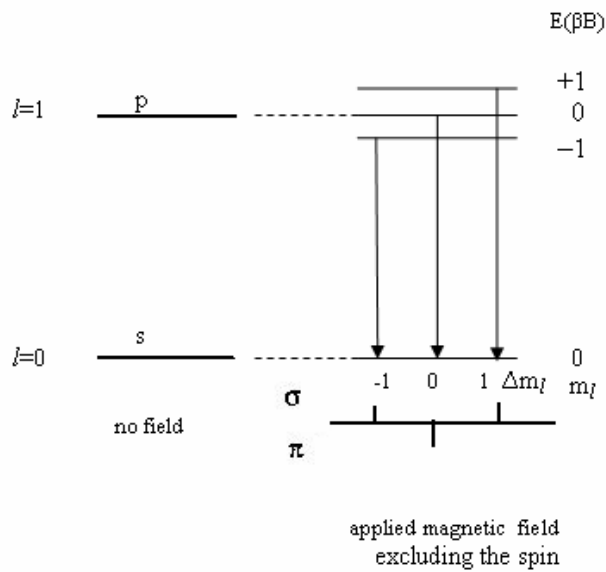
In principle, we should be required to choose unperturbed set which diagonalizes both fine structure and the magnetic energy.

A- $H_m \gg H_{LS}$ 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 $|\ell m_\ell s m_s\rangle$

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

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

and if we put the hydrogen atom in a magnetic field, the splitting, and the transitions, in the level $p \rightarrow s$ will be as follows:



- 1- The π lines ($\Delta m_{\ell} = 0$) are plane polarized with the direction of polarization parallel to the field.
- 2- The σ_{\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.

H.W. Work out the transition $d \rightarrow p$ in strong magnetic field (ignore the spin).

2- Including the spin, one finds

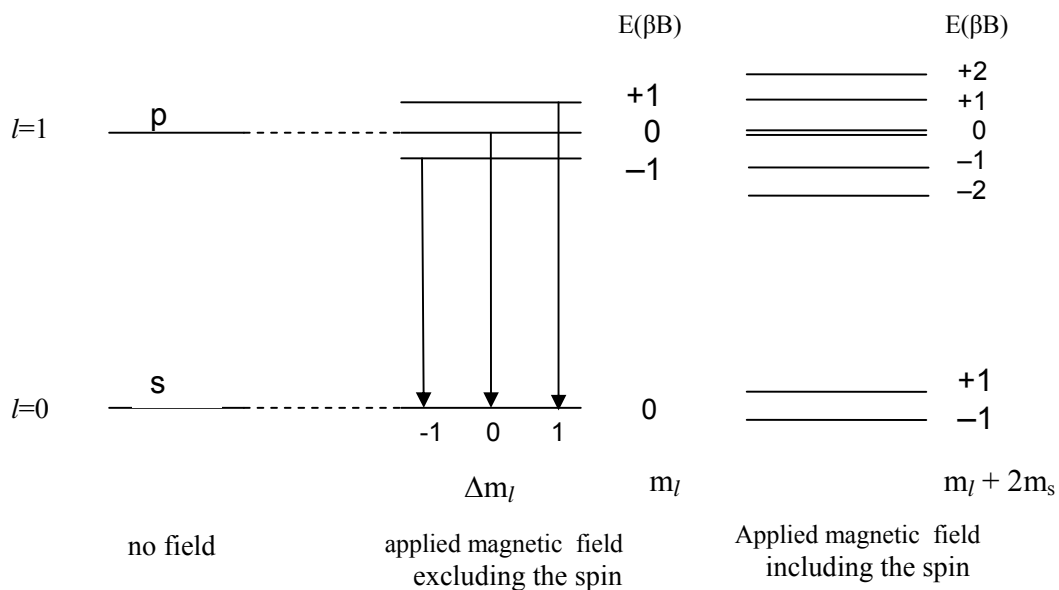
$$\begin{aligned} \langle H_m \rangle &= \beta B \langle \ell' m'_{\ell} s' m'_{s} | (\hat{L}_z + 2\hat{S}_z) | \ell m_{\ell} s m_s \rangle \\ &= \beta B (m_{\ell} + 2m_s) \delta_{\ell\ell'} \delta_{m_{\ell} m'_{\ell}} \delta_{ss'} \delta_{m_s m'_{s}} \end{aligned}$$

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

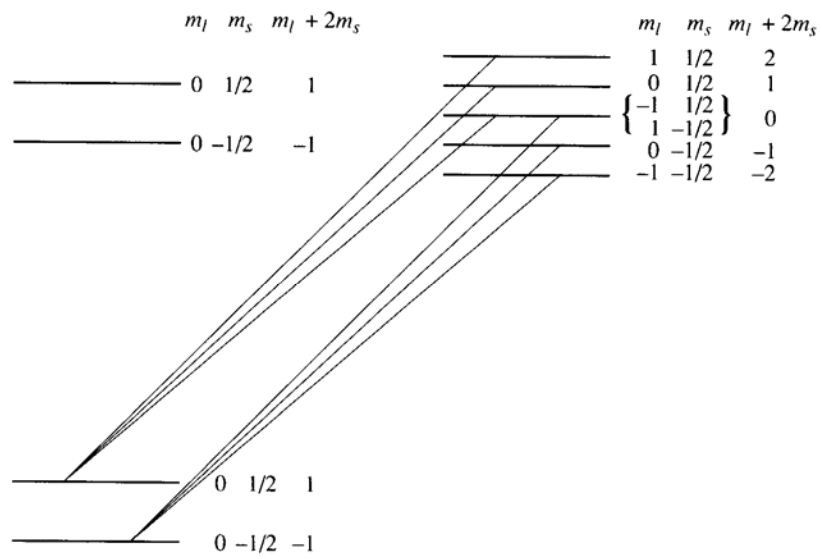
State	m_{ℓ}	m_s	$\beta B (m_{\ell} + 2m_s)$	degeneracy
s ($\ell = 0$)	0	1/2	1	1
	0	-1/2	-1	1

State	m_{ℓ}	m_s	$\beta B (m_{\ell} + 2m_s)$	degeneracy
p ($\ell = 1$)	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



H.W. Work out the splitting of the d-state in strong magnetig field (including the spin).



The splitting of $n = 2, \ell = 1$ and $n = 1, \ell = 0$ levels in a strong field and the allowed dipole transitions among them.

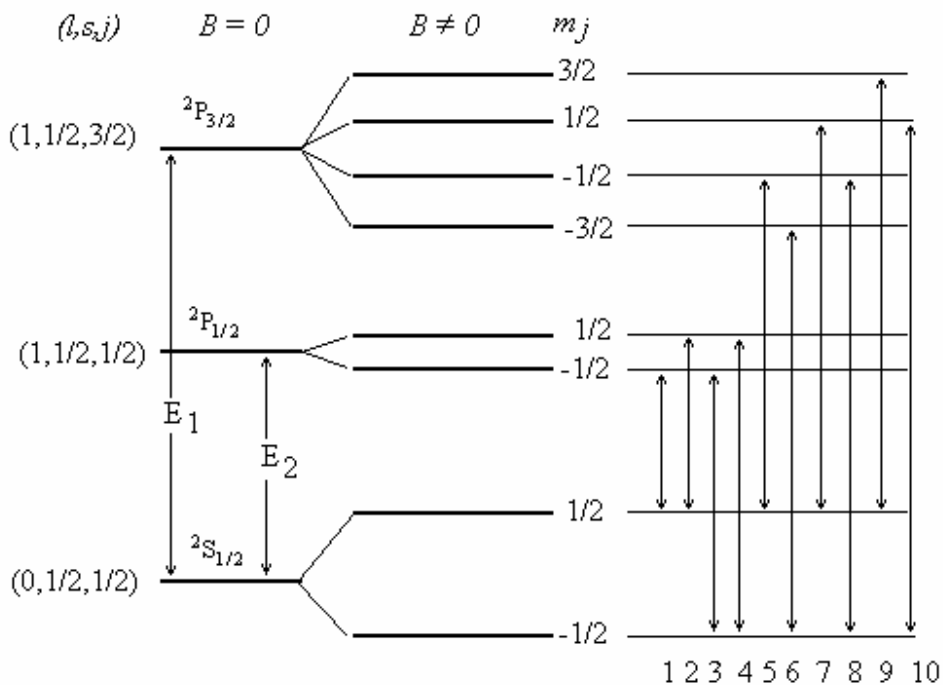
2- Weak magnetic field $H_m \ll H_{LS}$ (anomalous Zeeman effect).

The state which diagonalize the term $\vec{L}\vec{S}$ is $|\ell s j m_j\rangle$ and will be the representative state. The shift in energy due to the external magnetic field will be written in the form:

$$H_m = \beta(\vec{L} + 2\vec{S}) \cdot \vec{B} = \beta g_J (\vec{J} \cdot \vec{B}) = \beta g_J m_J B,$$

where g_J is called the Lande g-Factor.

In a magnetic field \mathbf{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 following Figure for $^2S_{1/2}, ^2P_{1/2}, ^2P_{3/2}$. 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 anomalous Zeeman effect of all $n = 2, \ell = 1$ and $n = 1, \ell = 0$ levels and the allowed dipole transitions among them.

Calculation of the Lande g_J factor

In external magnetic field, there are three precessional 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 $\vec{J} = |\vec{J}| \hat{k}$, \hat{k} is a unit vector along \vec{J} , it follows that the only surviving terms are:

$$\vec{L} \cdot \vec{B} \rightarrow (\vec{L} \cdot \hat{k})(\hat{k} \cdot \vec{B}) = \frac{(\vec{L} \cdot \vec{J})(\vec{J} \cdot \vec{B})}{|\vec{J}|^2}, \quad \vec{S} \cdot \vec{B} \rightarrow (\vec{S} \cdot \hat{k})(\hat{k} \cdot \vec{B}) = \frac{(\vec{S} \cdot \vec{J})(\vec{J} \cdot \vec{B})}{|\vec{J}|^2}$$

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

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

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

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

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 the spin $S = 0$, we have $J = L$, $g_J = 1$ and $M_J = \pm 1$. 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 $S \neq 0$, 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 $\Delta M_J = 0, \pm 1$ continues to limit the transitions, but the lines no longer coincide and form three neat groups. Notes that:

- 1- $g_J = 1, \quad J = L$
- 2- $g_J = 1 \pm \frac{1}{2L+1}, \quad J = L \pm \frac{1}{2}$
- 3- $g_{J,\max} = 1 + \frac{(L+S)(L+S+1) + S(S+1) - L(L+1)}{2(L+S)(L+S+1)} = 1 + \frac{S}{S+1}, \quad J_{\max} = L+S$
- 4- $g_{J,\min} = 1 + \frac{(L-S)(L-S+1) + S(S+1) - L(L+1)}{2(L-S)(L-S+1)} = 1 - \frac{S}{L-S+1}, \quad J_{\min} = L-S$

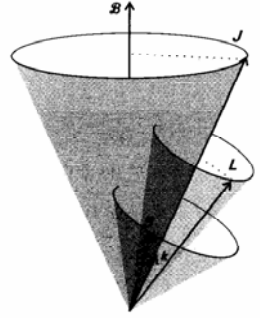
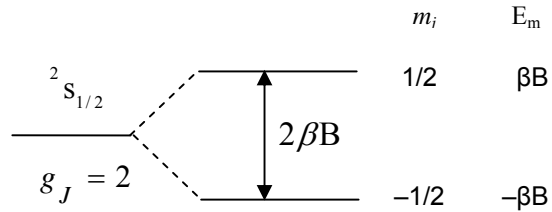


Fig. 7.23 The vector diagram used to calculate the Lande g -factor.

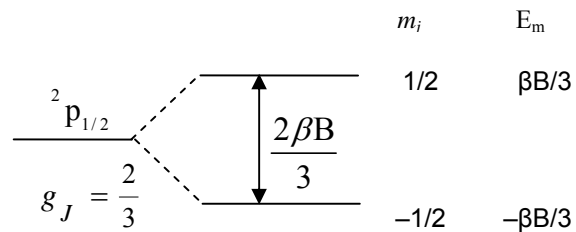
Example: Account for the form of the Zeeman effect when a magnetic field B is applied to the levels ${}^2S_{1/2}$, ${}^2P_{1/2}$, and ${}^2P_{3/2}$. (note that: $H_m = \beta g_J m_J B$)

Answer:

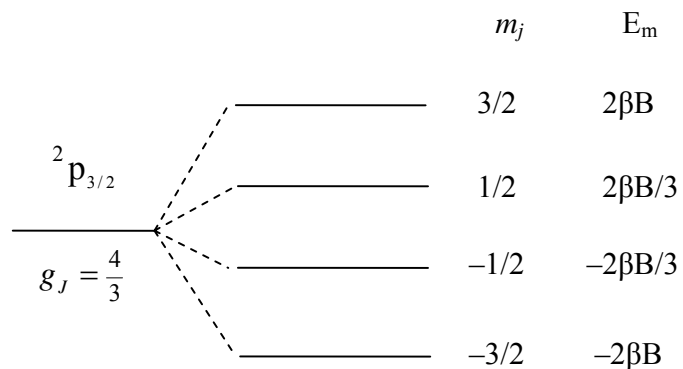
Splitting of ${}^2S_{1/2}$ in a weak magnetic field



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

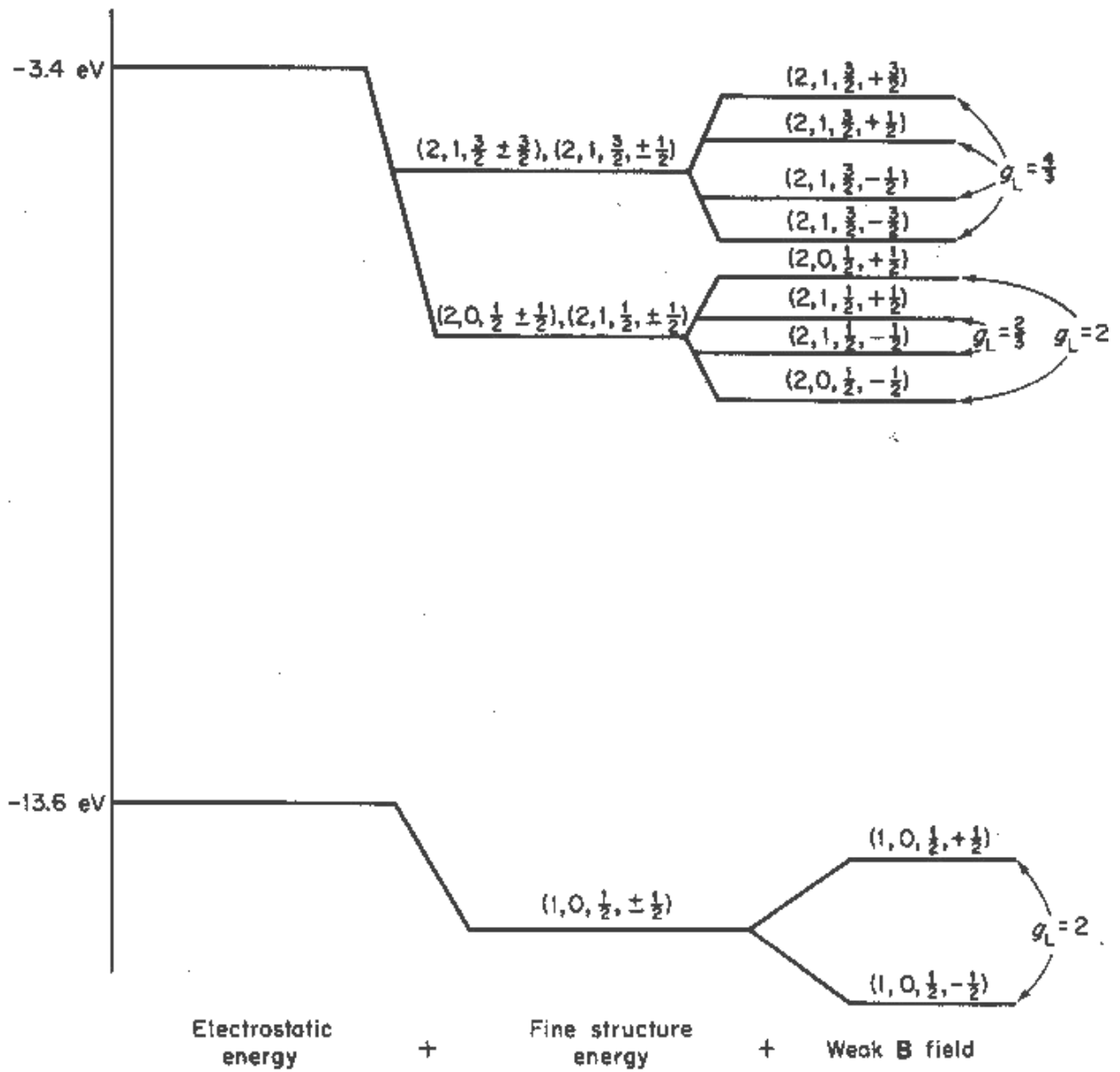


Splitting of ${}^2P_{3/2}$ in a weak magnetic field



H.W. Check the following table for the Calculation of Zeeman Splittings

Orbital state	ℓ	j	m_j	g_J	$\Delta E = g_J m_j (\beta B)$
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



The anomalous Zeeman effect (hydrogen). The parantheses refer to $(n \ell j m_j)$

Example: Account for the form of the Zeeman effect when a magnetic field B 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 $\frac{2}{3}\beta B$ in the ${}^2P_{1/2}$ term. The six

allowed transitions are summarized in Fig. 7.24, where it is seen that they form three doublets.

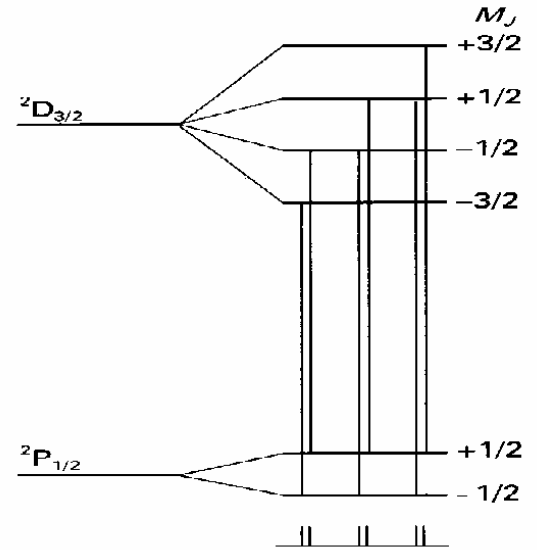
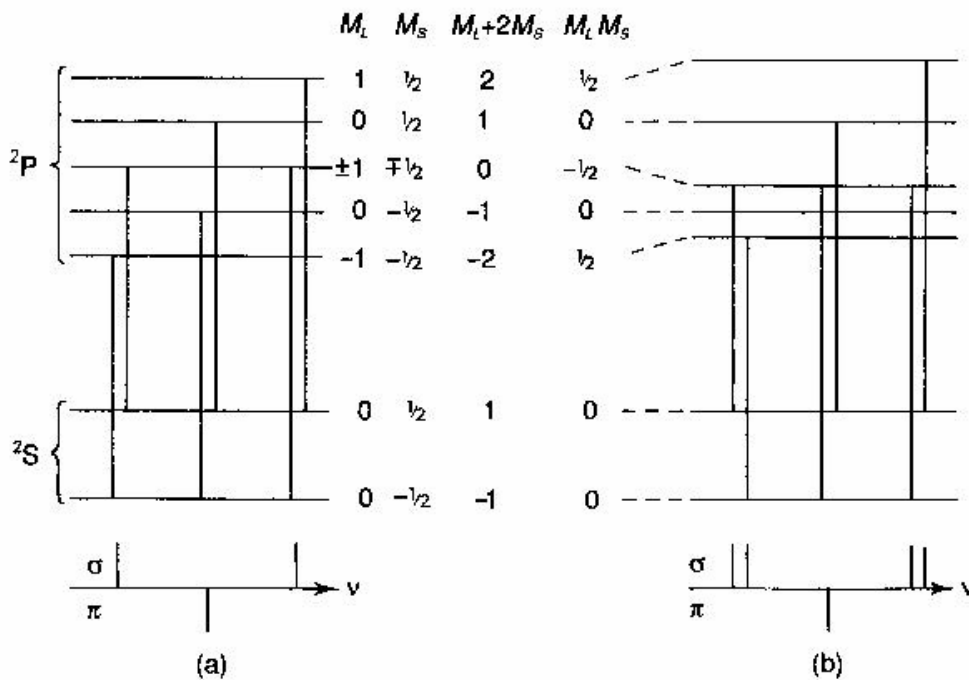


Fig. 7.24 The anomalous Zeeman effect. The splitting of energy levels with different g -values leads to a more complex pattern of lines than in the normal Zeeman effect.



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.