Chapter 10: Multi-Electron Atoms – Optical Excitations

To describe the energy levels in multi-electron atoms, we need to include all forces. The strongest forces are the forces we already discussed in Chapter 9:

- The forces between the electrons and the nucleus.
- The forces between the electrons.

However, a more accurate understanding of the energy levels in multi-electron atoms also requires the inclusion of weaker forces:

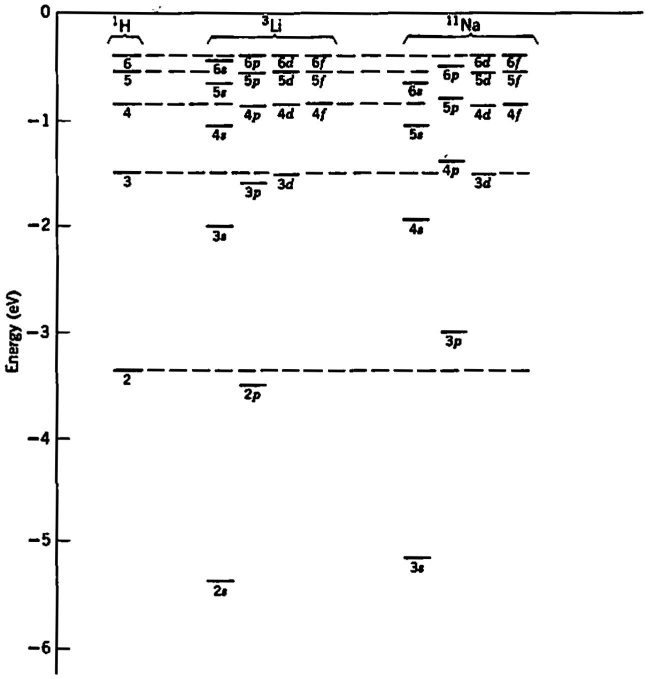
- The forces due to the coupling between orbital angular momenta.
- The forces due to the coupling between spin angular momenta (the exchange force).
- The forces due to the coupling between spring and orbital angular moment.
- The forces due to external magnetic fields (the Zeeman effect).

The energy levels in multi-electron atoms can be probed using:

- Optical spectra: transitions associated with weakly bound outer electrons (small energies).
- X-ray spectra: transitions associated with tightly bound outer electrons (large energies).

To start our study of optical excitations, let us first consider the alkali atoms. The energy levels of some states in the lightest alkali atoms are indicated in the Figure at the bottom of the page. In our discussion of alkali atoms we make the following assumptions:

- We ignore the core of filled sub-shells in the atom. These sub-shells have spherical symmetry and are difficult to excite.
- The electronic structure for the Alkali atoms shown in the Figure is as follows:
  - For H: 1 electron. The electron is located in a $1s^1$ configuration. The outer-most electron is in the $1s$ state.
  - For Li: 3 electrons. The electrons are located in a



$1s^2 2s^1$ configuration. The outer-most electron is in the $2s$ state.
  - For Na: 11 electrons. The electrons are located in a $1s^2 2s^2 2p^6 3s^1$ configuration. The outer-most electron is in the $3s$ state.
- The highest filled sub-shell in the Alkali atoms, except H and Li, is the p shell.
- The outermost electron in the Alkali atoms is located in an s shell. This electron is called **the optical electron.**

Based on detailed studies of the optical spectra of Alkali atoms, the following conclusions can be drawn:

- The spectra show **fine structure**. All levels are split, except the $\ell = 0$ levels.
- The splitting is related to the spin-orbit coupling (see Chapter 8) which introduces an energy shift equal to

$$\Delta E = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot\vec{L} = \frac{\hbar^2}{2m^2c^2}\left\{ j(j+1) - \ell(\ell+1) - s(s+1)\right\}\frac{1}{r}\frac{dV}{dr}$$

If $\ell = 0$, $j = s$ and the energy shift is 0.

If $\ell \neq 0$, there are two values of the energy shift:

$$j = \begin{cases} \ell + \frac{1}{2} & \Rightarrow \begin{cases} \Delta E = \frac{\hbar^2}{2m^2c^2}\left\{\left(\ell + \frac{1}{2}\right)\left(\ell + \frac{3}{2}\right) - \ell(\ell+1) - \frac{3}{4}\right\}\frac{1}{r}\frac{dV}{dr} = \\ \quad = \frac{\hbar^2}{2m^2c^2}\ell\frac{1}{r}\frac{dV}{dr} \end{cases} \\ \ell - \frac{1}{2} & \Rightarrow \begin{cases} \Delta E = \frac{\hbar^2}{2m^2c^2}\left\{\left(\ell - \frac{1}{2}\right)\left(\ell + \frac{1}{2}\right) - \ell(\ell+1) - \frac{3}{4}\right\}\frac{1}{r}\frac{dV}{dr} = \\ \quad = \frac{\hbar^2}{2m^2c^2}(-\ell - 1)\frac{1}{r}\frac{dV}{dr} \end{cases} \end{cases}$$

Looking at the calculated energy shift we make the following observations:

1. The splitting of the original energy level is asymmetric.
2. The splitting is proportional to $(1/r)(dV/dr)$. Since both $(1/r)$ and (dV/dr) become large when r becomes small, the expectation value of the energy shift will be dominated by the behavior of the wavefunctions at small r.
3. Since (dV/dr) at small r is proportional to Z, we expect that the energy shift increases when Z increases. This is indeed observed, as can be seen based on the information contained in the following table:

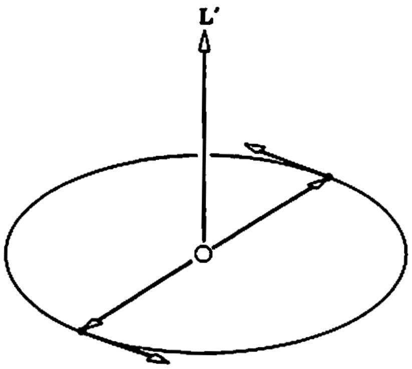
Atom	Spin-Orbit Splitting	$\frac{Z}{Z_{Li}}$	$\frac{\Delta E}{\Delta E_{Li}}$
^{3}Li	0.42×10^{-4} eV	1	1
^{11}Na	21×10^{-4} eV	3.7	50
^{19}K	72×10^{-4} eV	6.3	171
^{37}Rb	295×10^{-4} eV	12.3	702
^{55}Cr	687×10^{-4} eV	18.3	1636

The structure of atoms with several optical electrons is more complicated. The energy levels of such atoms can be determined using the Hartree approximation which shows that the energy level of each electron in the outer shell is determined by two quantum numbers n and ℓ. Since there are $(2\ell+1)$ values of m_ℓ and 2 values of m_s, there are $2(2\ell+1)$ combinations that have the same energy. However, some of the degeneracy is removed by considering the effect of the following interactions:

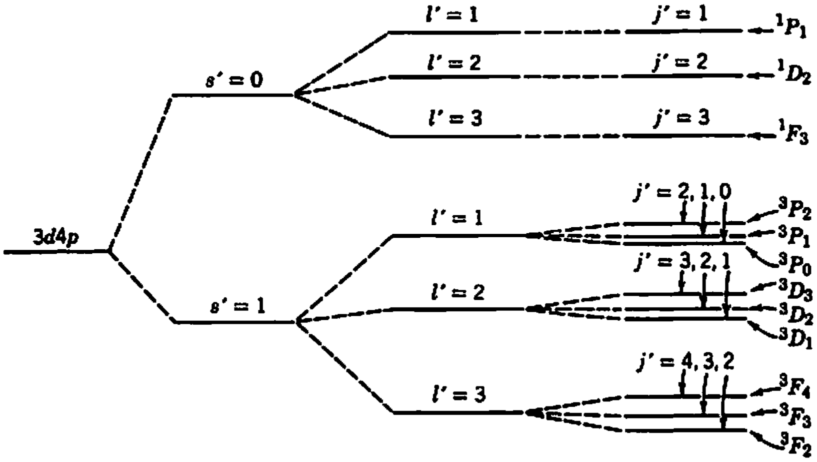
- The residual Coulomb interactions: this is a correction to the average affect of the Coulomb interactions due to all other electrons which has been included in the Hartree calculations.
- Spin-orbit interactions.

Let us first consider the residual Coulomb interactions:

- This interaction is not relevant in Alkali atoms since the average potential used in the Hartree calculations is a good approximation due to the spherical nature of the closed (sub)shells.
- The interaction depends on the distance between the electrons in the outer shell. First consider atoms with two optical electrons. These two electrons can be in either a triplet or a singlet spin state. Since the average distance between two electrons in the triplet state is larger than the average distance between two electrons in the singlet state, the repulsion between these electrons will be less when they are in the triplet state, $S_{12}=\sqrt{2}\hbar$, compared to the singlet state, $S_{12}=0$. We thus conclude that the energy shift due to residual Coulomb interactions is lower when S_{12} is larger. An example of the shift associated with spin is shown in the level scheme on Page 4.
- The angular momentum of the optical electrons also influences the energy of the states. Consider the classical picture of an atom with two optical electrons, shown in the Figure on the right. The Coulomb repulsion energy is minimized when the electrons are



on opposite sides of the orbit. In this case, the angular momentum associated with each electron is pointing in the same direction and the total angular momentum of this pair is maximized. This model leads to the following conclusion: states with maximum L_{12} have the lowest energy. The resulting shift in energy levels is shown in the following level scheme where a state with $\ell_{12} = 1$ have the highest energy and a state with $\ell_{12} = 3$ has the lowest energy.



Note: the spectroscopic notation used in this level scheme is $^{2S+1}L_J$.

Now consider the spin-orbit interaction:

- We already saw that the energy shift due to the spin-orbit interaction is given by the following expression:

$$\Delta E = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot\vec{L} = \frac{\hbar^2}{2m^2c^2}\left\{j(j+1)-\ell(\ell+1)-s(s+1)\right\}\frac{1}{r}\frac{dV}{dr}$$

  For a given ℓ and s, the energy shift is lower when the total angular momentum quantum number j is lower. This is the reason that the states in the lower right-hand corner of the level scheme shown above split according to this rule. For example, the order of the lowest three states is $j = 2, 3, 4$ (order of increasing energy). The spin-orbit effect does not change the energy of the states shown in the top-right corner of the Figure since $s = 0$ and $j = \ell$.

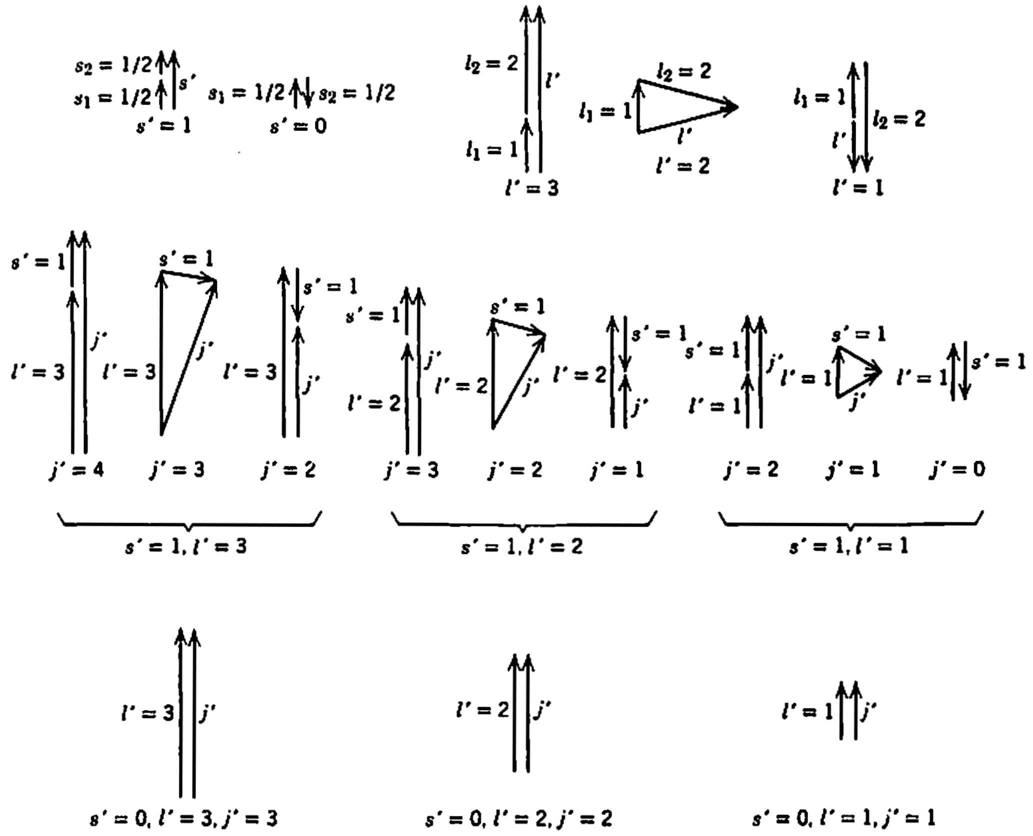
- If there are more than two optical electrons, the calculation of the angular momenta becomes more complicated:

$$\vec{S} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + ...$$

$$\vec{L} = \vec{L}_1 + \vec{L}_2 + \vec{L}_3 + ...$$

$$\vec{J} = \vec{J}_1 + \vec{J}_2 + \vec{J}_3 + ...$$

- When Z increases, the spin-orbit interaction increases and may exceed the Coulomb repulsion corrections.
- It is critical to understand the vector addition of the angular momenta of two electrons. Examining (and understanding) the vector additional diagrams shown in the following Figure is very important.

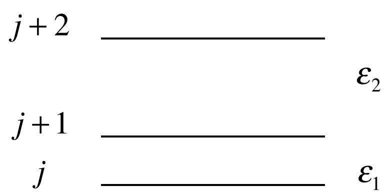


- The separation energy between energy levels of a multiplet depends on j:

$$\begin{aligned}\varepsilon_{(j+1)\to j} &= k\left\{(j+1)(j+2)-\ell(\ell+1)-s(s+1)\right\}-k\left\{j(j+1)-\ell(\ell+1)-s(s+1)\right\}= \\ &= k\left\{\left(j^2+3j+2\right)-\left(j^2+j\right)\right\}=2k(j+1)\end{aligned}$$

This prediction is called **the Lande interval rule** and can be used to determine j.

Example: consider the following the following levels that are part of a multiplet:



The Lande rule can be used to relate the energy differences to *j*;

$$\left.\begin{array}{l}\varepsilon_1 = 2k(j+1)\\ \varepsilon_2 = 2k(j+2)\end{array}\right\} \Rightarrow \frac{\varepsilon_1}{\varepsilon_2} = \frac{j+1}{j+2} = 1 - \frac{1}{j+2}$$

The measured energy levels are in good agreement with the Lande rule.

As an example, consider the special case of **carbon**. Carbon has 6 electrons in the following configuration: $1s^2\ 2s^2\ 2p^2$. The optical properties of carbon are determined by the properties of the $2p^2$ electrons. These electrons have the following quantum numbers:

$$n_1 = 2, \ell_1 = 1, s_1 = \frac{1}{2}$$
$$n_2 = 2, \ell_2 = 1, s_2 = \frac{1}{2}$$

The total spin and the total orbital angular momentum of these two electrons can take on the following values:

$$S_{12} = 0,1$$
$$L_{12} = 0,1,2$$

The total spin can thus have two possible values:

- $S_{12} = 0$. The total angular momentum of the two electrons can take on the following values:

$$\text{if } L_{12} = 0: \quad J_{12} = 0$$
$$\text{if } L_{12} = 1: \quad J_{12} = 1$$
$$\text{if } L_{12} = 2: \quad J_{12} = 2$$

- $S_{12} = 1$. The total angular momentum of the two electrons can take on the following values:

$$\begin{aligned}
&\text{if } L_{12} = 0: \quad J_{12} = 1 \\
&\text{if } L_{12} = 1: \quad J_{12} = 0,1,2 \\
&\text{if } L_{12} = 2: \quad J_{12} = 1,2,3
\end{aligned}$$

In our study of possible states in carbon we have not considered the impact of the exclusion principle. The two electrons in the 2*p* state have the same *n* and ℓ and in order to satisfy the exclusion principle, they must have different m_ℓ or m_s. Consider what happens when the electrons are in a spin triplet state. If they have the same m_s they must have different m_ℓ. But, this prevents the electrons from being in the L_{12} =2 state. To look at which states are possible we need to construct a table that lists all possible combinations of *m*. Consider two electrons in the *p* shell. The following table lists all possible combinations of the magnetic quantum numbers associated with these two electrons.

m_{ℓ_1}	m_{s_1}	m_{ℓ_2}	m_{s_2}	$m_{\ell_{12}}$	$m_{s_{12}}$	$m_{j_{12}}$
1	+½	1	-½	2	0	2
		0	+½	1	1	2
		0	-½	1	0	1
		-1	+½	0	1	1
		-1	-½	0	0	0
1	-½	0	+½	1	0	1
		0	-½	1	-1	0
		-1	+½	0	0	0
		-1	-½	0	-1	-1
0	+½	0	-½	0	0	0
		-1	+½	-1	1	0
		-1	-½	-1	0	-1
0	-½	-1	+½	-1	0	-1
		-1	-½	-1	-1	-2
-1	+½	-1	-½	-2	0	-2

As we can see from this table, a total of 15 possible configurations exist for these two electrons. Based on the information in the table we can draw the following conclusions:

- Since m_j can take on values between +2 and -2, the total angular momentum quantum number *j* cannot be 3. This is a consequence of the Pauli exclusion principle. We thus do not expect to see the $^3D_3$ level in carbon. But, we know that there must be D states since there are combinations with $m_{\ell_{12}} = 2$ in the table. Since the $^3D_1$ and $^3D_2$ states have combinations for which the electrons would have the same quantum numbers, we can also exclude these states. The only possible D state would thus be the $^1D_2$ state. This state has $j = 2$ and thus account for $(2j + 1) = 5$ combinations.

- Now consider P states. If the electrons are in a spin triplet state ($s = 1$) the following configurations exist:
    - $j = 2$: $m_j = -2, -1, 0, 1, 2$. Possible configurations: 5 $^3P_2$
    - $j = 1$: $m_j = -1, 0, 1$. Possible configurations: 3 $^3P_1$
    - $j = 0$: $m_j = 0$. Possible configurations: 1 $^3P_0$

  The total number of configurations is 9.

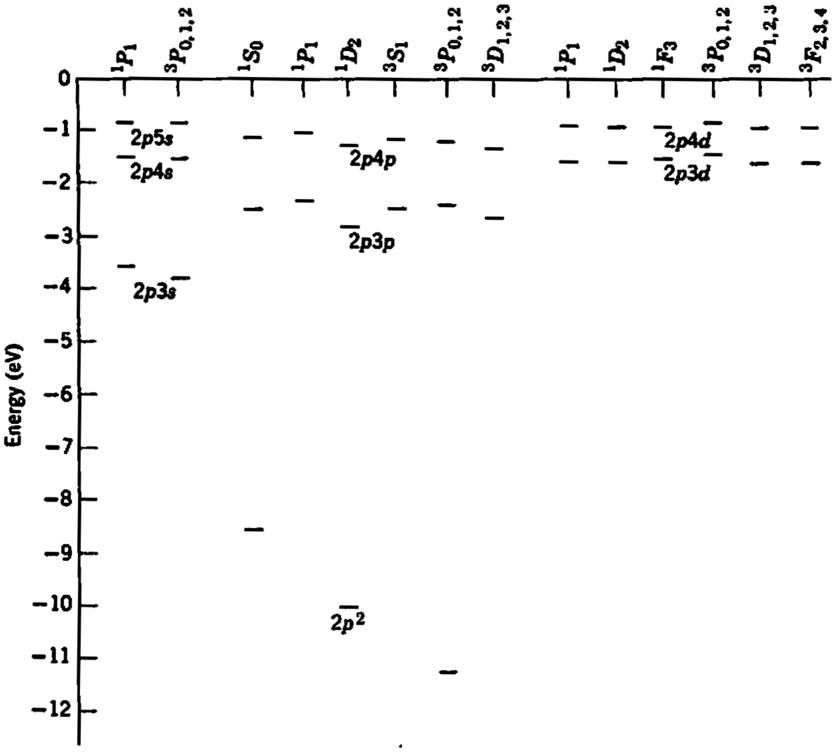
  The $^1P_1$ state is excluded on the basis of the Pauli exclusion principle (the total wavefunction has to be asymmetric and the $^1P_1$ state would be symmetric: an asymmetric spin wavefunction and an asymmetric spatial wavefunction).
- Combining the two previous sets of configurations, we see that we already account for 14 of the 15 configurations. In order to ensure that we account for all states, it is often convenient to convert the table of *m* values to the following summary table:

m_j	#	$^1D_2$	$^3P_{0,1,2}$	Not Assigned
2	2	1	1	0
1	3	1	2	0
0	5	1	3	1
-1	3	1	2	0
-2	2	1	1	0

  Since we are left to assign one state with $m_j = 0$, we conclude that this must be a $j = 0$ state. This state must be a $^1S_0$ state.

We thus conclude that the two *p* electrons can occupy the following states: $^1S_0$, $^3P_{0,1,2}$, and $^1D_2$. In order to make predictions about the energy ranking of these states, we make the following observations:

- Triplet spin states will have a lower energy that singlet spin states. The states with the lowest energies will thus be the $^3P_{0,1,2}$ states.



- States with a larger total orbital angular momentum will have a lower energy. This leads us to conclude the ordering of the $^1S_0$ and the $^1D_2$ spin singlet states in terms of energy is as follows: the $^1D_2$ state has the lowest energy.

The predictions made on the basis of the rules are in good agreement with the observed ordering of levels in the carbon atom, as shown in the Figure above.

For other configurations where one optical electron is promoted to a different sub shell,. The Pauli exclusion principle is satisfied by having the *n* number of the two electrons be different. As a consequence, we observe that there are 10 possible states for a 2*p* 3*p* configuration:

$^3D_{1,2,3}$	excluded for $2p\ 2p$
$^3P_{1,2,3}$	
$^3S_1$	excluded for $2p\ 2p$
$^1D_2$	
$^1P_1$	excluded for $2p\ 2p$
$^1S_0$	

The spectrum of light emitted when optical electrons make transitions indicates that not all possible transitions are allowed. The following transition rules are obeyed in the observed transitions:

1. Transitions involve the change of n and ℓ number of one electron. Transitions between states that require the change in quantum numbers of more than one electron are extremely unlikely to be observed.

2. The change in ℓ of the electron involved in the transition satisfies the following relation: $\Delta\ell = \pm 1$.
3. Changes in $s_{12}, \ell_{12}, j_{12}$ satisfy the following rules:

$$\begin{aligned}
&\Delta s_{12} = 0 && \text{Spin can change, but the probability is very low.}\\
&\Delta \ell_{12} = 0, \pm 1 &&\\
&\Delta j_{12} = 0, \pm 1 && \text{except when } j_{12} = 0 \text{ which requires } \Delta j_{12} = 0
\end{aligned}$$

When an atom is placed in an external magnetic field, its energy levels may be split due to the interaction between the atom's dipole moment and the external magnetic field. This effect was first observed by the Dutchman Pieter Zeeman and is called **the Zeeman effect.** The magnitude of the splitting is proportional to the magnitude of the external magnetic field:

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

The magnetic moment is determine by the properties of the optical electrons:

$$\begin{aligned}
\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S \quad &= -\frac{g_\ell \mu_b}{\hbar}\left\{\vec{L}_1 + \vec{L}_2 + \vec{L}_3 + ...\right\} - \frac{g_s \mu_b}{\hbar}\left\{\vec{S}_1 + \vec{S}_2 + \vec{S}_3 + ...\right\} = \\
&= -\frac{\mu_b}{\hbar}\left\{\vec{L}_1 + \vec{L}_2 + \vec{L}_3 + ...\right\} - \frac{2\mu_b}{\hbar}\left\{\vec{S}_1 + \vec{S}_2 + \vec{S}_3 + ...\right\} = \\
&= -\frac{\mu_b}{\hbar}\left\{\vec{L}_{tot} + 2\vec{S}_{tot}\right\}
\end{aligned}$$

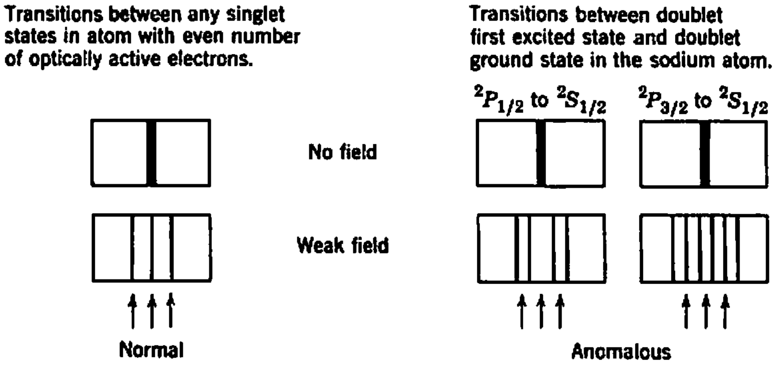
Note that since $\vec{J}_{tot} = \vec{L}_{tot} + \vec{S}_{tot}$ the total angular momentum is not parallel to the magnetic moment.

First consider what happens when $\vec{S}_{tot} = 0$. In this case:

- $\vec{J}_{tot}$ is anti parallel to $\vec{\mu}$.
- The splitting is proportional to $\vec{\mu} \cdot \vec{B}$. If we choose the z axis to be parallel to the magnetic field then $\vec{\mu} \cdot \vec{B}$ can be written as $\mu_z B$. The z component of the magnetic moment is equal to

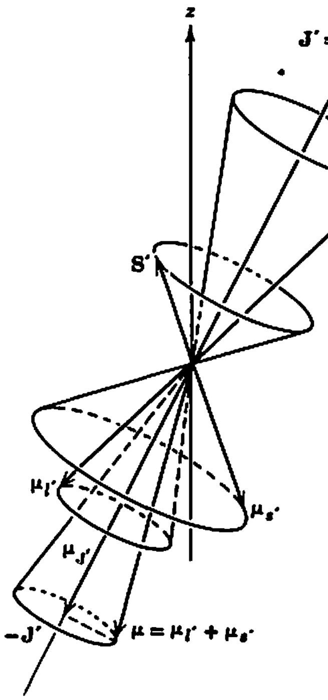
$$\mu_z = -\frac{\mu_b}{\hbar} j_z$$

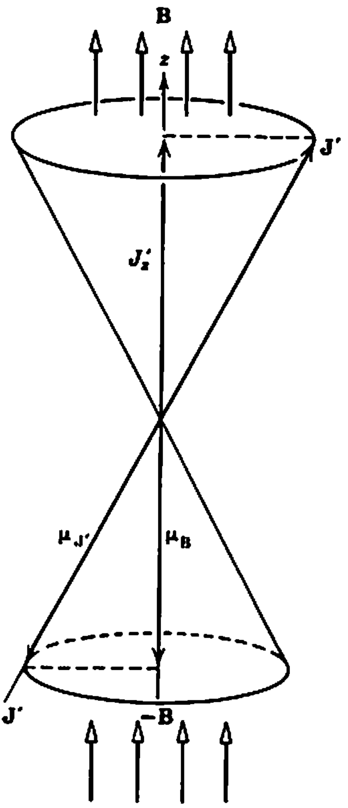
- For a given total angular momentum, there will be (2*j* + 1) different energy shifts. The external magnetic field will thus produce a regular spaced pattern of energy levels.
- The splitting that occurs when the total spin is 0 is called **normal Zeeman splitting** (see Figure below). By counting the number of lines, we can determine the value of *j*. For the example shown in the Figure, *j* = 1.



When the total spin of the optical electrons is not equal to zero the splitting becomes more complex. We note that:

- $\vec{J}$, $\vec{L}$, and $\vec{S}$ lie in one plane.
- $\vec{S}$ will precess due to the spin-orbit coupling. If there is no external field, the total





angular momentum will remain fixed in space, and a precession of the total spin about the total orbital angular momentum must be accompanied by a precession of the total orbital angular momentum. The plane defined by $\vec{J}$, $\vec{L}$, and $\vec{S}$ will thus precess about $\vec{J}$.

- The total magnetic moment lies in the plane defined by $\vec{J}$, $\vec{L}$, and $\vec{S}$ but it is not anti-parallel to $\vec{J}$.
- Due to the precession of $\vec{L}$ and $\vec{S}$ about $\vec{J}$, the magnetic moment will precess about $\vec{J}$.
- The energy shift due to the external field depends on $-\vec{\mu}\cdot\vec{B} = -\mu_B B$. The energy shift is complicated since the magnetic moment precesses about $\vec{J}$ and $\vec{J}$ precesses about $\vec{B}$. N general, the internal magnetic field is very much larger than the external magnetic field, and as consequence, the precession rate of the magnetic moment about $\vec{J}$ will be much higher than the precession rate of $\vec{J}$ about $\vec{B}$. The precession rate of $\vec{J}$ about $\vec{B}$ of depends on the projection of the magnetic moment onto $\vec{J}$. This projection is equal to

$$\begin{aligned}\mu_J &= \frac{\vec{\mu}\cdot\vec{J}}{J} = -\frac{\mu_b}{\hbar}\frac{\left(\vec{L}+2\vec{S}\right)\cdot\left(\vec{L}+\vec{S}\right)}{J} = -\frac{\mu_b}{\hbar}\frac{L^2+2S^2+3\vec{L}\cdot\vec{S}}{J} = \\ &= -\frac{\mu_b}{\hbar}\frac{L^2+2S^2+3\frac{\left(J^2-L^2-S^2\right)}{2}}{J} = -\frac{\mu_b}{\hbar}\frac{2L^2+4S^2+3\left(J^2-L^2-S^2\right)}{2J} = \\ &= -\frac{\mu_b}{\hbar}\frac{3J^2+S^2-L^2}{2J}\end{aligned}$$

The component of this magnetic moment parallel to the z axis will define the energy shift associated with the external magnetic field. The component of μ_J along the magnetic field is equal to

$$\mu_B = \mu_J\frac{\vec{J}\cdot\vec{B}}{JB} = \mu_J\frac{J_z}{J} = -\frac{\mu_b}{\hbar}\frac{3J^2+S^2-L^2}{2J^2}J_z$$

The resulting energy shift is equal to

$$\Delta E = -\vec{\mu}\cdot\vec{B} = -\mu_B B = \frac{\mu_b B}{\hbar}\frac{3J^2+S^2-L^2}{2J^2}J_z = \mu_b B g m_j$$

where

$$g = \frac{3j(j+1)+s(s+1)-\ell(\ell+1)}{2j(j+1)} = 1 + \frac{j(j+1)+s(s+1)-\ell(\ell+1)}{2j(j+1)}$$

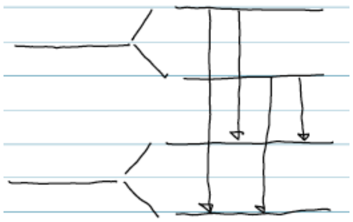
The factor g is called the **Lande factor**.

- Different levels will have different Lande factors and the splitting of different levels will thus be different.

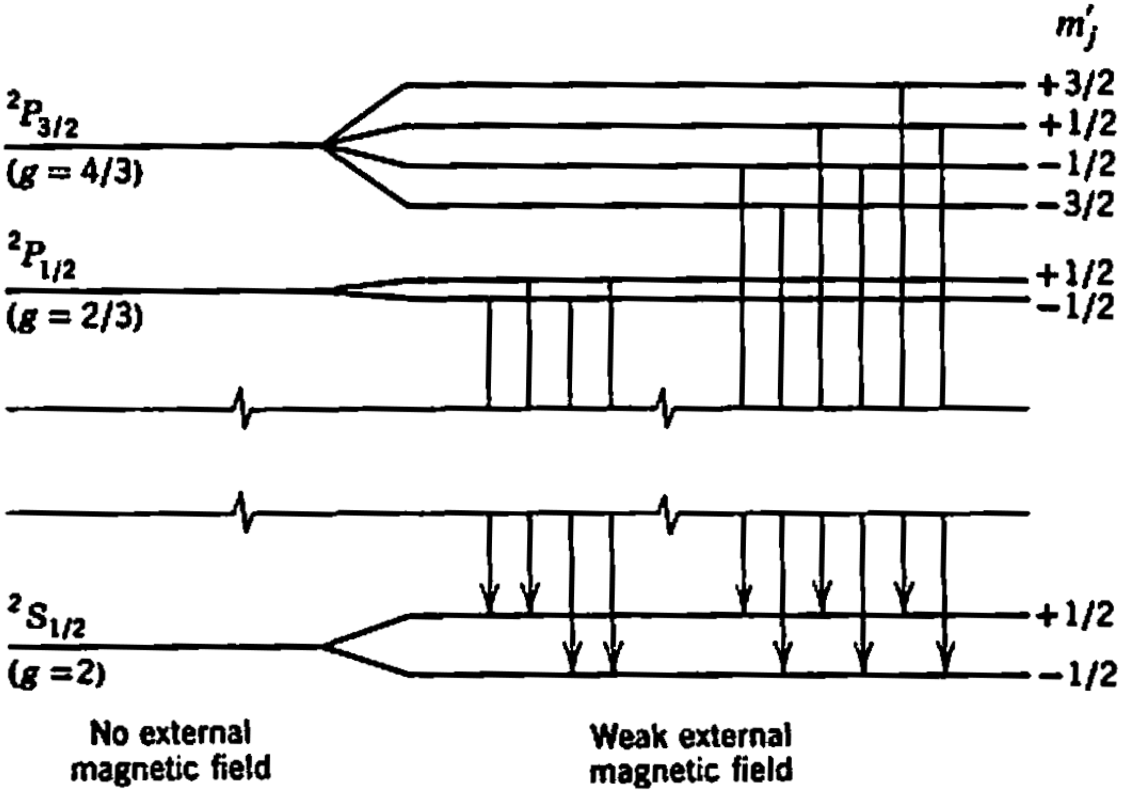
Transitions are allowed when

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

However, if $\Delta j = 0$, transitions from $m_j = 0$ to $m_j = 0$ are not allowed. Since the splitting depends on m_j, the transitions are sensitive to j. Consider the following examples:



- $j = 1/2$ to $j = 1/2$.
  Each level splits in two: $m_j = ½$ and $m_j = -½$. Applying the selection rule that $\Delta m_j = 0, \pm 1$ we recognize that there are 4 possible transitions.
- $j = 3/2$ to $j = 1/2$. The upper level splits into 4 levels; the bottom level splits into 2 levels. However, due to the selection rule $\Delta m_j = 0, \pm 1$, not all transitions will occur. For



example, a transition from *mj* = 3/2 to *mj* = -1/2 is not allowed. The total number of transitions in this case is 6.