Zeeman Effect

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Zeeman Effect

- First reported by Zeeman in 1896. Interpreted by Lorentz.
- Splitting of spectral lines into a number of components in the presence of magnetic field is called Zeeman effect.
- The extent of splitting depends on the strength of magnetic field and nature of spectral lines, whether singlet or multiplets.
- Types of Zeeman effect
  - Normal Zeeman effect
  - Anomalous Zeeman effect

The splitting of spectral lines in a strong magnetic field indicates that the energy of an electron is slightly modified when the atom is immersed in a magnetic field.

- Interaction between atoms and field can be classified into two regimes:

  Weak fields: *Zeeman effect*, either *normal* or *anomalous.*

  Strong fields: *Paschen-Back effect.*

  Normal Zeeman effect agrees with the classical theory of Lorentz.

  Anomalous effect depends on electron spin, and is purely quantum mechanical.

Normal Zeeman effect

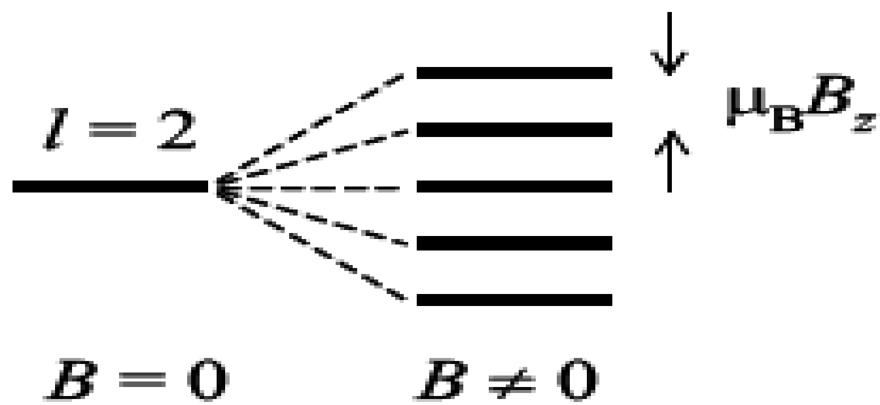
- Observed in atoms with no spin.
- Total spin of an *N*-electron atom is $\hat{S} = \sum_{i=1}^{N} \hat{s}_i$
- Filled shells have no net spin, so only consider valence electrons. Since electrons have spin 1/2, not possible to obtain $S = 0$ from atoms with odd number of valence electrons.
- Even number of electrons can produce $S = 0$ state (e.g., for two valence electrons, $S = 0$ or 1).
- All ground states of Group II (divalent atoms) have ns^2 configurations => always have $S = 0$ as two electrons align with their spins antiparallel.
- Magnetic moment of an atom with *no spin* will be due entirely to *orbital* motion:

$$\hat{\mu} = -\frac{\mu_B}{\hbar}\hat{L}$$

- Interaction energy between magnetic moment and a uniform magnetic field is: $$\Delta E = -\hat{\mu}\cdot\hat{B}$$
- Assume *B* is only in the *z*-direction: $$\hat{B} = \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix}$$
- The interaction energy of the atom is therefore,

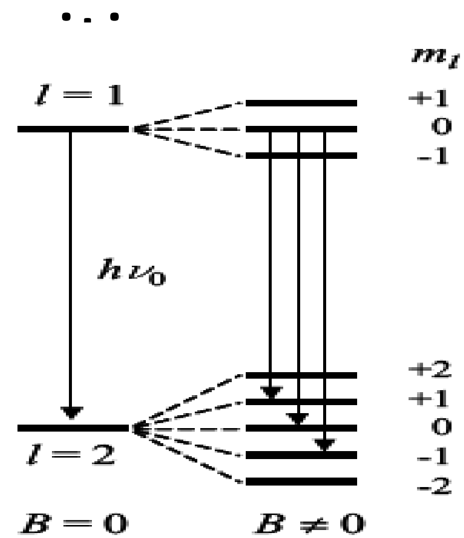
$$\Delta E = -\mu_z B_z = \mu_B B_z m_l$$

where m_l is the orbital magnetic quantum number. This equation implies that *B* splits the degeneracy of the m_l states evenly.



- selections rules for m_l: $\Delta m_l = 0, \pm 1$.

Consider transitions between two Zeeman-split atomic levels. Allowed tran



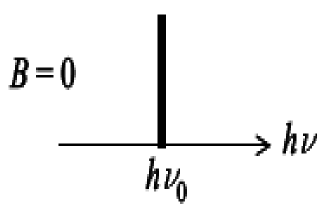
frequencies are therefore,

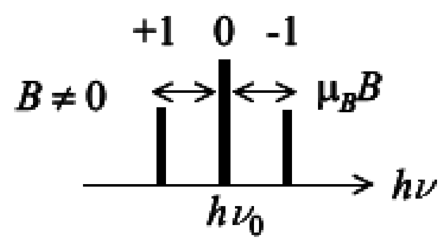
$$h\nu = h\nu_0 + \mu_B B_z \qquad \Delta m_l = -1$$

$$h\nu = h\nu_0 \qquad \Delta m_l = 0$$

$$h\nu = h\nu_0 - \mu_B B_z \qquad \Delta m_l = +1$$

Emitted photons also have a polarization, depending on which transition they result from.





- *Longitudinal Zeeman effect:* Observing along magnetic field, photons must propagate in *z*-direction.
  - Light waves are transverse, and so only *x* and *y* polarizations are possible.
  - The *z*-component ($\Delta m_l = 0$) is therefore absent and only observe $\Delta m_l = \pm 1$.
  - Termed σ-components and are circularly polarized.
- *Transverse Zeeman effect:* When observed at right angles to the field, all three lines are present.
  - $\Delta m_l = 0$ are linearly polarized || to the field.
  - $\Delta m_l = \pm 1$ transitions are linearly polarized at right angles to field.

- Last two columns of table below polarizations

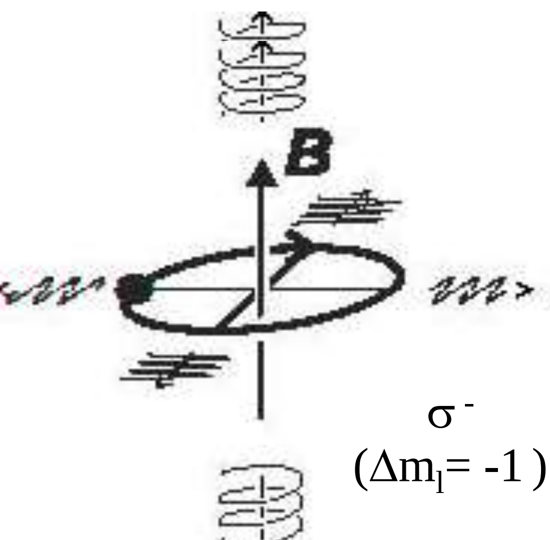
  observed in the longitudinal

  and transverse directions.

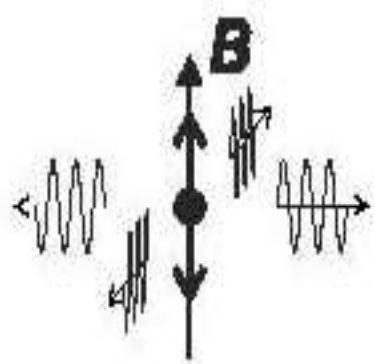
Δm_l	Energy	Polarization	
		Longitudinal observation	Transverse observation
+1	$h\nu_0 - \mu_B B$	σ^+	$\mathcal{E} \perp B$
0	$h\nu_0$	not observed	$\mathcal{E} \parallel B$
−1	$h\nu_0 + \mu_B B$	σ^-	$\mathcal{E} \perp B$

The direction of circular polarization in the longitudinal observations is defined relative to *B.*

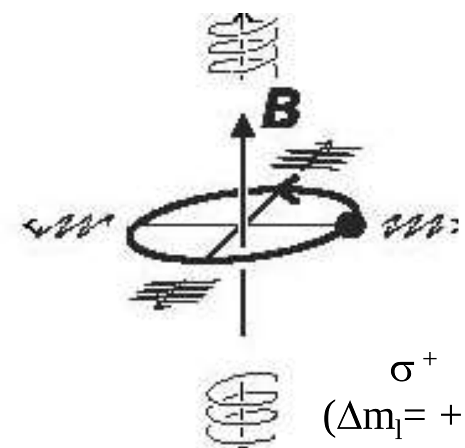
Interpretation proposed by Lorentz (1896)



σ^-
($\Delta m_l = -1$)

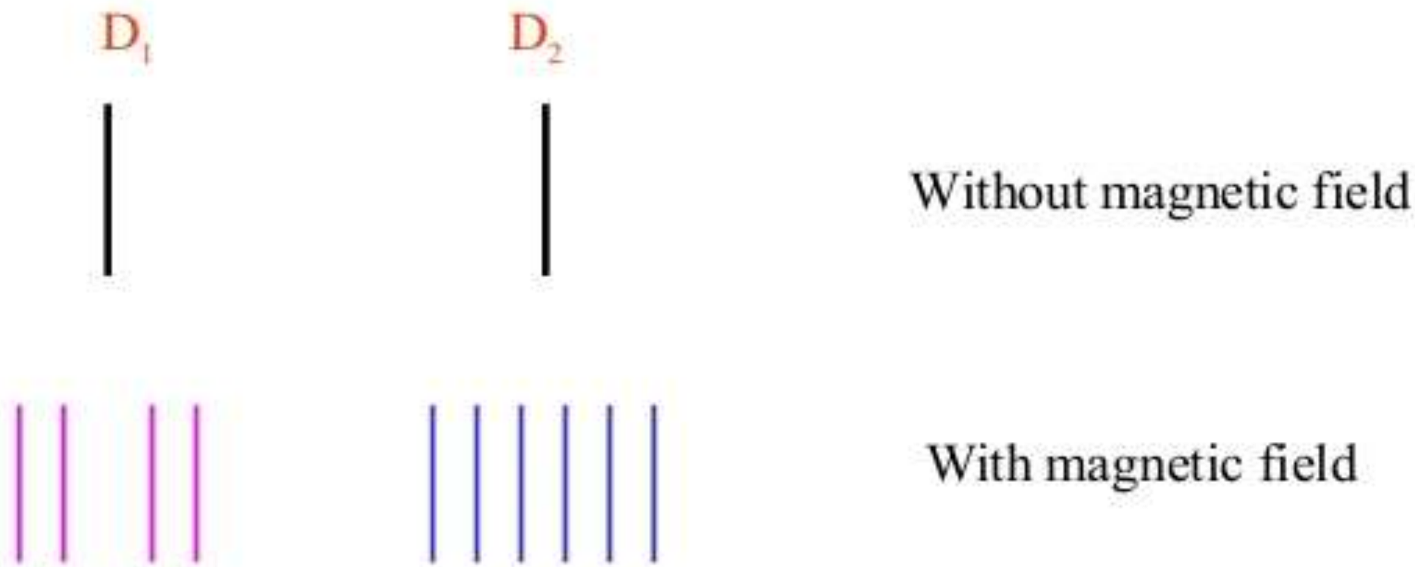


π ($\Delta m_l = 0$)



σ^+
($\Delta m_l = +1$)

The anomalous Zeeman effect



The D lines of sodium. The D_1 line splits into four components, the D_2 line into six in a magnetic field. The wavelengths of the D_1 and D_2 lines are 5896 and 5889 nm; the quantum energy increases to the right in the diagram.

In general case, the atomic magnetism is due to the superposition of spin and orbital magnetism, which results the anomalous Zeeman effect.

In cases of the anomalous Zeeman effect, the two terms involved in the optical transition have different g factors, because the relative contributions of spin and orbital magnetism to the two states are different. The g factors are determined by the total angular momentum j and are therefore called g_j factors. The splitting of the terms in the ground and excited states is therefore different, in contrast to the situation in the normal Zeeman effect.

The magnetic moments in the direction of the field are

$$(\mu_j)_{j,z} = -m_j g_j \mu_B$$

The magnetic energy is

$$V_{m_j} = -(\mu_j)_{j,z} B_0$$

The number of splitting components in the field is given by m_j and is again 2j+1. The distance between the components with different values of m_j – is-called Zeeman components – is no longer the same for all terms, but depends on the quantum numbers *l*, *s*, and *j*:

$$\Delta E_{m_j, m_{j-1}} = g_j \mu_B B_0$$

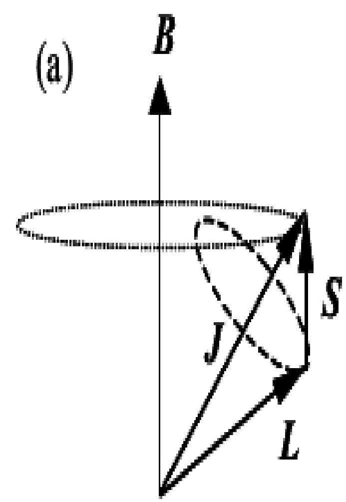
Anomalous Zeeman Effect

Discovered by Thomas Preston in Dublin in 1897.

Occurs in atoms with non-zero spin => atoms with odd number of electrons.

In *LS*-coupling, the spin-orbit interaction couples the spin and orbital angular momenta to give a total angular momentum according to

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



In an applied *B*-field, *J* precesses about *B* at the Larmor frequency.

L and *S* precess more rapidly about *J* to due to spin-orbit interaction. Spin-orbit effect therefore stronger.

- Interaction energy of atom is equal to sum of interactions of spin and orbital magnetic moments with *B*-field:

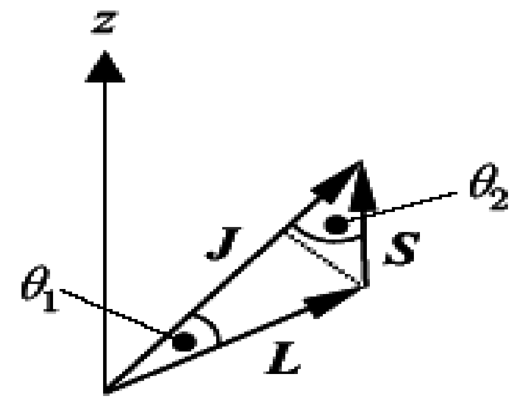
$$\Delta E = -\mu_z B_z$$
$$= -(\mu_z^{orbital} + \mu_z^{spin}) B_z$$
$$= \rangle \hat{L}_z + g_s \hat{S}_z \langle \frac{\mu_B}{\hbar} B_z$$

where $g_s = 2$, and the < … > is the expectation value. The normal Zeeman effect is obtained by setting $\hat{S}_z = 0$ and $\hat{L}_z = m_l \hbar$.

In the case of precessing atomic magnetic in figure on last slide, neither S_z nor L_z are constant. Only is well defined. $\hat{J}_z = m_j \hbar$

- Must therefore project *L* and *S* onto *J* and project onto *z*-axis =>

$$\hat{\mu} = -\Big\rangle |\hat{L}|\cos\theta_1 \frac{\hat{J}}{|\hat{J}|} + 2|\hat{S}|\cos\theta_2 \frac{\hat{J}}{|\hat{J}|}\Big\langle \frac{\mu_B}{\hbar}$$



The angles θ_1 and θ_2 can be calculated from the scalar products of the respective vectors:

$$\hat{L}\cdot\hat{J} = |L||J|\cos\theta_1$$

$$\hat{S}\cdot\hat{J} = |S||J|\cos\theta_2$$

which implies that

$$\hat{\mu} = -\Big\rangle \frac{\hat{L}\cdot\hat{J}}{|\hat{J}|^2} + 2\frac{\hat{S}\cdot\hat{J}}{|\hat{J}|^2}\Big\langle \frac{\mu_B}{\hbar}\hat{J} \qquad (1)$$

Now, using $\hat{S} = \hat{J} - \hat{L}$ implies that $\hat{S}\cdot\hat{S} = (\hat{J}-\hat{L})\cdot(\hat{J}-\hat{L}) = \hat{J}\cdot\hat{J} + \hat{L}\cdot\hat{L} - 2\hat{L}\cdot\hat{J}$

Therefore $\hat{L}\cdot\hat{J} = (\hat{J}\cdot\hat{J} + \hat{L}\cdot\hat{L} - \hat{S}\cdot\hat{S})/2$

- So that $$\left\rangle \frac{\hat{L}\cdot\hat{J}}{|\hat{J}|^2} \right\langle = \frac{\left[j(j+1)+l(l+1)-s(s+1)\right]\hbar^2/2}{j(j+1)\hbar^2}$$
$$= \frac{\left[j(j+1)+l(l+1)-s(s+1)\right]}{2j(j+1)}$$

Similarly, $\hat{S}\cdot\hat{J} = (\hat{J}\cdot\hat{J}+\hat{S}\cdot\hat{S}-\hat{L}\cdot\hat{L})/2$ and

$$\left\rangle \frac{\hat{S}\cdot\hat{J}}{|\hat{J}|^2} \right\langle = \frac{\left[j(j+1)+s(s+1)-l(l+1)\right]}{2j(j+1)}$$

We can therefore write Eqn. 1 as

$$\hat{\mu} = -\left(\frac{\left[j(j+1)+l(l+1)-s(s+1)\right]}{2j(j+1)} - 2\frac{\left[j(j+1)+s(s+1)-l(l+1)\right]}{2j(j+1)}\right)\frac{\mu_B}{\hbar}\hat{J}$$

This can be written in the form $\hat{\mu} = -g_j \frac{\mu_B}{\hbar}\hat{J}$

- where g_J is the *Lande g-factor* given by

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

This implies that $\mu_z = -g_j \mu_B m_j$

and hence the interaction energy with the *B*-field is

$$\Delta E = -\mu_z B_z = g_j \mu_B B_z m_j$$

Classical theory predicts that $g_j = 1$. Departure from this due to spin in quantum picture.

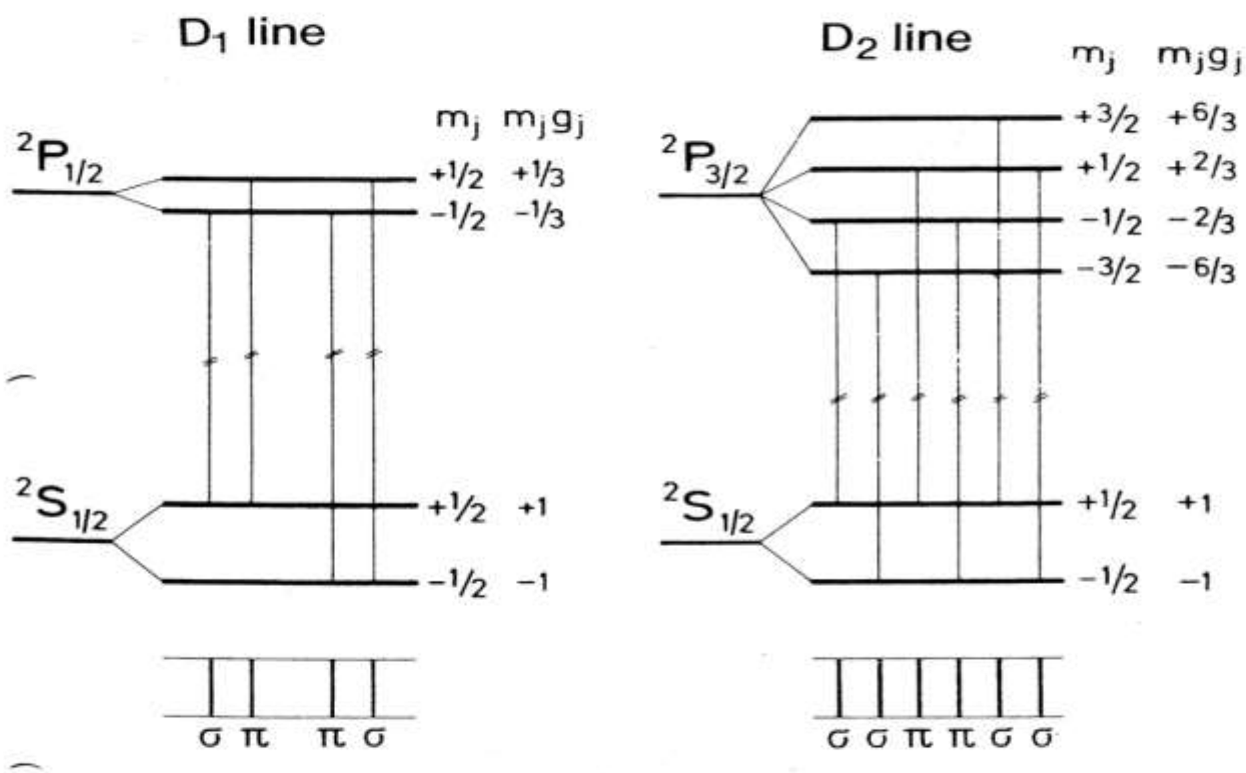
Spectra can be understood by applying the selection rules for *J* and m_j:

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

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

- Polarizations of the transitions follow the same patterns as for normal Zeeman effect.

- For example, consider the Na D-lines at right produced by $3p \rightarrow 3s$ transition.



COUPLING SCHEMES

LS coupling (Russell-Saunders coupling)

If the spin-orbit interactions $(\boldsymbol{s}_i \cdot \boldsymbol{l}_i)$ between the spin and orbital angular momenta of the individual electrons i are smaller than the mutual interactions of the orbital or spin angular momenta of different electrons coupling $(\boldsymbol{l}_i \cdot \boldsymbol{l}_j)$ or $(\boldsymbol{s}_i \cdot \boldsymbol{s}_j)$, the orbital angular momenta $\boldsymbol{l}_i$ combine to a total orbital angular momentum $\boldsymbol{L}$, and the spins combine to a total spin $\boldsymbol{S}$. $\boldsymbol{L}$ couples with $\boldsymbol{S}$ to form the total angular momentum $\boldsymbol{J}$.

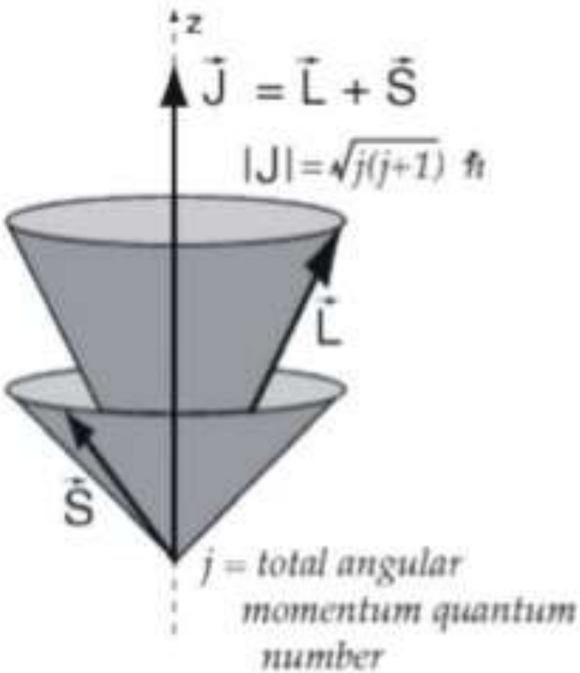
$$\vec{L} = \sum_i \vec{l}_i,$$

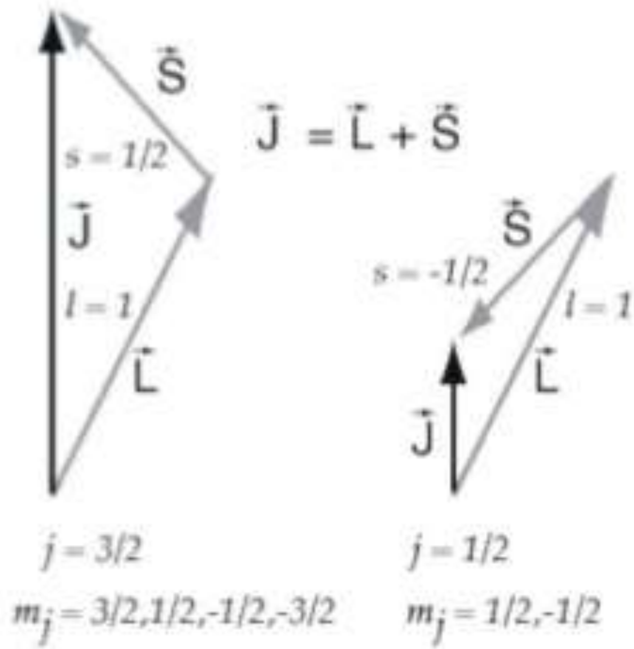
$$\vec{S} = \sum_i \vec{s}_i,$$

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

LS coupling gives a good agreement with the observed spectral details for many light atoms. For heavier atoms, another coupling scheme called j-j coupling provides better agreement with experiment.

The vector model:





For example for a two-electron system like the He atom

The orbital angular momentum L of the atom:

$$\vec{L} = \vec{l}_1 + \vec{l}_2, \qquad \left|\vec{L}\right| = \sqrt{L(L+1)}\hbar$$

$$L = l_1 + l_2, l_1 + l_2 - 1, \cdots, l_1 - l_2$$

The quantum number L determines the term characteristics:
L = 0, 1, 2, … indicates S, P, D, … terms.

It should be noted here that a term with L = 1 is called a P term but this does not necessarily mean that in this configuration one of the electrons is individually in a p state.

For the total spin angular momentum S:

$$\vec{S} = \vec{s}_1 + \vec{s}_2 \qquad with \qquad \left|\vec{S}\right| = \sqrt{S(S+1)}\,\hbar$$

The spin quantum number:
S = ½ + ½ = 1   or   S = ½ - ½ = 0

The interaction between ***S*** and the magnetic field $\boldsymbol{B_L}$, which arises from the total orbital angular momentum ***L***, results in a coupling of the two angular momenta ***L*** and ***S*** to the total angular momentum ***J***:

$$\vec{J} = \vec{L} + \vec{S}, \qquad \left|\vec{J}\right| = \sqrt{J(J+1)}\,\hbar$$

The quantum number J:
For S = 0, J = L;   singlet;
For S = 1, J = L +1, L, L – 1   triplet

jj coupling

jj coupling is the case for coupling of electron spin and orbital angular momenta is larger compared to the interactions ($\boldsymbol{l}_i \cdot \boldsymbol{l}_j$) and ($\boldsymbol{s}_i \cdot \boldsymbol{s}_j$) between different electrons. It occurs mostly in heavy atoms, because the spin-orbit coupling for each individual electron increases rapidly with the nuclear charge Z.

$$\vec{j}_1 = \vec{l}_1 + \vec{s}_1;$$

$$\vec{j}_2 = \vec{l}_2 + \vec{s}_2;$$

$$\cdots$$

$$\vec{J} = \sum \vec{j}_i \qquad with \left|\vec{J}\right| = \sqrt{J(J+1)}\hbar$$

In jj coupling, a resultant orbital angular momentum L is not defined. There are therefore no term symbols S, P, D, etc. one has to use the term notation (j_1, j_2) etc..

The number of possible states and the J values are the same as in LS coupling.

A selection rule for optical transitions:
$\Delta J = 0, \pm 1$, and a transition from J = 0 to J = 0 is forbidden.

Purely jj coupling is only found in very heavy atoms. In most cases there are intermediate forms of coupling (intermediary coupling), which the intercombination between terms of different multiplicity is not so strictly forbidden.

THANKS