Chapter 2

1. Russell-Saunders or *LS* coupling

The central field approximation, in which all the electrons are reckoned to move in a common spherically-symmetric field. The rest of their repulsion, the part which is not spherically symmetric, is called the residual electrostatic interaction. It is easy to write down the mathematical form of this residual electrostatic interaction. The precise complete Hamiltonian for the atom is:

$$H = \sum_i \left(\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \qquad \text{.....(1)}$$

while the approximate Hamiltonian used in the central field approximation was:

$$H_{\text{central}} = \sum_i \left(\frac{\mathbf{p}_i^2}{2m} + V(r_i) \right) \qquad \text{......(2)}$$

Therefore the residual electrostatic interaction is:

$$H_{\text{re}} = H - H_{\text{central}} = \sum_i \left(-\frac{Ze^2}{4\pi\epsilon_0 r_i} - V(r_i) \right) + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \qquad \text{.....(3)}$$

The upshot is that the quantum numbers on which the energy of the whole atom depends are now n_i; l_i; L; S, and this whole method of approximation is called *LS coupling* or Russell-Saunders coupling. The things which are coupled in this coupling are:

1. All the individual orbital angular momenta couple together to make $^\wedge$L.
2. All the individual spin angular momenta couple together to make $^\wedge$S.

2. Fine structure for many electrons

The central field approximation is the correct starting point for all atoms, and after that it have both the residual electrostatic interaction and the spin-orbit interaction:

$$H = H_{cf} + H_{re} + H_{so}$$ ……(4)

$$H_{so} = \sum_i \eta_i \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i .$$ …..(5)

r-dependence into η_i

There are three cases to consider:

$$\begin{array}{ll} \langle H_{re} \rangle \gg \langle H_{so} \rangle & \rightarrow LS \text{ coupling.} \\ \langle H_{re} \rangle \ll \langle H_{so} \rangle & \rightarrow jj \text{ coupling.} \\ \langle H_{re} \rangle \simeq \langle H_{so} \rangle & \rightarrow \text{no simple coupling scheme.} \end{array}$$

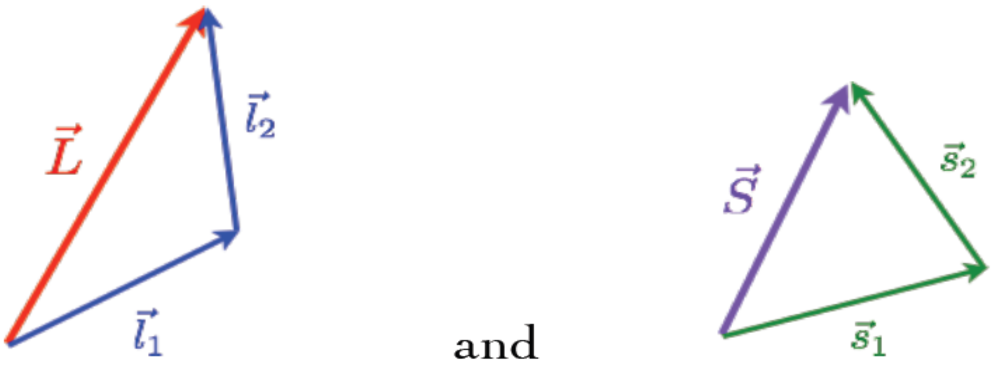
$$\vec{J} = \vec{L} + \vec{S}$$ ……(6)

Where:

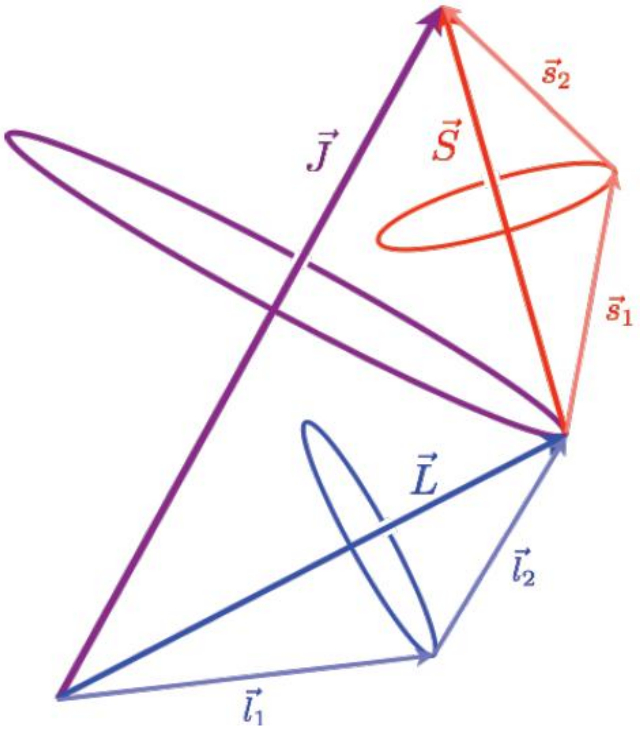
$$\begin{array}{l} \vec{L} = \sum_i \vec{l}_i \\ \vec{S} = \sum_i \vec{s}_i \end{array}$$ …….(7)

- $H_{\text{res}} > H_{\text{SO}}$

In this case, the interaction between the electrons is stronger than the spin-orbit interaction in each of them. example with a 2-electron atom:



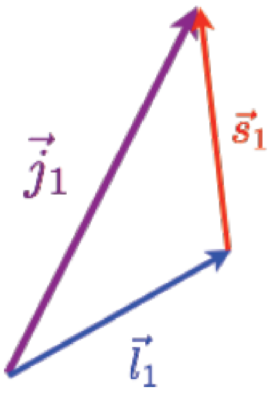
Then, *L* and *S* couple to a total *J*.



This situation is called "*LS*-coupling"

- $H_{\mathrm{SO}} > H_{\mathrm{res}}$

In this case, the individual coupling between the electrons, via the spin-orbit interaction, is stronger than the electrostatic interaction between them. example with a 2-electron atom:



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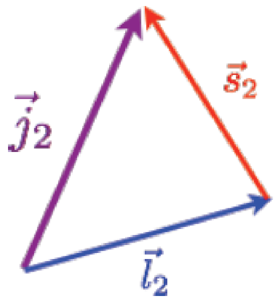
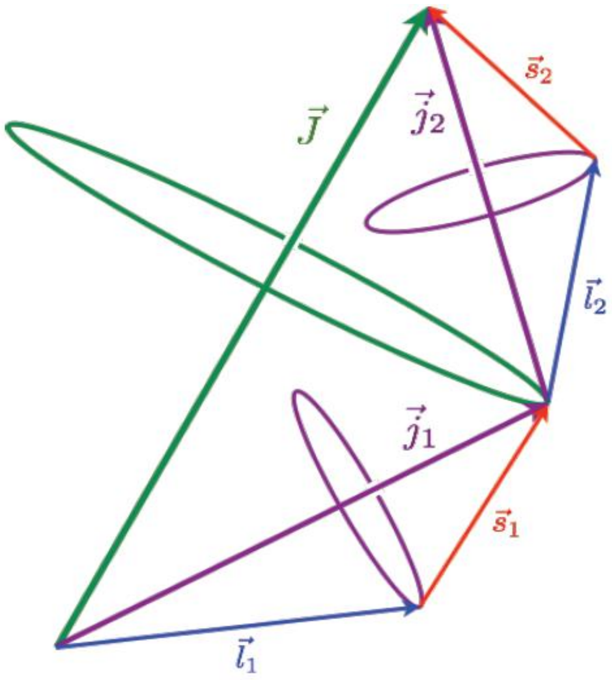


Then, j_1 and j_2 couple to a total J.



This situation is called “*jj*-coupling”.

For a filled shell :

$$M_S = \sum_i m_{s_i} \text{ and } M_L = \sum_i m_{l_i}$$

$$L = S = 0$$

Degenerescence in M_L and M_S

- (2L + 1)(2S + 1) degenerate states.

❖ "Landé's interval rule"

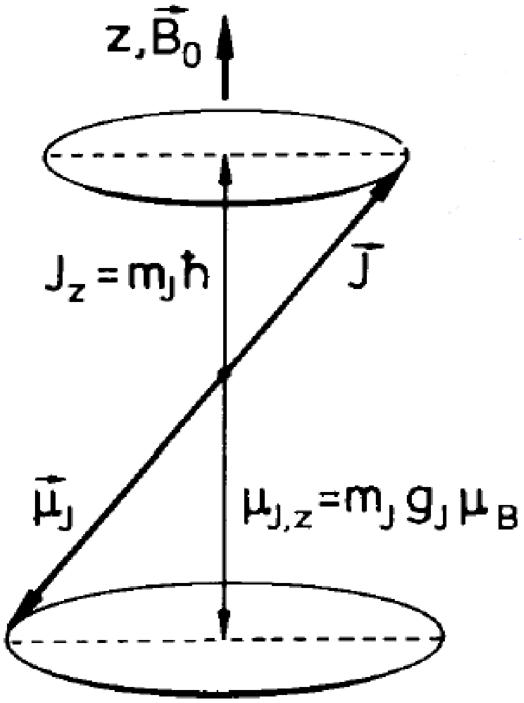
This rule cam be used as a test of how well system can be described by LS-coupling.

3. Zeeman Effect

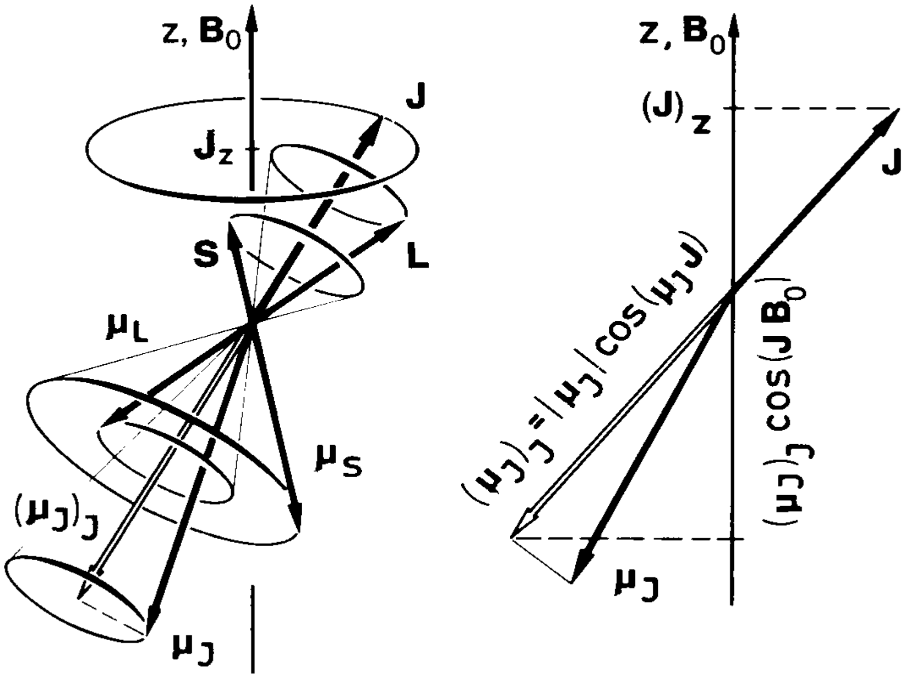
The Zeeman effect is the name given to the splitting observed in spectral lines when the source of those lines is placed in an external magnetic field. Splitting of a single spectral line into three components in the presence of an external magnetic field is called the normal Zeeman effect. Any time the *g*-values of the upper and lower states are the same, this pattern results. When the *g*-values are different, much more complicated patterns are possible. These, for historical reasons, are called the anomalous Zeeman effect.

g is the Land´e *g*-value defined as:

$$g \equiv 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad \text{……(8)}$$

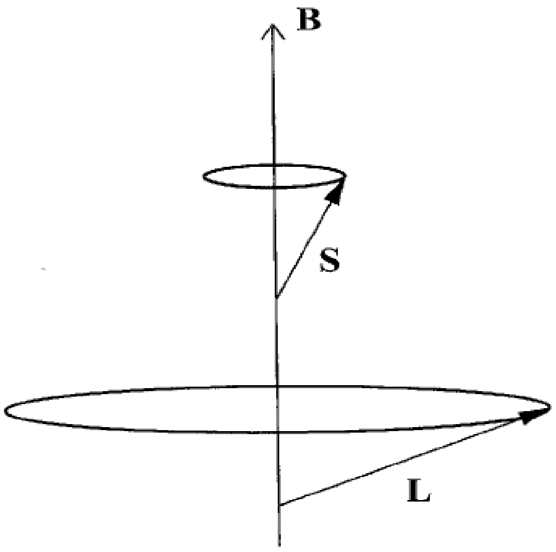


Normal Zeeman effect



Anomalous Zeeman effect: spin orbit coupling

When the applied field is very strong, the coupling between L and S may be broken in favour of their direct coupling to the magnetic field. The individual angular momenta, and therefore their magnetic moments, now precess independently about the field direction . As the electromagnetic field couples to the spatial distribution of the electrons (recall the form of the transition dipole moment), not to the magnetic moment due to the spin, the presence of the spin now makes no difference to the energies of the transitions. As a result, the anomalous Zeeman effect gives way to the normal Zeeman effect. This switch from the anomalous effect to the normal effect is called the Paschen–Back effect.



The Paschen-Back effect