Total Angular Momentum

First we're going to discuss single electron atoms.

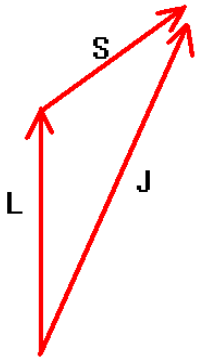
For an atom with L and S, the total angular momentum J is given by

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

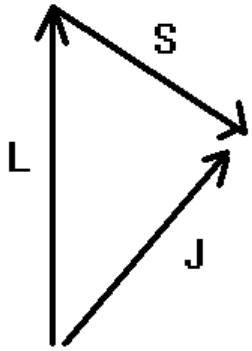
The eigenvalues of the angular momentum are given by:

$$J = \sqrt{j(j+1)}\hbar; J_z = m_j\hbar$$

The j quantum number can be obtained by looking at vector diagrams:



$$j = \ell + s = 1 + \tfrac{1}{2} = \tfrac{3}{2}$$



$$j = \ell - s = 1 - \tfrac{1}{2} = \tfrac{1}{2}$$

These are shown for an ℓ value of 1.

The common notation used to designate these states is:

$$nL_j$$

n=principle quantum number

L = (S,P,D,...)=orbital angular momentum

j=total angular momentum quantum number.

Now let's look at many electron atoms. The electrons fill the shells of the atoms according to Hund's rules:

(1) The total spin angular momentum S should be maximized to the extent possible without violating the Pauli exclusion principle

(2) So long as you don't violate rule 1, L should also be maximized.

In this discussion, your author considers shells with only 2 electrons outside a closed shell, which we will do also.

As an example of application of Hund's rules: the first 5 electrons to occupy a d subshell should all have the same value of m_s. Remember a d shell has $\ell = 2 \Rightarrow m_\ell = \{-2,-1,0,1,2\}$

(s:0,p:1,d:2,...)

By rule 2 the electrons will go into the state with the same m_s. This would serve to "align" the spins so that S total is maximized. These electrons will then have

$$m_\ell = 2, m_\ell = 1 \text{ or } m_\ell = -2, m_\ell = -1$$

in order to maximize L.

Now the interactions become more complicated. Each electron has spin-orbit interaction. In addition there is a Coulomb interaction between the two electrons. However, this

Coulomb interaction, when calculated, does not necessarily take into account the identical nature of the electrons which results in a lowering of this interaction energy known as the exchange interaction. Additionally, there are additional electron-electron interactions arising from spins and the orbital angular momentum on one electron from the other. As you might imagine, this interaction also needs to take into account the identical nature of the electrons which gives rise to a second form of the exchange interaction. I guess if you count all these interactions up, you've got something like this:

Coulomb Interaction: $3:\text{protons} \Leftrightarrow \text{electron}_1 : \text{protons} \Leftrightarrow \text{electron}_2 : \text{electron}_1 \Leftrightarrow \text{electron}_2$

Spin orbit interaction: $2:\ \text{protons} \Leftrightarrow \text{electron}_1 : \text{protons} \Leftrightarrow \text{electrons}_2$

electron response to spin orbit of other electron:

$2:\text{electron}_1 \Leftrightarrow [\text{electron}_2 \Leftrightarrow \text{Pr otons}] : \text{electron}_2 \Leftrightarrow [\text{electron}_1 \Leftrightarrow \text{Pr otons}]$

Electron response to spin of other electron: $2:\text{electron}_1 \Leftrightarrow \text{electron}_2 : \text{electron}_2 \Leftrightarrow \text{electron}_1$

Of course, you'd imagine that the proton responds to the electronic magnetic moments. It does. We won't worry about that now.

There are also at least 3 exchange interactions and additionally the proton interactions will need to be modified because of this also.

Finally the protons in the nucleus have spin and thus this produces a magnetic moment to which the electrons must respond.

It's a pretty complicated picture all in all. We'll work with only the most significant of these interactions.

For our 2 electron system, we label the electrons as 1 and 2, so that we have:

L_1S_1 and L_2S_2

Of course, you know that ultimately we can't label the electrons so don't be surprised when a correction is necessary to take this into account (it's that exchange interaction again).

The total angular momentum is going to be given by:

$$\vec{J} = \vec{L}_1 + \vec{L}_2 + \vec{S}_1 + \vec{S}_2$$

There are two schemes called LS coupling and jj coupling for combining the four angular momenta to form J. The decision of which scheme to use depends on relative strengths of the various interactions. jj coupling predominates for heavier elements.

LS or Russell Saunders Coupling

Used for most atoms when the magnetic field is weak.

The LS coupling says that the angular momenta combine and the spin momenta combine:

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

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

The total angular momentum is then:

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

One of Hund's rules states that the electron spins combine to make S a maximum. This occurs because of the mutual repulsion of the electrons, which want to be as far away from each other as possible in order to have the lowest possible energy ... except for those funny situations where they want to be close to each other and form pairs (not within single atoms).

If the two electrons in the same subshell have the same m_s then they must have different m_L states. The lowest energy states normally occur with the maximum L. It is the aligned direction that keeps the electrons as far away from the nucleus as possible. If the angular momenta where misaligned, they would pass each other more often thus resulting in a higher interaction energy.

For the case of two electrons the total spin angular momentum quantum number may be S=0 or S=1 depending upon whether the electrons are parallel or antiparallel.

Consider two electrons: one is in the 4p subshell while the other is in the 4d subshell.

We have the following possibilities for L and S:

$$\{S_1 = \tfrac{1}{2}, S_2 = \tfrac{1}{2}, L_1 = 1, L_2 = 2\}$$

The singlet states will be when S=0. This then means that the spins are antialigned. For this state, however, we have several possible values for L:

L=1, L=2 and L=3

For a given value of L there are 2S+1 values of J, because J goes from L-S to L+S (for L>S).

For L<S there are fewer than 2S+1 possible values of J. The value of 2S+1 is called the multiplicity of the state.

The notation for 2 electron atoms becomes:

$$n^{2S+1}L_J$$

For two electrons, we have singlet states (S=0) and triplet states (S=1) which refer to the multiplicity 2S+1.

We can construct the following table:

S	L	J	Symbol
0 (singlet)	1	1	4^1P_1
	2	2	4^1D_2
	3	3	4^1F_3
1 (triplet)	1	2	4^3P_2
	1	1	4^3P_1
	1	0	4^3P_0
1 (triplet)	2	3	4^3D_3
	2	2	4^3D_2
	2	1	4^3D_1
1 (triplet)	3	4	4^3F_4
	3	3	4^3F_3
	3	2	4^3F_2

Anomalous Zeeman Effect

We have earlier discussed the normal Zeeman Effect which shows the splitting of the spectral line into 3 components in the presence of an external magnetic field. (remember, that's the theory, but not what Stern Gerlach observed for the reason that they had an L=0 state). It was soon observed that often more than the 3 closely spaced optical lines could be observed. This is called the anomalous Zeeman effect. It can now be explained.

The interaction that splits the energy levels in an external magnetic filed B_{ext} is still caused by the $\vec{\mu} \bullet \vec{B}$ interaction. However, the magnetic moment is due not only to the orbital contribution μ_ℓ, but it must also depend upon the spin magnetic moment $\vec{\mu}_s$ as well. The 2J+1 degeneracy (due to m_J) for a given total angular momentum state J is removed by the effect of the external magnetic field. If the external magnetic field B_{ext} is small in comparison with the internal magnetic field, the L and S precess about J while J precesses slowly about B_{ext}. The total magnetic moment is given by:

$$\vec{\mu} = \vec{\mu}_\ell + \vec{\mu}_s = -\frac{e}{2m}\vec{L} - \frac{e}{m}\vec{S}$$

You can find the average magnetic moment about J and then interact this average moment with B to find the interaction energy:

$$V = \frac{e\hbar B_{ext}}{2m} g m_J = \mu_B B_{ext} g m_J$$

g here is the Lande g factor:

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

The total magnetic angular momentum numbers m_J range from –J to J in integral steps. The external B field splits each J into 2J+1 equally spaced levels separated by V (above). Finally for photon transitions between energy levels, we have the previous selection rules but need to add one more:

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

but

$m_{J_1} = 0 \rightarrow m_{J_2} = 0$ is forbidden when $\Delta J = 0$

These types of hyperfine structure are often observed in EPR spectra.