

10 Atomic Term Symbols and Coupling of Angular Momentum

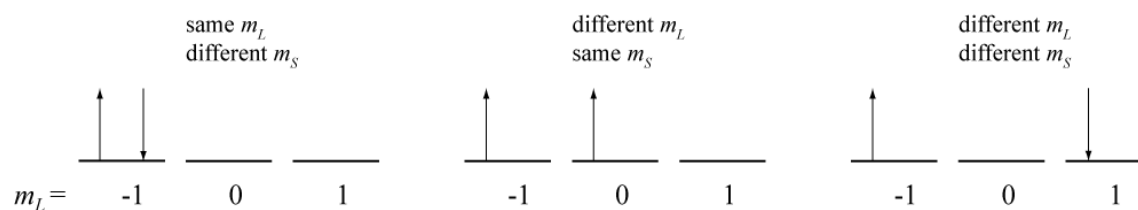
In many electron atoms, each electron has both a spin and an orbital angular momentum. In the zeroth-order picture where we neglect inter-electronic repulsion, the energy of an electron in an atom (*i.e.*, the energy of a particular orbital) depends only on the n quantum number of that electron or orbital. In this approximation, a particular electronic configuration (in which we specify only n and l for each electron) has a specific, well-defined energy.

However, when we specify the electronic configuration of an atom, there are many different values of the projections of both the spin and orbital angular momenta (m_l and m_s) for a given n and l . (Remember, for hydrogen, the energy is independent of m .)

Let's consider the example of the ground state of carbon, which has an electronic configuration of

$$1s^2 2s^2 2p^2$$

The two $2p$ electrons can be in any of the three $2p$ orbitals ($2p_{-1}$, $2p_0$, $2p_{+1}$) and have different m_l and can have either spin up or spin down (different m_s).



When we take into consideration inter-electronic repulsion, the energy of the atoms depends upon these quantum numbers as well *i.e.*, the inter-electronic repulsion lifts the degeneracy.

We therefore need a way to label the states of an atom in a more precise way in order to account for these differences. We need to label a state not only by its configuration, but also in a manner that indicates the projections of the angular momenta of the individual electrons, because each state labeled in this way will have a different net angular momentum and a different energy.

There is no analytical way to differentiate these states, since the electronic Schrödinger equation is not exactly solvable. However, having some qualitative principles will allow us to predict which states will be higher in energy than others. This is done using atomic term symbols.

The approach that we will consider is called **Russell-Sanders coupling** or **L-S coupling** and is simply a method by which one determines the resultant angular momenta from many electrons.

The Russell-Saunders scheme determines the total orbital angular momentum, L , and the total spin angular momentum, S , of all the electrons, and then adds these two vectors to get a total electronic angular momentum, J .

The result of coupling these angular momenta in this way (*i.e.*, the resulting state) is designated by an atomic term symbol.

The term symbol has the form: $^{2S+1}L_J$

where : L is the total orbital angular momentum quantum number

S is the total spin quantum number

J is the total angular momentum quantum number

We will see that the total orbital angular momentum quantum number L will be an integer ≥ 0 .

In a manner analogous to the way we indicate the orbital angular momenta of individual electrons by letters ($s, p, d, f, \dots$), we indicate the total L by letters

$$L = \begin{array}{ccccc} 0 & 1 & 2 & 3 & 4 \\ S & P & D & F & G \end{array}$$

The total S will turn out to be integral or half-integral, so the left superscript $2S+1$ will be an integer.

The quantity $2S+1$ is called the multiplicity, since if $L \geq S$, there are $2S+1$ possible values of J .

Examples of atomic term symbols (otherwise just called terms) are

$$^3S \quad ^2D \quad ^1P$$

These symbols represent states of an atom with the same electronic configuration but with different energy.

These are read as "triplet S ", "doublet D ", and "singlet P ".

At this point it may seem a bit mysterious why we chose to add the angular momenta in this way (that is, why we chose first to find the total L and total S and then combine them to find total J).

Let me digress a moment to talk about good quantum numbers and constants of motion. We know that the square of the magnitude of the total angular momentum operator, $\hat{J}^2$, commutes with the Hamiltonian (if the potential only depends on the distance not the angles), it is a constant of the motion. This is true no matter how we couple angular momenta. (For a quantity to be constant in time it must commute with $\hat{H}$ so its eigenfunctions have trivial time dependence.)

If we neglect inter-electronic repulsion, the angular momentum operator of each electron commutes with the Hamiltonian and hence is a conserved quantity or a constant of motion. This means that the angular momentum quantum numbers of each electron have meaning since they are time independent.

However, if you include inter-electronic repulsion in a multi-electron system, the orbital angular momentum operators of the individual electrons no longer commute with $\hat{H}$. Therefore the quantum numbers l_i for the individual electrons are no longer good quantum numbers and the angular momenta of the individual electrons need not be conserved (*i.e.* they are no longer constants of the motion).

However, it turns out that for atoms of atomic number less than about 40, the sum of the orbital angular momentum

$$\mathbf{L} = \sum_i \mathbf{l}_i$$

will still be a constant of the motion. This says that the individual orbital angular momentum vectors can change in time, but their vector sum remains constant.

The same holds true for spin angular momentum. The total spin angular momentum

$$\mathbf{S} = \sum_i \mathbf{s}_i$$

will also be a constant of the motion.

Why does the coupling scheme outlined above work for atoms with $Z \leq 40$? The coupling scheme I have presented in which we first couple the orbital angular momentum and the spin together and then couple these to get the total angular momentum only holds in the case in which we neglect relativistic terms in the Hamiltonian. That is, L and S are only good quantum numbers when we neglect the relativistic spin-orbit coupling term.

The spin-orbit term in the Hamiltonian has the form

$$\hat{H}_{so} = \sum_j \xi(r_j) \mathbf{l}_j \cdot \mathbf{s}_j$$

and it enters if we do a relativistic treatment of quantum mechanics. It basically arises from the fact that a moving electron creates a magnetic field which has a magnitude that is proportional to the orbital angular momentum, l_j of the electron. This magnetic field interacts with the spin magnetic moment of the electron which is proportional to the spin, s_j

One can easily show that $\hat{L}^2$ and $\hat{S}^2$ (where these are the operators for the total angular momentum) do not commute with this term in the Hamiltonian.

In the Russell-Sanders or L - S coupling scheme outlined above we are neglecting the H_{so} term and assume

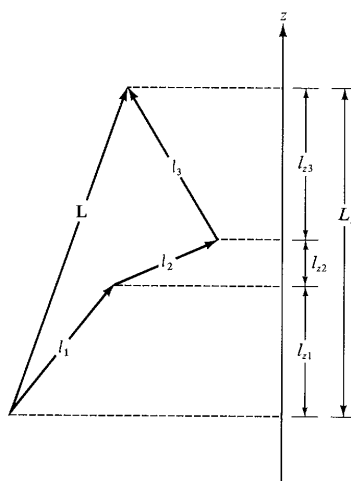
$$[\hat{L}^2, \hat{H}] = 0 \quad [\hat{S}^2, \hat{H}] = 0$$

This assumption (and hence the coupling scheme) is best when the atomic number is low (<40).

The average velocity of the electron depends on Z . Higher atomic number means faster $\langle v \rangle$ and hence, it's more likely that relativistic terms will become important. So in this approximation (which is quite good for low Z), we can characterize an atomic state with a total orbital angular momentum quantum number, L , where $L(L+1)\hbar^2$ is the square of the magnitude of $\mathbf{L}$.

Because L and S are constants of the motion, it is meaningful to label states by them.

To get the quantum numbers corresponding to the total orbital or total spin angular momentum, we cannot simply add the individual quantum numbers. The angular momenta are vector quantities, and we have to add them vectorially. However, the projections of the angular momentum vectors on the z -axis add like scalar quantities, and from this we can find the quantum numbers for the total angular momentum.



Thus,

$$L_z = \sum_i l_{zi} = \sum_i m_{li} \hbar = M_L \hbar \quad \text{where} \quad M_L = \sum_i m_i$$

and

$$S_z = \sum_i s_{zi} = \sum_i m_{si} \hbar = M_S \hbar \quad \text{where} \quad M_S = \sum_i m_{si}$$

Note: I will use M_L for M to emphasize that it is orbital angular momentum.

The goal is to couple a set of angular momentum vectors by adding the z-components to get a total z-component (i.e. M_L and M_S), and then determine what the corresponding total angular momentum quantum numbers are (L and S). From these we can determine the Term Symbol. Each term symbol will represent a state of different energy.

We need to be able to derive the *Terms* for a given electronic configuration.

1) First consider closed subshells (full number of electrons)

The total spin will always equal zero for a closed shell. (note that shells are defined by n , subshells by l)

For each electron with $m_s = 1/2$ there is another with $m_s = -1/2$

So

$$M_S = \sum_i m_{si} = 0 \quad \text{for a filled subshell and } S=0$$

Similarly, the total orbital angular momentum L will = 0 for a closed subshell

For every electron in an orbital with quantum number m , there will be one with quantum number $-m$, since m runs from l to $-l$.

$$M_L = \sum_i m_{li} = 0 \quad \text{for a filled subshell.}$$

So for a totally closed subshell

$$L = 0 \quad S = 0 \quad \text{and we have only a } {}^1S_0$$

If we have a configuration with a closed subshell and an open one, we need only consider the open subshells. (The closed ones don't contribute to L and S).

2) Consider two electrons in different subshells

One doesn't have to worry about the Pauli principle since they will have different values of n or l or both. (Remember, no two electrons can have all the same quantum numbers.)

Ignore closed subshells.

Write down all the possible combinations of quantum numbers of the open shell electrons. By summing the m and m_s to get M_L and M_S you can then find the possible values of S and L and the terms.

3) When we have two electrons in the same subshell (same as n and l), we have some restrictions.

For instance for a $1s^2 2s^2 2p^2$ carbon ground state, one can make a list of possible values of the m quantum numbers, see below. Certain values are not valid, however, because of the Pauli Exclusion Principle.

For instance, one can't have

$$m_1 = 1 \quad m_{s1} = 1/2$$

$$m_2 = 1 \quad m_{s2} = 1/2$$

Or you can't have both

$$m_1 = 1 \quad m_{s1} = 1/2$$

$$m_2 = 1 \quad m_{s2} = -1/2$$

and

$$m_1 = 1 \quad m_{s1} = -1/2$$

$$m_2 = 1 \quad m_{s2} = 1/2$$

If you allowed both of these, it implies that you can distinguish between electrons. By summing the m and m_s to get M_L and M_S you can then find the possible values of S and L and the terms.

There is one last part to these term symbols: the subscript J which is the total electronic angular momentum. The total angular momentum $\mathbf{J}$ is the vector sum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. We know this commutes with H so J will be a good quantum number

J can take the values

$$J = L + S, L + S - 1, \dots, |L - S|$$

You can see this by coupling just two angular momentum vectors.

J is written as a subscript in the term symbol.

For 3P $L = 1, S = 1$ J can range from $J = 2, 1, 0$

so we get $^3P_0, ^3P_1, ^3P_2$ These are called levels.

In the absence of spin-orbit interaction, different levels have the same energy, but $\hat{H}_{so}$ splits them slightly. Once we have determined the states which correspond to a particular electronic configuration, how do we decide which is lowest in energy?

Hund's Rules

- 1) The highest in multiplicity is lowest (least inter-electronic repulsion)
- 2) If there are two states with the same multiplicity, the one with the largest L is the lowest.
- 3) If the subshell < half filled the state with the lowest J is lowest in energy, if the subshell > half filled state with highest J is lowest in energy.

This works well for ground state configuration, but not always as well for excited configurations.



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Example:

Let us have a look at an example, the carbon atom. The 6 electrons of the carbon atom give rise to the following electronic configuration $1s^2 2s^2 2p^2$. We have just seen that the filled subshells do not contribute to the total orbital and spin angular momentum, since they have $L=S=0$. So we only have to consider the two electrons in the $2p$ shell. If we take into account the Pauli Exclusion Principle we can write down the following table for the different values of m and m_s to give M_l and M_s .

	m_1	m_{s1}	m_2	m_{s2}	M	M_s	M_J
1	+1	$+\frac{1}{2}$	+1	$-\frac{1}{2}$	+2	0	+2
2	+1	$+\frac{1}{2}$	0	$+\frac{1}{2}$	+1	+1	+2
3	+1	$+\frac{1}{2}$	0	$-\frac{1}{2}$	+1	0	+1
4	+1	$+\frac{1}{2}$	-1	$+\frac{1}{2}$	0	+1	+1
5	+1	$+\frac{1}{2}$	-1	$-\frac{1}{2}$	0	0	0
6	+1	$-\frac{1}{2}$	0	$+\frac{1}{2}$	+1	0	+1
7	+1	$-\frac{1}{2}$	0	$-\frac{1}{2}$	+1	-1	0
8	+1	$-\frac{1}{2}$	-1	$+\frac{1}{2}$	0	0	0
9	+1	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1	-1
10	0	$+\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	0
11	0	$+\frac{1}{2}$	-1	$+\frac{1}{2}$	-1	+1	0
12	0	$+\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	0	-1
13	0	$-\frac{1}{2}$	-1	$+\frac{1}{2}$	-1	0	-1
14	0	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	-1	-2
15	-1	$+\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0	-2

We must now deduce the possible values of L and S from the values of M and M_s in the table above. The largest value is 2 and this value occurs only with M_s is 0. Therefore there must be a state with $L=2$ and $S=0$. This state accounts for the entries 1, 3, 5, 12 and 15 in the table. Remember, an $L=2$ state with $S=0$ has M values of -2, -1, 0, +1 and +2 and $M_s=0$.

If we take these entries out of the table we are left with:

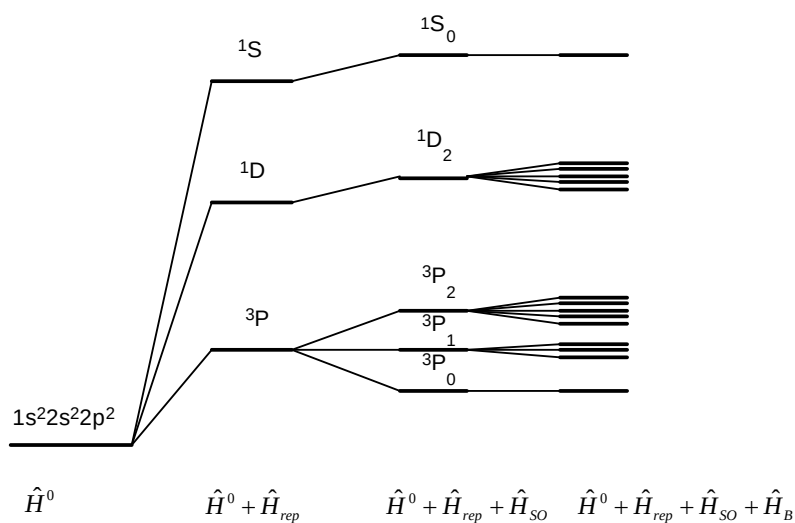
	m_1	m_{s1}	m_2	m_{s2}	M	M_s	M_J
2	+1	$+\frac{1}{2}$	0	$+\frac{1}{2}$	+1	+1	+2
4	+1	$+\frac{1}{2}$	-1	$+\frac{1}{2}$	0	+1	+1
6	+1	$-\frac{1}{2}$	0	$+\frac{1}{2}$	+1	0	+1
7	+1	$-\frac{1}{2}$	0	$-\frac{1}{2}$	+1	-1	0
8	+1	$-\frac{1}{2}$	-1	$+\frac{1}{2}$	0	0	0
9	+1	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1	-1
10	0	$+\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	0
11	0	$+\frac{1}{2}$	-1	$+\frac{1}{2}$	-1	+1	0
13	0	$-\frac{1}{2}$	-1	$+\frac{1}{2}$	-1	0	-1
14	0	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	-1	-2

The largest value of M remaining is $M=1$, implying $L=1$. This $L=1$ state has as possible M values, $M=0, \pm 1$. Each of these values occurs with a value of $M_s=0$ or ± 1 . So what we have is a state with $L=1$ and $S=1$. If we remove the nine entries in the table corresponding to this state we are only left with entry 10 with $M=0$ and $M_s=0$ implying $L=0$ and $S=0$.

All that has to be done now is to assign term values to these states.

$$\begin{array}{llll}
 L=2, S=0 & \Rightarrow & J=2 & \Rightarrow & {}^1D_2 \\
 L=1, S=1 & \Rightarrow & J=0,1,2 & \Rightarrow & {}^3P_0, {}^3P_1, {}^3P_2 \\
 L=0, S=0 & \Rightarrow & J=0 & \Rightarrow & {}^1S_0
 \end{array}$$

The ordering of the different states according to Hund's rule are given in the figure below.



To close out and summarize our discussion of atoms, let us step back for a moment and look at the effect of the different terms in the Hamiltonian.

- 1) To zeroth-order there is only one state for a particular electron configuration.
- 2) If we consider electron repulsion, it splits the different terms. This says that states with different amounts of orbital and spin angular momentum will have different amounts of electron repulsion.
- 3) If we add spin orbit interaction, we split different J values.
- 4) If we add Zeeman term (*i.e.*, due to an external magnetic field), split m_j 's.

