

8.4: Angular Momentum Coupling

Any system that has more than one source of angular momentum will be subject to coupling between those forms of angular momentum. For example, consider the emission from an excited hydrogen atom, for which the electron is in the 2p subshell the atom emits a photon as the electron relaxes to be in the ground 1s subshell. In fact, this transition is doubled as two lines can be observed if viewed at high enough resolution.

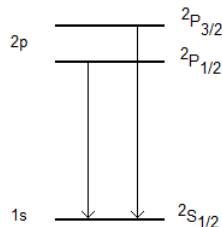


Figure 8.4.1

The transition is depicted in the above energy level diagram. The upper (2p) state is shown to be split into two components, one labeled $^2P_{3/2}$ and one $^2P_{1/2}$. The lower state has only one component, labeled $^2S_{1/2}$. Part of the job of quantum mechanics will be to describe this splitting. The explanation comes in the form of angular momentum coupling.

There are two sources of **angular momentum** in the electronic wavefunction of the atom: the orbital angular momentum ($l = 1$) and the electron spin angular momentum ($s = \frac{1}{2}$). These angular momenta can couple to yield a total angular momentum $J = \frac{3}{2}$ or $\frac{1}{2}$. The resultant angular momentum can be determined by the two angular momentum vectors adding in parallel or antiparallel. The result is to split the state into two components.

Term Symbols

Angular momentum in atoms can be summarized using a **term symbol**. The term symbol will indicate a number of different types of angular momentum such as the total orbital angular momentum, total spin angular momentum and the total (spin + orbit) angular momentum. In the limit that **Russell-Saunders coupling** (which will be described in detail shortly) provides a good description of the atom, the term symbol used will be of the form

$$(2S+1)L_J$$

where S is the total spin angular momentum and $(2S+1)$ is the spin degeneracy, L is the total orbital angular momentum, and J gives the total of the spin-orbit angular momentum. (The convention will be followed that lower-case letters are used to indicate one-electron properties and upper-case letters are used to describe total atom properties.)

L and S must be calculated using vectorial sums of the single-electron angular momenta (whether orbital or spin.) The vectorial sums can yield several values depending on the angle between the vectors. The possible magnitudes of the resultant vectors will be quantized, with the range of magnitudes being given by a **Clebsch series**. Consider the addition of the angular momentum vectors for two electrons in $p(l = 1)$ subshells.

$$\begin{aligned} \mathbf{L} &= \mathbf{l}_1 \oplus \mathbf{l}_2 \\ &= l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \dots, |l_1 - l_2| \end{aligned}$$

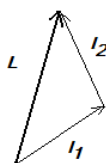


Figure 8.4.2

As such, the possible values of \mathbf{L} for a p^2 configuration are

$$\begin{aligned}\mathbf{L} &= \mathbf{l}_1 \oplus \mathbf{l}_2 \\ &= 1 \oplus 1 \\ &= 2, 1, 0\end{aligned}$$

As in the case of one-electron orbital angular momenta, the total orbital angular momentum is signified using a letter. The following table shows which letters are used.

One-electron			Total Atom	
l	Designation	\mathbf{L}	Designation	
0	s	0	S	
1	p	1	P	
2	d	2	D	
3	f	3	F	
4	g	4	G	

The possible values of \mathbf{S} , are given by $s_1 \oplus s_2$. (For all electrons, $1s = \frac{1}{2}$.)

$$\mathbf{S} = s_1 \oplus s_2 = \frac{1}{2} \oplus \frac{1}{2}$$

So the possible values of $(2\mathbf{S} + 1)$ are 3 and 1. In other words, both triplet and singlet states arise from a p^2 configuration.

However, not all possible combinations of \mathbf{L} and $(2\mathbf{S} + 1)$ are possible. In fact, only those values that arise from distinguishable combinations of **microstate** quantum number combinations are possible.

The Microstate Method

The number of distinguishable microstates for a given electronic configuration is given by

$$\frac{G!}{N!(G-N)!}$$

where G is the number of spin-orbit states possible for a single electron and N is the number of electrons. For a p^2 configuration, $G = 6$ and $N = 2$. So the number of microstates is given by

$$\frac{6!}{2! \cdot 4!} = \frac{6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(2 \cdot 1) \cdot (4 \cdot 3 \cdot 2 \cdot 1)} = 15$$

So there are 15 possible microstates possible. Each microstate will be characterized by a value of m_l and m_s for each electron under consideration. A complete set of microstates for a p^2 configuration is shown in the table below. m_l and m_s are indicated for electrons 1 and 2 in the atom. Notice that only distinguishable combinations are shown!

	m_L		m_S		Designation		
	1	2	1	2			
1	+1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+2	0	1D
2	+1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	3P
3	+1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	1D
4	+1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3P
5	+1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	1D

	m_L			m_S	Designation		
6	+1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	3P
7	+1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	3P
8	+1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	3P
9	+1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	3P
10	0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	1S
11	0	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	3P
12	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	1D
13	0	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	3P
14	0	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	3P
15	-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	1D

The “Designation” column in the above table is really for bookkeeping only. For example, it should be noted that there are two microstates that yield $m_L = +1$, $m_S = 0$. One has been designated 1D and the other 3P . In fact, the wavefunctions needed to describe these term symbol components require linear combinations of both microstates.

The resulting microstates for a p^2 configuration are 1D , 3P and 1S . The methodology for determining this from the table of microstates is as follows:

1. Find the largest value of m_L and the largest value of m_S that corresponds to that value.
2. From these, find L and S for the term symbol.
3. Mark combinations of m_L and m_S that match the pattern for a given term symbol.
4. Repeat from step 1 for remaining microstates. Keep repeating until there are no microstates left.

It is very important to approach this process methodically or errors will occur in determining microstate-term symbol correlations.

Utilizing this methodology to work through the above table, we start with the largest value for m_L which is +2. The largest value of m_S that goes with it is 0. This indicates L and S values of 2 and 1 respectively. $L = 2$ indicates a D state. $S = 0$ indicates that $(2S + 1) = 1$ (or a singlet state.) So the resulting term is 1D . This will have components of $m_L = +2, +1, 0, -1, -2$. Each will have $m_S = 0$. This accounts for five of the microstates.

The largest value of m_L for the remaining microstates is $m_L = +1$. the largest value of m_S that goes with $m_L = +1$ is $m_S = +1$. This correlates to $L = 1$, $S = 1$ or a 3P state. There are nine combinations of microstates for this term symbol, one each for each combination of $m_L = +1, 0, -1$ and $m_S = +1, 0, -1$.

After these combinations are marked, the only remaining combination is $m_L = 0$, $m_S = 0$, which corresponds to a 1S state.

The number of microstates used for a given term symbol can be determined from $(2L + 1)$ and $(2S + 1)$, the orbital and spin degeneracies respectively. Consider the following table. Notice that the total of $(2L + 1)(2S + 1)$ is the same as the number of original microstates.

	$(2L + 1)$	$(2S + 1)$	$(2L + 1)(2S + 1)$
1D	5	1	5
3P	3	3	9

	$(2L + 1)$	$(2S + 1)$	$(2L + 1)(2S + 1)$
1S	1	1	1
Total			15

Spin-Orbit Coupling

The one thing that has not been determined from the microstates themselves is the total angular momentum \mathbf{J} , which is given by the vectorial sum of \mathbf{L} and \mathbf{S} . \mathbf{J} values must be determined for each term separately. This coupling of spin and orbit angular momenta will split the term states further.

$$\mathbf{J} = \mathbf{L} \oplus \mathbf{S}$$

	\mathbf{L}	\mathbf{S}	\mathbf{J}	Terms
1D	2	0	2	1D_2
3P	1	1	2, 1, 0	$^3P_2, ^3P_1, ^3P_0$
1S	0	0	0	1S_0

Again, the values of the spin-orbit degeneracies, given by $(2J+1)$ can be used to determine if the coupling scheme has been done properly.

	\mathbf{J}	$(2J+1)$
1D_2	2	5
3P_2	2	5
3P_1	1	3
3P_0	0	1
1S_0	0	1
Total		15

Again, notice that the total matches the original number of microstates.

The Hole Rule

When dealing with a subshell that is more than half filled, it is oftentimes easier (or at least less tedious) to employ the **hole rule**. The hole rule involves treating electron holes rather than the electrons themselves. Consider ${}_6C$ and ${}_8O$ as an example of complementary atoms. Carbon has a p^2 configuration and oxygen a p^4 configuration. (Added together, that makes a p^6 configuration, which closes the p-subshell and is why the two atoms are complementary.)

For each microstate in the p^2 system, there exists one in the p^4 system that when added together would complete the p-subshell. An example is shown below.

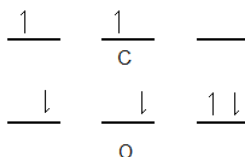


Figure 8.4.3

This relationship ensures that the exact same symmetry relationships hold for the p^4 system as for the p^2 system. Hence, the term symbols that arise from a p^4 system are 1D , 3P and 1S . With spin-orbit coupling, the 3P will split into three components, 3P_0 , 3P_1 and 3P_2 . Of these, 3P_2 will have the lowest energy according to Hund's rule 3b, as these terms arise from a system where the subshell is more than half filled.

Hund's Rules

Hund's rules are used to determine the lowest energy state within the manifold of states generated from a given electronic configuration. The rules can be summarized as follows:

1. The lowest energy state will be the one with the largest value of **S**.
2. For multiple states with the same largest value of **S**, the lowest energy state will have the largest value of **L**.
3. For states with the same values of **L** and **S**, the lowest energy state will have
 - a. The smallest value of **J**, if the term arises from an electronic configuration in which the subshell is less than half filled
 - b. The largest value of **J**, if the term arises from an electronic configuration in which the subshell is more than half filled

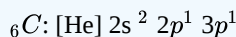
For the case of a p^2 configuration, the largest value of **S** generated is $S = 1$, for the 3P state. And within this state, the lowest energy term will be 3P_0 , since p^2 corresponds to a subshell that is less than half filled.

✓ Example 8.4.1: Nonequivalent Electrons

Determine the term symbols that arise from the p^3 configuration of $_7\text{N}$.

Solution

Consider a carbon atom in an excited state where the electronic configuration is given by



This is an example of a pp configuration (which is different than a p^2 configuration since the two electrons have different values of the principle quantum number n . In this case, a number of microstate combinations become distinguishable that would not be before. A complete set of microstates for a pp configuration is given in the table below. In this case, since the electrons are not equivalent, it is possible for both to be in orbitals where $m_l = +1$ with $m_s = +\frac{1}{2}$ since they are in different subshells.

	m_L		m_S		Designation		
	2p	3p	2p	3p			
1	+1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	+2	+1	3D
2	+1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+2	0	3D
3	+1	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	+2	0	1D
4	+1	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	+2	-1	3D
5	+1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	3D
6	+1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	3D
7	+1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	1D
8	+1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	3D
9	+1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3D
10	+1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	3D
11	+1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	1D

	m_L		m_S	Designation			
12	+1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	3D
13	0	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	+1	+1	3P
14	0	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	+1	0	3P
15	0	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	+1	0	1P
16	0	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	+1	-1	3P
17	0	0	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3S
18	0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	3S
19	0	0	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	1S
20	0	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	3S
21	0	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	3D
22	0	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	3D
23	0	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	1D
24	0	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	3D
25	-1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	0	+1	3P
26	-1	+1	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	3P
27	-1	+1	$-\frac{1}{2}$	$+\frac{1}{2}$	0	0	1P
28	-1	+1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	-1	3P
29	-1	0	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	+1	3P
30	-1	0	$+\frac{1}{2}$	$-\frac{1}{2}$	-1	0	3P
31	-1	0	$-\frac{1}{2}$	$+\frac{1}{2}$	-1	0	1P
32	-1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	3P
33	-1	-1	$+\frac{1}{2}$	$+\frac{1}{2}$	-2	+1	3D
34	-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	3D
35	-1	-1	$-\frac{1}{2}$	$+\frac{1}{2}$	-2	0	1D

			m_L	m_S	Designation		
36	-1	-1	$-\frac{1}{2}$	$-\frac{1}{2}$	-2	-1	3D

In this example, there are more term symbols generated due to the fact that the electrons are not in the same subshell. The resulting term symbols are 3D , 3P , 3S , 1P , 1P and 1S . As such, this set of microstates includes some combinations of m_l and m_s which would not be possible if the two electrons were in the same subshell.

This page titled [8.4: Angular Momentum Coupling](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Patrick Fleming](#).