

8.8: Term Symbols Gives a Detailed Description of an Electron Configuration

Learning Objectives

- Understand how electron configurations results in different manifestations of angular momenta (both orbital and spin)
- Describe the manifestations in atoms via atomic term symbols

Atoms have quantum numbers that are directly analogous to the electronic quantum numbers.

The Total Orbital Angular Momentum Quantum Number: L

One might naively think that you could get the total angular momentum of an atom (L) by simply adding up the l values of the individual electrons. The problem with this idea is that the angular momenta of the various electrons are not necessarily pointing in the same direction. Let's consider the case of adding two 2p-orbitals together (i.e., with $l = 1$ quantum numbers).

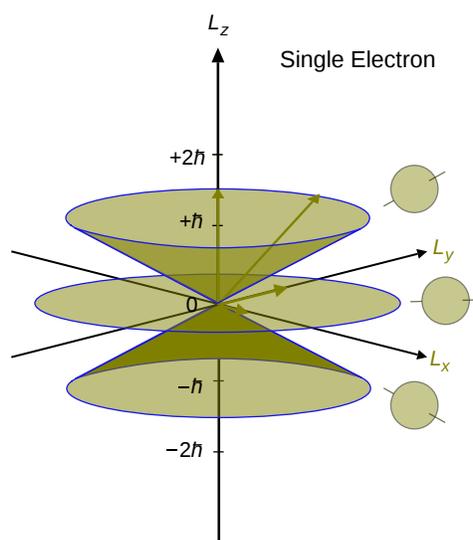


Figure 8.8.1 : The three possible angular momenta vectors for a p-orbital.

As discussed in Section 6.3, each of these electrons has $\sqrt{2\hbar}$ of angular momentum, but oriented in three different directions given by three different m_l values of 1, 0, and -1 (Figure 8.8.1).

$$L = \sum_i^n l_i \quad (8.8.1)$$

However, we must recognize that while the magnitude of angular momentum is a scalar (represented by l), angular momenta are really vector quantities and to add them together will require vector addition (vs. scalar addition) to do properly and must address all possible orientations of l for each electron.

For example, if two electrons are revolving in the same direction as each other (i.e., same m_l values), one would add just their l values together

$$L(\text{same direction}) = \sqrt{2\hbar} + \sqrt{2\hbar} = 2\hbar$$

If the two electrons were revolving in opposite direction (e., opposite m_l values, you subtract their values.

$$L(\text{same direction}) = \sqrt{2\hbar} - \sqrt{2\hbar} = 0$$

If they are revolving at some off-angle relative to each other (one revolving in a plane and one off plane), you would partially subtract them.

$$L(\text{same direction}) = \sqrt{2\hbar} + 0 = \sqrt{2\hbar}$$

To figure out all of the possible combinations of l for a pair of electrons, simply add them together to get the co-aligned case, subtract them to get the opposing case, and then fill in all the numbers in between to get the off-angle cases. For the two p-orbital case, there are no other possibilities (remember that l and hence L must be non-negative since they represent the magnitude of angular momenta (addressing the m_l values is a different story as we discuss below).

If you prefer to have a formula for the possibilities of L , you can use this:

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, \dots, |l_1 - l_2| \quad (8.8.2)$$

Technically, Equation 8.8.2 should include all electrons in a system, not just two, to account for all possible combinations of orbital angular momenta, however, there are some tricks that aid in applying this equations to address larger multi-electron atoms. First, electrons in s-orbitals have no orbital angular momentum, so they can be ignored. Second, if block of orbitals are completely filled (e.g., all six p-block spin-orbitals or all 10 d-block spin-orbitals), then the orbital angular momentum vector of each electron will be countered by another electron in the system; these are called **closed-shell** systems. Systems with partially unfilled blocks are called **open-shell** systems.

Hence, conveniently for chemists, an atom's electronic state depends entirely on its unfilled sub shells. Because electrons distribute themselves in a symmetric manner, the inner shell electrons end up canceling out each other's momenta. For an atom in the configuration $1s^2 2s^2 2p^2$, only the two p-electrons matter. For an atom in the configuration $1s^2 2s^1 2p^1$, we have to examine only the 2s and 2p electrons (and can ignore the s electrons too).

✓ Example 8.8.1 : Total Orbital Angular Momentum of Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both open-shell electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 2, 1, 0.

✓ Example 8.8.2 : Total Orbital Angular Momentum of Unknown Species

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We can ignore the electrons in the $[Xe]$ core and the electrons in the 6s block. So all we have to consider is the f electron $l = 3$ and d electron $l = 2$.

The two extremes possible (Equation 8.8.2) are

$$3 + 2 = 5$$

and

$$3 - 2 = 1$$

The possible combinations are thus 5, 4, 3, 2, and 1.

The Total Magnetic Quantum Number: M_l

The Total Magnetic Quantum Number M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much total angular momentum there is in the system, M_l tells you which direction it is pointing. Like L , a given configuration can have several possible values of M_l , depending on the electrons' relative orientation. Unlike L , M_l is allowed to have negative values. To list the possible M_l values for a two electron system, take the case where both m_l are positive, then take the case where they are both negative, and then fill in the numbers in between (Figure 8.8.1).

$$M_l = m_{l1} + m_{l2}, m_{l1} + m_{l2} - 1, \dots, -m_{l1} - m_{l2} \quad (8.8.3)$$

Note that there is no absolute value function in Equation 8.8.3 like in Equation 8.8.2.

✓ Example 8.8.3 : Total Magnetic Quantum Number of the Zirconium Ground State

What are the possible values M_l of a zirconium atom with the $[Kr]5s^24d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

The Total Spin Magnetic Quantum Number: M_s

M_s is the sum total of the z-components of the electrons' inherent spin. Do not confuse it with M_l , which is the sum total of the z-component of the **orbital angular momentum**. It is easily computed by finding all of the possible combinations of m_s . Since m_s for each individual electron can only be +1/2 or -1/2, this isn't too complicated.

$$M_s = m_{s1} + m_{s2}, m_{s1} + m_{s2} - 1, \dots, m_{s1} - m_{s2} \quad (8.8.4)$$

✓ Example 8.8.4 : Total Spin Magnetic Quantum Number of the Carbon Ground State

What are the M_s values for $1s^22s^22p^2$?

Solution

$M_s = 1, 0, -1$

The Total Intrinsic Spin Quantum Number: S

The sum total of the spin vectors of all of the electrons is called S . The difference between S and M_s is subtle, but vital for understanding multiplicity. M_s measures the total z-component of the electrons' spins, while S measures the entire resultant vector. The values of S are computed in a manner very similar to M_s . Because S measures the magnitude of a vector, it cannot ever be negative.

$$S = |s_1 + s_2|, |s_1 + s_2 - 1|, \dots, |s_1 - s_2| \quad (8.8.5)$$

✓ Example 8.8.5 : The Hydrogen Ground State

Find S for $1s^1$.

Solution

S clearly has to be $\frac{1}{2}$ since that's the spin of a single electron and there's only one electron to worry about.

✓ Example 8.8.6 : The Beryllium Excited State

Find S for $1s^22s^12p^1$.

Solution

$S = 1, 0$

✓ Example 8.8.7 : The Carbon Ground State

Find S for carbon atoms with the $1s^22s^22p^2$ electron configuration.

Solution

$S = 1, 0$ This is the same as the previous problem. Notice that S is not affected by which orbitals the electrons are in. S only cares about how many **open-shell electrons** (i.e., unpaired electrons) there are, not about where they are. This is because S measures an inherent property of the electrons themselves

✓ Example 8.8.8

Find S for nitrogen atoms with the $1s^22s^22p^3$ electron configuration.

Solution

We have not done a three electron case yet, but they are not hard. Find all the combinations for a single pair first, and then factor in the third electron. For two electrons, we already know that the two possible S values are $S=1,0$. A third electron can either add or subtract $\frac{1}{2}$ from these values, so the final S can be $S = 3/2, 1, 1/2$.

The Total Angular Momentum Quantum Number J

The total orbital angular momentum of an atom (measured in terms of l), and the total spin angular momentum of an atom (measured in S) combine to form total angular momentum, a number that is quantized by the number J . L and S do not necessarily have to be pointing in the same direction (Figure 8.8.1), so J can range from $L + S$ to $|L - S|$.

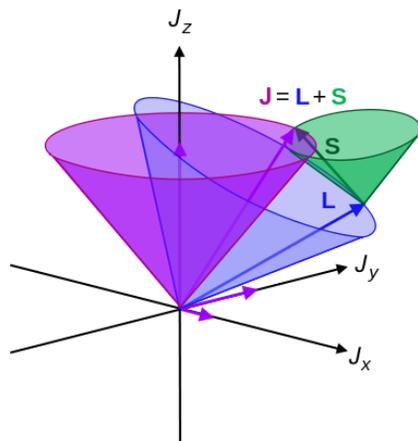


Figure 8.8.1 : Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

Table 8.8.1 : Quantum Numbers and associated ranges

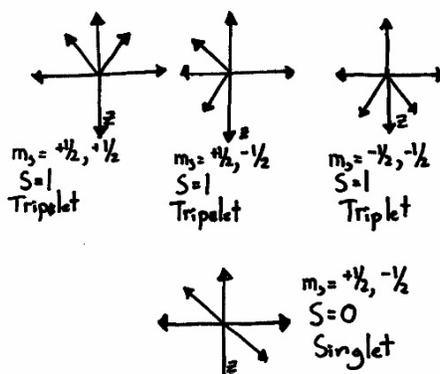
Symbol	Name	Allowed Range
l	Total orbital angular momentum	$ l_1 + l_2 , \dots, l_1 - l_2 $
M_l	Magnet Quantum number	$[m_{l1} + m_{l2}, \dots, -m_{l1} - m_{l2}]$
M_s	Spin Magnetic Quantum Number	$[m_{s1} + m_{s2}, \dots, m_{s1} - m_{s2}]$
S	Inherent Spin Number	$ s_1 + s_2 , \dots, s_1 - s_2 $
M	Multiplicity	$2S+1$
J	Total Angular Momentum	$L + S, \dots, L - S $

Multiplicity

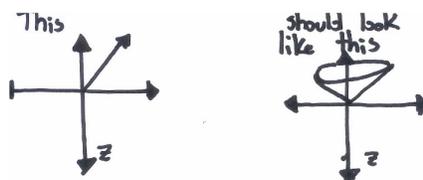
Multiplicity is a simple - sounding concept that defies simple explanations. You know from your first - year education that a singlet is when the net spin (S) is equal to zero (e.g. all the electrons are spin paired), and a triplet happens when the net spin is equal to 1 (e.g. two electrons are pointing in the same direction). They are called “singlet” and “triplet” because there are 3 ways to combine a pair of electron spins to get $S=1$, but only one way to get $S = 0$. If you draw a picture of the possible ways that two electrons can arrange their spins, you get something like this:



Figure 8.8.1 : When we call an electron spin “up,” what we really mean is that it has a positive z-component (e.g. $m_s = +\frac{1}{2}$).



While this picture is an improvement over the simple up-down model, it is still misleading. The three spin axes of an electron share a Heisenberg Uncertainty Principle. The more you know about S_x , the less you can know about either S_y or S_z . The same is true for all other combinations of x, y and z. Since we have defined S_z as a known and fixed value, the values of S_x and S_y must be **completely unknown**. This causes the x and y orientations of the electrons to become smeared out across all possible values:



Constructing Term Symbols

Atomic term symbols contain two pieces of information. They tell you the total orbital angular momentum of the atom (l), and they tell you the multiplicity (M). l is denoted by a simple code, similar to the code used to delineate the types of atomic orbitals:

- $L = 0 \rightarrow S$
- $L = 1 \rightarrow P$
- $L = 2 \rightarrow D$
- $L = 3 \rightarrow F$

Note that while the notation is similar, L does NOT say anything about what types of orbitals the electrons are in. A state that has the term symbol P does NOT necessarily have an open p-shell. The multiplicity is indicated by appending a number to the upper left of the symbol. A $L = 2$, $M = 3$ state would be represented by 3D . The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration. An atom that only has closed shells will always be $1S$.

Each term symbol represents a discrete energy level. We can place these levels in the correct order by using these simple rules:

- 1: High multiplicity values mean low energy
- 2: If there is a tie, high l values mean low energy
- 3a: If there is still a tie and the shell is less than half full, then low J means low energy
- 3b: If the shell is more than half full, then high J means low energy

These rules reliably predict the ground state. They have only erratic agreement with experiment when ordering the other levels.

✓ Example 8.8.9 : Hydrogen Ground State

What are the term symbols for the microstates possible for $1s^1$ electronic configuration of hydrogen?

Solution

Since there is only one electron, this is a simple problem. $L = 0$ and $M = 1$, so the only possible term symbol is 2S . With only one electron, $S = 1/2$, so $J = 0 + 1/2 = 1/2$. Only one microstate exists for this configuration and it has a term symbol of ${}^2S_{1/2}$.

✓ Example 8.8.10 : Boron

What are the term symbols for the microstates possible for $1s^2 2s^2 2p^1$ electronic configuration of boron?

Solution

There still only one open shell electron, so $L = 1$, $M = 1$ and $S = \frac{1}{2}$. We get a term symbol of the type 2P , which gets split into separate symbols because $J = 3/2$ and $1/2$. Two possible microstates exist for this system with term symbols of $^2P_{3/2}$ and $^2P_{1/2}$.

✓ Example 8.8.11 : Beryllium Excited State

What are the term symbols for the microstates possible for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

Now we have two electrons to worry about. Since $l_1 = 0$ and $l_2 = 1$, the only possible combination is $L = 1$. The possible combinations of S are: $S = 1, 0$. This means that $M = 3$ or $M = 1$. The term symbols will be of the form 1P and 3P . For the 1P state, $L = 1$ and $S = 0$, so $J = 1$. For the second state, $L = 1$ and $S = 1$, so $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of 1P_1 and $^3P_2, ^3P_1$, and 3P_0 .

✓ Example 8.8.12 : Zirconium

What are the term symbols for the microstates possible for the $[Kr]5s^2 4d^2$ ground-state electronic configuration of zirconium?

Solution

This is a much harder problem. We will need to use a special technique to disentangle all of the possible combinations of l and M . Let's start by listing the relevant quantum numbers for the two open-shell electrons:

$l_1 = 2$	$l_2 = 2$
$m_{l1} = 2, 1, 0, -1, -2$	$m_{l2} = 2, 1, 0, -1, -2$
$m_{s1} = \frac{1}{2}, -\frac{1}{2}$	$m_{s2} = \frac{1}{2}, -\frac{1}{2}$

Let's combine these numbers to generate the atomic quantum numbers:

$$L = 4, 3, 2, 1, 0$$

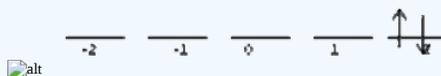
$$M_l = 4, 3, 2, 1, 0, -1, -2, -3, -4$$

$$M_s = 1, 0$$

We know that there will at least one each of S, P, D, F and G. It isn't immediately clear which of these will be singlets and which will be triplets. To figure this out, we need to systematically examine the possible microstates. It turns out that there are **45** possible ways to put distribute two electrons between 5 d orbitals. That's a lot! The easiest way to list the states is to organize them into a chart:

$M_s = -1$	$M_s = 0$	$M_s = +1$

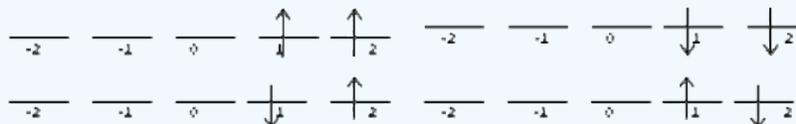
Attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_l = 4$? It turns out there is only one possible combination that does this:



This state has $M_s = 0$. This means that there is only 1 microstate that corresponds to $M_l = 4$ and $M_s = 0$, and none that correspond to $M_l = 4$ and $M_s = \pm 1$. We add this microstate to the chart like this:

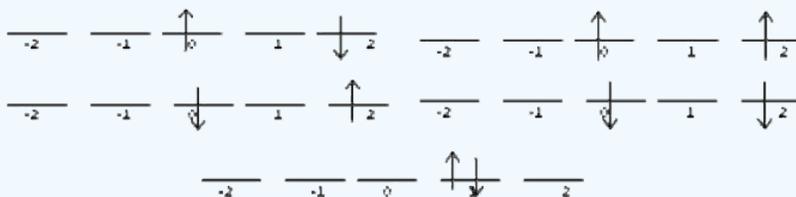
M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0

Now, how many ways are there to get $M_l = 3$?



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1

For $M_l = 2$, we find the following states:



M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1
2	1	3	1

You should be able to draw the microstates on your own by now. You should find 8 states, four of which are singlet and four of which are triplets.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1
2	1	3	1

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2

There are only nine possible ways to arrange the electrons to get $M_l = 0$

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2

The rest of the chart will be symmetric to the first half, so we do not need to do any more work:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	0	1	0

Now that we have a listing of all of the microstates, we need to figure out how to divide them up between the term symbols. It turns out that each term symbol can have, at most, one microstate from each box on the chart. The term symbols always end up claiming a “box” of microstates, centered on the middle of the chart. This is easier shown than said.

Attacking the chart from the top, we can see that the $M_l = 4$ $M_s = 0$ state clearly belongs to a 1G symbol. The $M_l = -4$ $M_s = 0$ box also clearly belongs to this symbol. If I connect these states with a “box,” I get this:

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
4	0	1	0
3	1	2	1

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	\emptyset	\pm	\emptyset

The strickthrough configurations all belong to the 1G state. Let's subtract them from the chart to indicate that they are not available for other term symbols.

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1

The next row indicates a $L = 3$ state. Because there are three M_s values available, this is a **triplet**. The term symbol will be 3F , which reduces the chart down to

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	2	4	2
0	2	5	2
-1	2	4	2

The next state will be 1D . Leaving us with

M_l	$M_s = -1$	$M_s = 0$	$M_s = +1$
1	1	1	1
0	1	2	1
-1	1	1	1

Next is a 3P state. The chart is getting pretty small now with

M_l	$M_s = 0$
	0

The last remaining microstate comprises the 1S term symbol.

The total listing is

$${}^1G, {}^3F, {}^1D, {}^3P, {}^1S.$$

Assigning J values, we get

$${}^1G_4, {}^3F_4, {}^3F_3, {}^3F_2, {}^1D_2, {}^3P_2, {}^3P_1, {}^3P_0, {}^1S_0$$

If you can do this problem, you can do almost any atomic term symbol.

Note

The secret to writing the term symbols for an atom is to discover what combinations of l and M are possible for that atom with that specific electronic configuration.

Shortcuts

There is a deep symmetry that connects different electronic configurations. It turns out that a p^1 configuration has the same term symbols as a p^5 . Similarly, $p^2 = p^4$. A similar relationship can be used to figure out high electron number term symbols for the d and f orbitals.

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