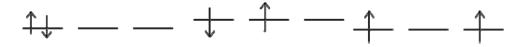
Term symbols: why bother?

Since your freshmen year, you have been using electron configuration notation. It is an easy and intuitive way to write electronic states, and can even be used to express excited states. For example, the ground state of C is $1s^22s^2p^2$ We could write an excited state as $1s^22s^2p^13s^1$

What's wrong with this?

This notation is not specific enough. $1s^22s^2p^2$ is NOT a single state. There are 36 different microstates that have this same configuration. Here are a few of them:



Notice that they have different multiplicities and angular momenta. The energies of these states are NOT the same. Unless we want to write out all of the microstates every time we talk about electronic states, we need to invent a compact notation that can sum up all of this information in a concise and useful way.

The principal quantum number n

n is a measure of the quantized energy of the electron. It tells you which energy level the electron occupies. The lowest possible value is one, and there is no theoretical limit to how high it can go (although in practice, reaching very high levels of n causes ionization, at which point it stops making sense to talk about energy levels). The principal number can be used to calculate the quantized energy by this (hopefully familiar) formula:

$$E_n = RhcZ^2/n^2$$

where R is the Rydberg constant and Z is the atomic number

The orbital angular momentum quantum number I (little "el")

I is the quantum number that determines the magnitude of the electron's angular momentum. I does not say anything about the direction of the angular momentum. The formula is:

 $L^2 = h^2 I(I + 1)$ where L^2 is the magnitude of the angular momentum

Electrons in higher energy levels (e.g. higher n numbers) have a wider range of I values to choose from. L can be any integer number between n-1 and 0. For example, an electron in n = 4 could have an I value of 3, 2, 1 or 0. But there is a better way to think about I.

The angular momentum q # tells you which type of orbital the electron is in. It follows a very simple code:

 $l=0 \rightarrow s$ orbital

 $l=1 \rightarrow p$ orbital

l=2 → d orbital

 $l=3 \rightarrow f$ orbital

You should know from general chemistry that the first energy level only has an s orbital, that the second energy level has s and p orbitals, and so on. So you don't really need a formula to figure out which combinations of I and n are possible. You should realize right away that n=1 I = 2 is impossible, because there aren't d orbitals on the first energy level!

Note that these rules imply that different types of orbitals grant different amounts of angular momentum to any electrons that occupy them. s orbitals are extremely symmetric, so they have a low value of L^2 [$\hbar^2 O(0+1) = \hbar^2$]. f orbitals are flatter and more planar, so they have higher amounts of angular momentum [$\hbar^2 S(3+1) = 9\hbar^2$]

The magnetic quantum number m_l

 m_l tells you which direction the electron's angular momentum is pointing. It can be used to calculate how much of the momentum is projecting onto the z axis of the atom:

L_z = m₁ ħ where L_z is the z-component of the angular

No Projection

Some projection

on to 2

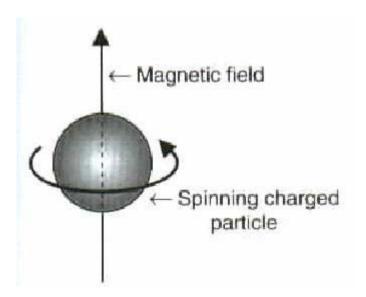
Fill projection

momentum

 m_l tells you which sub-orbital the electron is in. It can range in value from l to -l. Again, you shouldn't need a formula to realize what combinations make sense. You should know that there is only one s orbital per level, three p orbitals, five d orbitals, and so on.

Interlude: inherent spin

All particles have a property called spin. Spin is the inherent angular momentum of a particle. We often pretend that spin is the angular momentum that comes from the particle rotating about its own axis. For many purposes, this is a very good approximation to the truth. For example, an electron's spin causes it to project a magnetic field, which is what you would expect from a rotating charged body



However, the magnetic dipole produces this way does not exactly match with what classical physics would predict.

There are other important diffences between the quantum mechanical concept of spin and the classical concept of rotation. Most significantly, spin is a fixed value. All electrons everywhere have the exact same spin. It cannot be made to "spin faster" or "spin slower." It is a fixed physical property, like mass or charge.

All particles have a spin quantum number, called s, that can be used to calculate the inherent angular momentum. The formula is:

$$S^2 = \hbar \sqrt{s(s + 1)}$$

Electrons all have an s value of ½, so the inherent angular momentum of an electron is:

$$\int_{S^2 = h\sqrt{2(\frac{1}{2} + 1)}}^{\frac{1}{2}} = h\frac{\sqrt{3}}{2}$$

This number will be the same for all electrons everywhere. Please note that the inherent angular momentum is different from the normal angular momentum that we were discussing earlier. The first one comes from the electron's spin, and the second one comes from the electron's motion about the orbital.

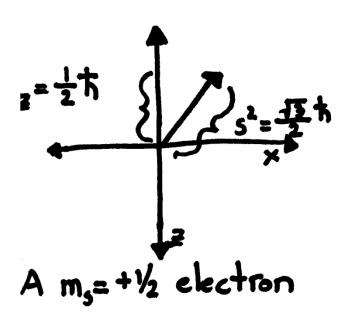
The spin magnetic quantum number ms

All electrons have the same amount of inherent angular momentum, but angular momentum is a vector quantity and can point in different directions. Just like how m_I told you

which direction the electron's orbital angular momentum was pointing in, m_s tells you which way the electron's inherent angular momentum points.

When in an orbital, electron spins can only be oriented in two directions, which we commonly call "up" and "down." There are no in between states allowed. When the electron is oriented along the positive z-axis, m_s is equal to $\frac{1}{2}$. When the spin is pointed along the negative z-axis, m_s is equal to $-\frac{1}{2}$.

The words up and down are misleading. The electron spins are not pointing directly along the z-axis. Moreover, an "up" electron is not necessarily pointing peg opposite to a "down" electron. How is this possible? It is because the spin axis is at an angle:



When we say that an electron is oriented "up," what we mean is that the z-component of its inherent spin is pointing up, not that the whole vector is literally pointing straight up the z-axis. The spin magnetic quantum number can be used to calculate exactly how much of the electron's inherent angular momentum is oriented along the z-axis by this simple formula:

$$S_7 = m_s \hbar$$

Since the only possible values for m_s are ½ and -½, S_z will always be equal to either $\frac{\hbar}{2}$ or $-\frac{2}{3}$

The illustration above is a better way thinking of electron orientation than the simple up and down model, but it is still misleading. The diagram shows the electron in a definite

orientation, but electrons are quantum mechanical objects and are subject to quantum uncertainty. We will return to this issue when we start talking about multiplicity.

Symbol	Name	Allowed Range	Associated property	Formula	Notes
n	Principal quantum number	[1,∞]	energy	$E_n = RhcZ^2/n^2$	Indicates energy level
I	orbital angular momentum	[n,0]	Angular momentum (scalar)	L ² = ħ ² l(l + 1)	Indicates type of orbital
m _l	magnetic quantum	[1,-1]	Angular momentum (z-component)	$L_z = m_l \hbar$	Indicates sub- orbital
m _s	spin magnetic quantum number	½ or -1/2	Spin momentum (z-component)	S _z = m _s ħ	Indicates spin direction
S	Inherent spin number	1/2	Spin (scalar)	S ² =ħ√ s(s + 1)	s = 1/2 for all electrons, no matter what

Atomic Term Symbols

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 $1s^22s^2p^2$, only the two p-electrons matter. For an atom in the configuration $1s^22s^12p^1$, we have to examine the 2s and 2p electrons.

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 by simply adding up the I values of the individual electrons. The problem with this idea is that the momenta of the various electrons are not necessarily pointing in the same direction. If two electrons are revolving in the same direction as each other, you would add their I values. If they were revolving opposite to each other, you would subtract them. If they are revolving at some off-angle relative to each other, you would partially subtract them.

To figure out all of the possible combinations of I 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. If you prefer to have a formula, you can use this:

$$L = |I_1 + I_2|, |I_1 + I_2 - 1|, ..., |I_1 - I_2|$$

Examples: What are the possible L values for 1s²2s²2p²?

Both open-shell electrons are I = 1. The possible combinations are 2,1,0

What about configuration [Xe] 6s² 4f¹ 5d¹?

We have an I=3 and an I=2 electron. 3+2=5 and 3-2=1. The possible combinations are 5,4,3,2,1

The total magnetic quantum number M_I

 M_l is the total z-component of all of the relevant electrons' orbital momentum. Where L told you how much angular momentum there was, 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 (if you think carefully about what L and M_l mean, you will see why this is the case). To list the possible M_l values, 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. Here's a formula: $M_l = m_{l1} + m_{l2}$, $m_{l1} + m_{l2} - 1$, ..., $-m_{l1} - m_{l2}$

Example: What are the possible values M_1 of 40 [Kr] $5s^2 4d^2$?

Both open-shell electrons are I=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 $\pm 1/2$ or $\pm 1/2$, this isn't too complicated.

$$M_s=m_{s1}+m_{s2},\,m_{s1}+m_{s2}-1$$
 , ... , m_{s1} - m_{s2}
 Example: What are the M_s values for $1s^2\,2s^2\,2p^2\,?$

$$M_s=1,0,-1$$

The total inherent 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. S measures the *entire* resultant vector.

The values of S are computing in a manner very similar to M_s . Because S measures the magnitude of a vector, it cannot ever be negative. $S = |s_1 + s_2|, |s_1 + s_2 - 1|, ..., |s_1 - s_2|$

Examples: Find S for 1s¹

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.

Find S for
$$1s^2 2s^1 2p^1$$

S = 1,0
Find S for $1s^2 2s^2 2p^2$

S=1,0 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 there are, not about where they are. This is because S measures an inherent property of the electrons themselves.

Find S for 1s²2s²2p³

We haven't done a three electron case yet, but they aren't 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 ½ from these values, so the final S is 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 (measure in S) combine to form total angular momentum, a number that is quantized by the number J. L and do not necessarily have to be pointing in the same direction, so J can range from L + S to |L - S|.

Symbol	Name	Allowed Range
L	Total orbital	$[_1 + _2 , _1 - _2]$
	angular	
	momentum	
M _I	magnetic	[m _{l1} + m _{l2} , -m _{l1} - m _{l2}]
	quantum	
M_s	spin magnetic	$[m_{s1} + m_{s2} , m_{s1} - m_{s2}]$
	quantum	
	number	
S	Inherent spin	$[s_1 + s_2 , s_1 - s_2]$
	number	
М	Multiplicity	2S+1
J	Total angular	[L + S, L - S]
	momentum	

Interlude: 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:



If you are like me when I first studying multiplicity, you just let out an exasperated sigh. It's very obvious that the first and last pairs should have S=1, but the two middle pairs are antiparallel. Shouldn't there be two singlet states and two triplet states? Why is one of the middle pairs counted as a singlet and the other one as a triplet?fpredicti

The confusion arises from taking the Pauli notation too literally. Like we saw earlier, electrons don't' really align their spins "up" and "down." They align them at angles. When we call an electron spin "up," what we really mean is that it has a positive z-component (e.g. $m_s = +\frac{1}{2}$).

m₃=
$$\frac{1}{2}$$
, $\frac{1}{2}$
S=1
Tripelet
Tripelet
Tripelet
Tripelet

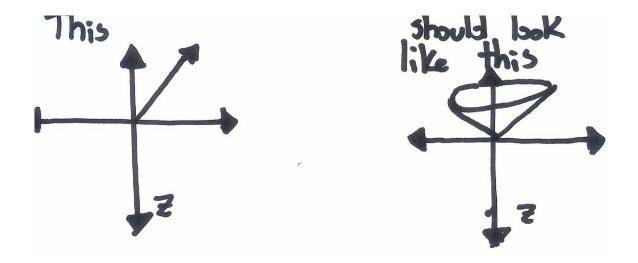
m₃= $\frac{1}{2}$, $\frac{1}{2}$

m₃= $\frac{1}{2}$, $\frac{1}{2}$

S=1
Tripelet
Tripelet

S=0
Singlet

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:



Putting it all together

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.

An atom that only has closed shells will always be ¹S.

Examples: What are the term symbols for 1s¹?

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, $S = \frac{1}{2}$, so $J = 0 + \frac{1}{2} = \frac{1}{2}$. The final term symbol is $^2S_{\frac{1}{2}}$

What are the term symbols for $1s^22s^22p^1$? 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 2 P,. which gets split into separate symbols because J = 3/2 and ½. The term symbols are 2 P_{3/2} and 2 P_{1/2}

What about $1s^22s^12p^1$?

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=3,1. 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. The final term symbols are 1P_1 and 3P_2 , 3P_1 , and 3P_0

What about [Kr] 5s² 4d²?

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 be listing the relevant quantum numbers for the two electrons:

$$\begin{split} I_1 &= 2 & I_2 &= 2 \\ m_{|1} &= 2,1,0,-1,-2 & m_{|2} &= 2,1,0,-1,-2 \\ m_{s1} &= \frac{1}{2},-\frac{1}{2} & m_{s2} &= \frac{1}{2},-\frac{1}{2} \end{split}$$

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

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

 $M_1 = 4,3,2,1,0,-1,-2,-3,-4$
 $M_s = 1,0$

We know that there will at least one each of S, P, D, F and G. It isn't immiediately 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:

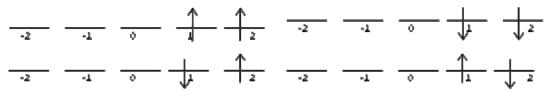
	M_s		
-1	0	1	

I recommend attacking the chart one row at a time. Ask yourself, how many ways can I arrange the two electrons to give me $M_1 = 4$? It turns out there is only one possible combination that does this:

This state is 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 $M_s = +/-1$. We represent this on the chart like this:

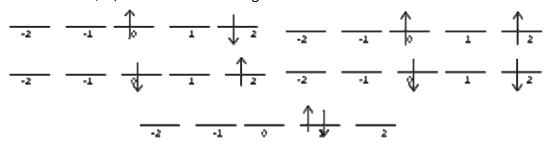
M_s				
-1	0	1		
0	1	0		

Now, how many ways are there to get $M_1 = 3$?



-1	M_s	1
0	1	0
1	2	1

For M_I=2, we find the following states:



M_s				
-1	0	1		
0	1	0		
1	2	1		
1	3	1		

 M_i =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_s

0	1	0
1	2	1
1	3	1
2	4	2

 $M_{l} \! = \! 0 \,$ There are only nine possible ways to arrange the electrons to get $M_{l} \! = \! 0 \,$

N	I_s	
-1	0	1
0	1	0
1	2	1
1	3	1
2	4	2
2	5	2

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

N	l _s	
-1	0	1
0	1	0
1	2	1
1	3	1
2	4	2
2	5	2
2	4	2
1	3	1
1	2	1
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, I can see that the M_I = 4 M_s = 0 state clearly belongs to a 1G symbol. The M_I =-4 M_s =0 box also clearly belongs to this symbol. If I connect these states with a "box," I get this:

M_s		
-1	0	1
0	1	0
1	2	1
1	3	1
2	4	2
2	5	2
2	4	2
1	3	1
1	2	1
0	1	0
		l

The circles stated all belong to the ¹G state. I'm going to subtract them out of the chart to indicate that they aren't available for other term symbols.

-1	M _s 0	1
1	1	1

1	2	1
2	3	2
2	4	2
2	3	2
1	2	1
1	1	1

The next row indicates a L=3 state. Because there are three M_s values available, I know that it is a triplet. The term symbol will be 3F and will use up the following microstates:

	M_s		
-1	0	1	
1	1	1	
1	2	1	
2	3	2	
2	4	2	
2	3	2	
1	2	1	
1	1	1	

Which reduces the chart down to

0	1	0
1	2	1
1	3	1
1	2	1
0	1	0

The next state will be ¹D:

-1	M _s 0	1
0	1	0
1	2	1
1	3	1
1	2	1
0	1	0

Leaving us with

-1	M _s 0	1
1	1	1
1	2	1
1	1	1

Next is a ³P state:

M_s		
-1	0	1
1	1	1
1	2	1
1	1	1

The chart is getting pretty small now:

The last remaining microstate comprises the 1 S term symbol. The total listing is 1 G, 3 F, 1 D, 3 P, 1 S. Assigning J values, we get 1 G₄ 3 F₄ 3 F₃ 3 F₂ 1 D₂ 3 P₂ 3 P₁ 3 P₀ 1 S₀

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

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.

Predicting energy levels

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.

Molecular quantum numbers

The quantum numbers for diatomic molecules are similar from the atomic quantum numbers. Be cautious, because the rules for finding the possible combinations are different.

The total orbital angular momentum quantum number

For the molecular case, this number is called Λ instead of L. It follows the same naming convention as L, except that instead of using capital English letters, it uses capital Greek letters:

 $\Lambda = 0 \rightarrow \Sigma$

 $\Lambda = 1 \rightarrow \Pi$

 $\Lambda = 2 \rightarrow \Delta$

 $\Lambda = 3 \rightarrow \Phi$

Unlike L, there is not a general formula for finding the possible combinations of Λ . You have to examine the individual microstates. This is easier than it sounds.

The total magnetic quantum number M_L

 M_L works like M_I , except that there is no formula for finding the combinations.

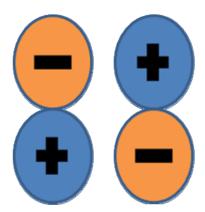
The total spin magnetic quantum number Ms

 M_S works exactly like M_s . Electrons can either point with or against the z-axis, and being in a molecular orbital versus an atomic orbital doesn't change this. M_S can range from $m_{s1} + m_{s2}$ to $m_{s1} - m_{s2}$

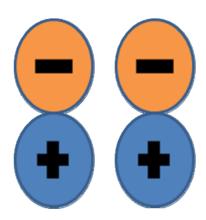
Two new components: parity and reflection

Molecular orbitals are more complex than atomic ones and require more modifiers to completely define.

Parity (sometimes called "inversion") tells you if the orbital is symmetric or anti-symmetric when an inversion operation is performed. Symmetric cases are called "gerade." Anti-symmetric cases are called "ungerade." Some examples:



This pi orbital is gerade



This pi orbital is ungerade

To determine whether or not a given state is g or u, find the parity of each individual open-shell electron and uses these simple rules:

$$g + g \rightarrow g$$

Example: What is the parity of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

Since both open shell electrons are ungerade, the overall parity is g. Helpful hint: bonding sigma orbitals and anti-bonding pi orbitals are always gerade. Anti-bonding sigmas and bonding pis are always ungerade. Draw them and see for yourself.

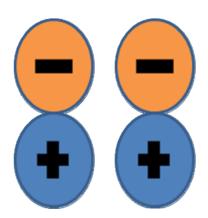
Reflection determines if a given orbital is symmetric or anti-symmetric upon reflection through a plane that contains both nuclei. The choice of symmetry planes is arbitrary. As long as you pick a plane and stick with it, you will always get the right answer. When an orbital is symmetric, it is labeled +. When an orbital is anti-symmetric, it is labeled -. To find the overall reflection of a state, use these rules:

- $(+)(+) \to +$
- (+)(-) → -
- (-)(-) → +

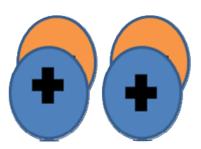
Reflection only applies to Σ states! For $\Lambda > 0$, there are no reflection labels! If you experiment with the rules, you will quickly realize why this is the case.

Example: What is the reflection of the state $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 2\pi_u^1 2\pi_u^1$?

You need to know what the orbitals look like. Draw a picture and then pick a plane. For this example, I'll use the plane of the page, but the orthogonal plane would have worked just as well.



The "vertical" orbital is +



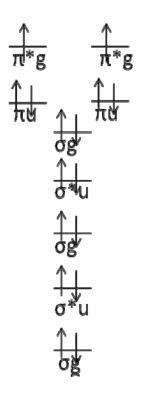
The "horizontal" orbital is -

Since one is + and one is -, the overall reflection is -. Try using the orthogonal plane and convince yourself that you still get the same answer.

All together now

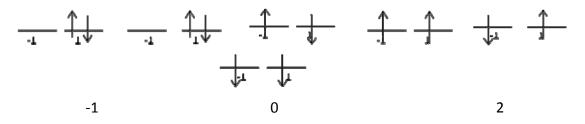
What are the term symbols for O₂?

The molecular orbital diagram for O is:



Where I chose arbitrary configurations for the last two electrons.

There are two open-shell electrons occupying the anti-bonding π_g orbitals. These are the only electrons that matter. It is easiest to simply draw all of the permutations and figure out the bounds on Λ and M_L by inspection. If we do this, it is easy to see that Λ = 2,0 and that M_L = 2,0,-2



0	1	0
1	2	1
0	1	0

The top row is a Λ =2 M_S=0 state, so it is $^1\Delta$. Both electrons are in the rightmost orbital. This orbital is gerade, and (g)(g) = g, so the parity label is g. We do not assign reflection labels to non Σ states, so the term symbol is $^1\Delta_g$

After removing the used up microstates, the chart becomes

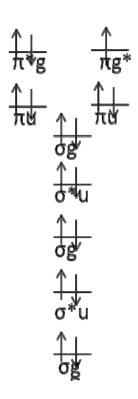
-1	0	2
1	1	1

This is a Λ =0 state with three possible spin configurations, so it is ${}^3\Sigma$. We know that the electrons are in different sub-orbitals (if you can't see this, try drawing all of the possible combinations that give Λ =0). Both of the orbitals are gerade, so the overall parity is gerade. One of the orbitals will be +, the other will be -. The final answer is

$$^{1}\Delta_{g}$$
 $^{3}\Sigma_{g}^{+}$

Write the term symbols for O_2 .

Draw the diagram.



There are only two possible configurations. It should be easy to see that the term symbol is $^2\Pi_{\rm g}.$