<u>Term states for a p^2 configuration</u>

For a p electron, m_l can take values -1, 0, 1, and m_s can take values +1/2, -1/2.
(From now on, I will designate the '+1/2' as just '+' and '-1/2' as just '-'.

The possible combinations of m_l and m_s for a given electron, say electron 1, are
(-1,+), (0,+), (1,+), (-1,-), (0,-), (1,-).
(You can work this out in another way. The degeneracy for l=1 state is **3**, i.e. [2l+1]. The spin degeneracy for single electron, s=1/2 is, **2**, i.e. [2s+1]. Hence the total degeneracy is [2l+1].[2s+1] = 6, which is what you wrote out explicitly above.)

Likewise for electron 2, the possible combinations are again six, as given above.
(-1,+), (0,+), (1,+), (-1,-), (0,-), (1,-).

If you take two electrons together, you will have 36 possible combinations, i.e. 6 x 6. However, not all possible combinations are allowed, as some combinations will be ruled out based on Pauli principle and the concept of indistinguishability. But anyway, let us write out all the possible 36 and then rule out the ones that should be ruled out.
m_l^1 = is the m_l for electron 1
m_l^2 = is the m_l for electron 2
m_s^1 = is the m_s for electron 1
m_s^2 = is the m_s for electron 2
m_L = sum of m_l^1 and m_l^2 and refers to the atom containing the two electrons. (Note the subscript "L" is upper case)
m_S = sum of m_s^1 and m_s^2 and refers to the atom containing the two electrons. (Note the subscript "S" is upper case).

In the table below, we will rule out (as we said earlier) certain microstates, based on two conditions.

First, we can't have those microstates, in which $m_l^1 = m_l^2$ **AND** $m_s^1 = m_s^{1.}$ If both quantum numbers are the same, that would violate the Pauli exclusion principle. Hence those must be excluded (such as entry 1 in Table 1).

Second, if two microstates differ only in the label of the electrons, then one of them must be excluded. What this means is the following:
if one microstate has (m_l^1, m_s^1) of (0,+) and (m_l^2, m_s^2) of (+1,-) (Entry 23 in Table 1)
and another microstate has (m_l^1, m_s^1) of (+1,-) and (m_l^2, m_s^2) of (0,+), (Entry 28 in Table 1)
you will see that the in the second microstate, the quantum numbers of the first and second electrons are simply exchanged compared with the first. Since the two electrons are indistinguishable, there is no way you can tell the two microstates apart from one another. Hence only one of them must be taken and the second rejected.

Based on the two conditions, you should reject certain microstates and only the allowed ones must be considered to derive the term states.

Now let us start the enumeration.

Table 1

No.	m_l^1	m_s^1	m_l^2	m_s^2	m_L	m_S	Allowed or not	Remarks
1.	-1	-	-1	-	-2	-1	x	Both electrons have identical quantum numbers
2	-1	-	-1	+	-2	0	√	OK
3	-1	-	0	-	-1	-1	√	OK
4	-1	-	0	+	-1	0	√	OK
5	-1	-	+1	-	0	-1	√	OK
6	-1	-	+1	+	0	0	√	OK
7	-1	+	-1	-	-2	0	x	Same as entry 2 - Indistinguishability
8	-1	+	-1	+	-2	1	x	Both electrons have identical quantum numbers
9	-1	+	0	-	-1	0	√	OK
10	-1	+	0	+	-1	1	√	OK
11	-1	+	+1	-	0	0	√	OK
12	-1	+	+1	+	0	1	√	OK
13	0	-	-1	-	-1	-1	x	Same as entry 3 - Indistinguishability
14	0	-	-1	+	-1	0	x	Same as entry 9 - Indistinguishability
15	0	-	0	-	0	-1	x	Both electrons have identical quantum numbers
16	0	-	0	+	0	0	√	OK
17	0	-	+1	-	+1	-1	√	OK
18	0	-	+1	+	+1	0	√	OK
19	0	+	-1	-	-1	0	x	Same as entry 4 - Indistinguishability
20	0	+	-1	+	-1	1	x	Same as entry 10 - Indistinguishability
21	0	+	0	-	0	0	x	Same as entry 16 - Indistinguishability
22	0	+	0	+	0	1	x	Both electrons have identical quantum numbers
23	0	+	+1	-	+1	0	√	OK
24	0	+	+1	+	+1	1	√	OK
25	+1	-	-1	-	0	-1	x	Same as entry 5 - Indistinguishability
26	+1	-	-1	+	0	0	x	Same as entry 11 - Indistinguishability
27	+1	-	0	-	+1	-1	x	Same as entry 17 - Indistinguishability
28	+1	-	0	+	+1	0	x	Same as entry 23 - Indistinguishability
29	+1	-	+1	-	+2	-1	x	Both electrons have identical quantum numbers
30	+1	-	+1	+	+2	0	√	OK
31	+1	+	-1	-	0	0	x	Same as entry 6 - Indistinguishability
32	+1	+	-1	+	0	1	x	Same as entry 12 - Indistinguishability
33	+1	+	0	-	+1	0	x	Same as entry 18 - Indistinguishability
34	+1	+	0	+	+1	1	x	Same as entry 24 - Indistinguishability
35	+1	+	+1	-	+2	0	x	Same as entry 30 - Indistinguishability
36	+1	+	+1	+	+2	1	x	Both electrons have identical quantum numbers

All shaded entries are disallowed.

Now collect all the allowed microstates that you wrote down above and arrange them to see how many microstates you have for each combination of (m_L,m_S) values. A total of 15 microstates is got.

Table 2

m_L	m_S	No of states	Got from entries
-2	0	1	2
-1	-1	1	3
-1	0	2	4,9
-1	1	1	10
0	-1	1	5
0	0	3	6,11,16
0	1	1	12
1	-1	1	17
1	0	2	18,23
1	1	1	24
2	0	1	30

You can rewrite the above information more elegantly as follows, if you see that for the atom, you have five values for m_L (-2, -1, 0, 1, 2) and three values for m_S = (1,0,-1). We will call this the "dot-diagram."

Table 3

	m_S		
m_L	-1	0	1
-2		•	
-1	•	••	•
0	•	•••	•
1	•	••	•
2		•	

I have put as many dots as I have microstates corresponding to that combination of (m_L,m_S). For example, I have three states corresponding to $m_L = 0$ and $m_S = 0$. Hence I have three dots in the corresponding square. (I hope you see the nice symmetry in the pattern!!)

No comes the tricky part. From the above information, how do you figure out what term states are present. It is easy if you go backwards at this point. Keep table 4 carefully aside and we will come back to that later. We will now see what I mean by going "backwards".

Now let us do another exercise.

If I told you have a ^1S state what does that mean. It means that L=0 and S=0 and therefore the allowed m_L and m_S values for this term state are $m_L = 0$ and $m_S = 0$. In other words, a ^1S state is signaled if you have with you a microstate where $m_L = 0$ and $m_S = 0$. In the "dot-diagram", this information can be represented as:

Table 4

m_L	-1	0	1
-2			
-1			
0		•	
1			
2			

What would you have if you have a ^3P state. It means that L=1 and S=1 and therefore the allowed m_L and m_S values for this term state are m_L = -1,0,+1 and m_S = -1,0,+1. This would mean 9 combinations: (-1,-1), (-1,0), (-1,+1), (0,-1), (0,0), (0,+1), (+1,-1), (+1,0), (+1,+1), where the first entry is an m_L value and the second is an m_S value. In other words, a collection of these 9 states immediately means a ^3P state. In a "dot-diagram", the ^3P state would be represented as:

Table 5

m_L	-1	0	1
-2			
-1	•	•	•
0	•	•	•
1	•	•	•
2			

Supposing I gave you two states, a ^3P and a ^1S. You know their individual dot diagrams. What would the combined dot diagram look like, for both ^3P and a ^1S? It would simply be a collection of the 10 states, 9 for ^3P and 1 for ^1S and would like the following.

Table 6

m_L	-1	0	1
-2			
-1	•	•	•
0	•	••	•
1	•	•	•
2			

Now let us add one more complication. What would you have, if you have a ^1D state. It means that L=2 and S=0 and therefore the allowed m_L and m_S values for this term state are m_L = -2, -1,0,+1, +2 and m_S = 0. This would mean 5 combinations: (-2,0), (-1,0), (0,0), (-1,0), (-2,0). In other words, a collection of these 5 states immediately means a ^1D state. In a "dot-diagram", the ^1D state would be represented as:

Table 7

m_L	-1	0	1
-2		•	
-1		•	
0		•	
1		•	
2		•	

What would the dot diagram look like if you had a collection of a ^3P, ^1S and a ^1D state. Just combine all the dot-diagrams. What you will get is the following.

Table 8

m_L	-1	0	1
-2		•	
-1	•	••	•
0	•	•••	•
1	•	••	•
2		•	

Compare this with what you got from Table 1, after you wrote all the microstates for p^2 configuration, then collected and systematized them through a dot diagram (Table 3). It is exactly the same; which simply means that the dot diagram you got from the microstates of a p^2 configuration (Table 3) is just representative of a ^3P, a ^1S and a ^1D state. This should clarify how you work out term symbols.

Even though working backwards makes it easier to understand the process, it is not the best way, because if you had new problem, you wouldn't know which term states to compare with. Having understood the method, we will now see how we can take Table 3 and work out the term states.
I will reproduce Table 3 again for you.

Table 3

	m_S		
m_L	-1	0	1
-2		•	
-1	•	••	•
0	•	•••	•
1	•	••	•
2		•	

A quick examination of Table 3, tells you that you have a microstate with m_L=-2 and m_S = 0. This immediately tells me, that I must have a ^1D state. But a ^1D state must also have other microstates corresponding to (-1,0), (0,0), (-1,0), (-2,0). From Table 3, remove all the dots corresponding to these microstates. Table 3 will now become

Table 3a

	m_S		
m_L	-1	0	1
-2			
-1	•	•	•
0	•	••	•
1	•	•	•
2			

From what remains, you will see that you have an entry for m_L= -1 and m_S = -1; this immediately tells you that you must have a ^3P state. This means that all the nine microstates corresponding to this term state must be removed. Table 3a now becomes

Table 3b

	m_S		
m_L	-1	0	1
-2			
-1			
0		•	
1			
2			

Only one microstate remains, which must naturally be due to ^1S.

Exercise 1:
As an exercise, take all the states that you rejected in Table 1, which must be 21 in number. Build a dot diagram corresponding to these rejected microstates and see what term states they correspond to.

If no Pauli restrictions were to be imposed, then combining two p electrons should have given you the following term states: ^3D, ^1D, ^3P, ^1P, ^3S, ^1S. (Why?) Of these, only three were allowed: ^1D, ^3P, ^1S, when you imposed the Pauli principle restrictions. Three were rejected; namely ^3D, ^1P, ^3S. These are just the same states you should get when you did Exercise 1 above.

Exercise 2:

If instead of a p^2 configuration, which implies that both electrons have the *same* principal quantum number, I gave you a 2p3p configuration. This is also p^2 stuff, which means that all the m_l^1, m_l^2 , m_s^1 and m_s^2 values you wrote out above are still valid. But the principal quantume number is now different. Hence the Pauli principle is straightway taken care of and you don't have to throw away any states in Table 1. There is no question of indistinguishability as the two electrons with different 'n' values can be told apart. Hence all 36 microstates are allowed and hence the term states for this configuration are ^3D, ^1D, ^3P, ^1P, ^3S, ^1S. Convince yourself of this point.

Exercise 3:

Now you can work out the term states for the d^2 configuration.