

[LS combinations] - the cases of 2p3p and 2p²

- **Equivalent and Nonequivalent Electrons**

Nonequivalent electrons are those differing in either n or l values, whereas equivalent electrons have the same n and l values.

- For instance, consider the combination of two p electrons.

(1) If they have different values of n (i.e., if they are nonequivalent electrons), then the combination is simple (e.g., 2p3p).

$$S = 0, 1, \quad L = 0, 1, 2 \quad \rightarrow \quad {}^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D$$
$$\rightarrow \quad 6 \text{ spectroscopic terms}$$

$$\rightarrow \quad {}^1S_0, {}^1P_1, {}^1D_2, {}^3S_1, {}^3P_{0,1,2}, {}^3D_{1,2,3}$$
$$\rightarrow \quad 10 \text{ spectroscopic levels}$$

We can have $(2J+1)$ states for each J value. Therefore, we have 36 states available in total.

$$\rightarrow \quad 1 + 3 + 5 + 3 + 9 + 15 = 36$$
$$(\quad = 3^2 \times 2^2) \text{ distinguishable states}$$

There are two possible states $m_s = \pm 1/2$ for spin of each electron, and three possible states $m_l = -1, 0, 1$ for orbital angular momentum of each electron. Therefore, we can expect that there are $2^2 \times 3^2 = 36$ distinguishable states.

(2) If two p electrons have the same n values and thus equivalent. Then all the 36 states are not available: some are ruled out by the Pauli exclusion principle, and some are ruled out because they are not distinguishable from others.

There are two ways to obtain the spectroscopic terms:

The first way is to use a table, as in the right-hand side.

- We can find there are 15 distinguishable states allowed. The following table shows the states that are excluded by Pauli's exclusion principle and labels only distinguishable states.

m_{l1}	m_{l2}	m_{s1}	m_{s2}	Label	m_{l1}	m_{l2}	m_{s1}	m_{s2}	Label
+1	+1	$+\frac{1}{2}$	$+\frac{1}{2}$	OUT	0	-1	+	+	11
		+	-	1			+	-	12
		-	+	1			-	+	13
		-	-	OUT			-	-	14
+1	0	+	+	2	-1	+1	+	+	6
		+	-	3			+	-	8
		-	+	4			-	+	7
		-	-	5			-	-	9
+1	-1	+	+	6	-1	0	+	+	11
		+	-	7			+	-	13
		-	+	8			-	+	12
		-	-	9			-	-	14
0	+1	+	+	2	-1	-1	+	+	OUT
		+	-	4			+	-	15
		-	+	3			-	+	15
		-	-	5			-	-	OUT
0	0	+	+	OUT					
		+	-	10					
		-	+	10					
		-	-	OUT					

OUT : Pauli excluded states.

Only distinguishable states are labelled.

Label	M_S	M_L	M_J	Level
1	0	+2	+2	(1) 1D_2
2	+1	+1	+2	(2) 3P_2
3	0	+1	+1	(1) 1D_2
4	0	+1	+1	(2) 3P_2
5	-1	+1	0	(2) 3P_2
6	+1	0	+1	(3) 3P_1
7	0	0	0	(1) 1D_2
8	0	0	0	(3) 3P_1
9	-1	0	-1	(3) 3P_1
10	0	0	0	(5) 1S_0
11	+1	-1	0	(4) 3P_0
12	0	-1	-1	(1) 1D_2
13	0	-1	-1	(2) 3P_2
14	-1	-1	-2	(2) 3P_2
15	0	-2	-2	(1) 1D_2

- We must now compare these states with the states expected in the LS multiplet: 1S_0 , 1P_1 , 1D_2 , 3S_1 , $^3P_{0,1,2}$, $^3D_{1,2,3}$.
 - Of these, we immediately see that 3D_3 state cannot be present, since this would require M_J values of +3 and -3. This in turn rules out the presence of 3D_2 and 3D_1 , since if one possible combination of a given L and S is present, all must be.
 - State 1 can come only from an LS term having $L \geq 2$ and $S \geq 0$; from this we conclude that the 1D_2 term must be present.
 - State 2 requires the present of an LS term with $L \geq 1$ and $S \geq 1$. Of the available combinations, this requires that $^3P_{0,1,2}$ be present.
 - We now found how many independent LS terms are known to be present. We have from $^3P_{0,1,2}$, $1+3+5 = 9$ states; from 1D_2 , 5 states; a total of 14.
 - Those states requires M_J values of +2, +1, 0, -1, -2; +1, 0, -1; 0; and +2, +1, 0, -1, -2, respectively.
 - These account for all of the M_J values in the table except for one, whose M_J value is zero. This then requires 1S_0 , to be present.
- \Rightarrow Finally, we obtain 1S_0 , 1D_2 , $^3P_{0,1,2}$.

The second method is to use the Pauli principle.

This is much simpler than the above method.

Recall that the Pauli principle states that **the total eigenfunction must be antisymmetric with respect to the exchange of two particles**. Therefore, we can have only two distinct cases:

- (a) symmetric function for the spin + antisymmetric function for the orbital angular momentum $\Rightarrow {}^3P$
- (b) antisymmetric function for the spin + symmetric function for the orbital angular momentum $\Rightarrow {}^1S, {}^1D$

Note that among the six terms ${}^1S, {}^1P, {}^1D, {}^3S, {}^3P, {}^3D$, the following terms are all excluded.

1P is antisymmetric for both spin and orbital angular momenta

3S is symmetric for both spin and orbital angular momenta

3D is also symmetric for both spin and orbital angular momenta

Because

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|---|--|
| $S = 0 \rightarrow s_1 = 1/2, s_2 = -1/2$ | : Product of two spin functions are antisymmetric w.r.t. the exchange |
| $S = 1 \rightarrow s_1 = 1/2, s_2 = 1/2$ | : Product of two spin functions are symmetric. |
| $L = 1 \rightarrow l_1 = 1, l_2 = 0$ | : The first wavefunction is antisymmetric and the second one is symmetric.
Therefore, their product is antisymmetric w.r.t. the exchange. |
| $L = 2 \rightarrow l_1 = 1, l_2 = 1$ | : Both are antisymmetric. Therefore, their product is symmetric. |