

# [LS combinations] - 2p3p

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- **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.

- **Consider the combination of two p electrons.**

(1) **2p3p** - Two electrons are nonequivalent.

In this nonequivalent case, all possible spectroscopic combinations are available.

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

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

We can have  $(2J+1)$  states for each  $J$  value.

Therefore, 36 distinguishable states are available in total.

$$\rightarrow \quad 1 + 3 + 5 + 3 + 9 + 15 = 36$$

There are two possible states  $m_s = \pm 1/2$  for spin of each electron, and three states  $m_l = -1, 0, 1$  for orbital angular momentum of each electron.

Thus, we expect that there will be  $2^2 \times 3^2 = 36$  distinguishable states.

## 2p<sup>2</sup>

(2) **2p<sup>2</sup>** - Two electrons are equivalent.

Then, all the 36 states are not available. Some are ruled out by Pauli exclusion principle, and some are ruled out because they are not distinguishable from others.

- The first step is to make a table to label the states for a single electron (e.g., a, b, c, d, e, f), as shown in Table 1.

Table 1

Label	m <sub>l</sub>	m <sub>s</sub>
a	+1	+1/2
b	0	+1/2
c	-1	+1/2
d	+1	-1/2
e	0	-1/2
f	-1	-1/2

Table 2

	States	$M_L$	$M_S$
1	ab	1	1
2	ac	0	1
3	ad	2	0
4	ae	1	0
5	af	0	0
6	bc	-1	1
7	bd	1	0
8	be	0	0
9	bf	-1	-1
10	cd	0	0
11	ce	-1	0
12	cf	-2	0
13	de	1	-1
14	df	0	-1
15	ef	-1	-1

- Next step is to make a table for the combination of  $(M_L, M_S)$  of two electrons, as shown in Table 2. Here,  $M_L = m_{l1} + m_{l2}$ , and  $M_S = m_{s1} + m_{s2}$ .
  - According to Pauli's exclusion principle, the states that have two identical states (aa, bb, cc, dd, ee, and ff) are not allowed.
  - Notice also that "ab" and "ba" states are identical and thus the "ba" state is ignored. Other identical combinations are also ignored.
- Following the above two rules, we construct Table 2 which contains 15 distinguishable states.

Table 3

States	$M_L$	$M_S$	Term 1	Term 2	Term 3
ab	1	1		$^3P$	
ac	0	1		$^3P$	
ad	2	0	$^1D$		
ae	1	0	$^1D$		
af	0	0	$^1D$		
bd	1	0		$^3P$	
be	0	0		$^3P$	
cd	0	0			$^1S$

- In addition to the above two rules, we can recognize that every “negative” values have always their “positive” counterparts.
  - Therefore, it is more convenient to remove the states with negative values. This gives us Table 3, which contains only 8 states.
- Now, we pick the states starting with the largest  $M_L$  and and the largest  $M_S$ .
  - (ad)  $M_L = 2$  and  $M_S = 0$ : The presence of the  $M_L = 2, M_S = 0$  indicates that a  $^1D$  term is among the possible terms. To this term we must further assign states with  $M_L = 1, 0$  and  $M_S = 0$ . What is left?
  - (ab)  $M_L = 1$  and  $M_S = 1$ : This is the next largest values. The combination  $M_L = 1, M_S = 1$  indicates that a  $^3P$  term is among the possible terms. To this term we must further assign states with  $M_L = 1, 0$  and  $M_S = 1, 0$ . What is left?
  - (cd)  $M_L = 0$  and  $M_S = 0$ : This is the only remaining combination. This that a  $^1S$  term is among the possible terms.
  - **Finally, we obtain 3 terms  $^1D$ ,  $^3P$ , and  $^1S$ .**
  - **The 3 terms are split into 5 levels :  $^1D_2$ ,  $^3P_{0,1,2}$ , and  $^1S_0$ .**

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*When we have only two electrons, we can use the Pauli principle to obtain the terms.*

This method is much simpler than the above method. However, this method is not easy to apply to the case of three electrons.

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

$S = 0 \rightarrow s_1 = 1/2, s_2 = -1/2$  : 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.

### (3) 2p<sup>3</sup> - Three electrons are equivalent.

- According to Pauli's exclusion principle, any states that include two identical states (aaa, aab, aac, add, bbc, bcc, etc) are not allowed.
- We have only seven states that have non-negative values, as shown in Table 4.

Table 4

States	M <sub>L</sub>	M <sub>S</sub>	Term 1	Term 2	Term 3
abc	0	3/2			<sup>4</sup> S
abd	2	1/2	<sup>2</sup> D		
abe	1	1/2	<sup>2</sup> D		
abf	0	1/2	<sup>2</sup> D		
acd	1	1/2		<sup>2</sup> P	
ace	0	1/2		<sup>2</sup> P	
bcd	0	1/2			<sup>4</sup> S

Table 1

Label	m <sub>l</sub>	m <sub>s</sub>
a	+1	+1/2
b	0	+1/2
c	-1	+1/2
d	+1	-1/2
e	0	-1/2
f	-1	-1/2

- Now, we pick the states starting with the largest  $M_L$  and then the largest  $M_S$ .
  - (abd)  $M_L = 2$  and  $M_S = 1/2$ : This indicates that a <sup>2</sup>D term is among the possible terms. To this term we must further assign states with  $M_L = 1, 0$  and  $M_S = 1/2$ . What is left?
  - (acd)  $M_L = 1$  and  $M_S = 1/2$ : This indicates the presence of a <sup>2</sup>P term. To this term we must further assign states with  $M_L = 0$  and  $M_S = 1/2$ . What is left?
  - (abc)  $M_L = 0$  and  $M_S = 3/2$ : This indicates the presence of a <sup>4</sup>S term.
  - *Finally, we obtain three terms (<sup>2</sup>D, <sup>2</sup>P, and <sup>4</sup>S) and five levels : <sup>2</sup>D<sub>3/2, 5/2</sub>, <sup>2</sup>P<sub>1/2, 3/2</sub>, and <sup>4</sup>S<sub>3/2</sub>.*