

**Angular Momentum Coupling Schemes**

We have so far considered only the coupling of the spin and orbital momentum of a single electron by means of the spin-orbit interaction. We now consider the case of two electrons, or more, for which there are four constituent momenta.

**Multiplicity (Statistical weight)**

For the uncouple state  $|n \ell m_\ell s m_s\rangle$ ,  $\ell$  takes the values:  $0, 1, \dots, n - 1$  for a given  $n$ , and  $m_\ell$  takes the values:  $-\ell, -\ell + 1, \dots, \ell$  for a given  $\ell$ . So, the multiplicity of the state  $\ell$  can be given by:

$$\omega_\ell = \sum_{m_\ell=-\ell}^{\ell} 1 = (2\ell + 1) = \hat{\ell}$$

For the spin  $s$ , the multiplicity is given by:

$$\omega_s = \sum_{m_s=-s}^s 1 = (2s + 1) = \hat{s}$$

So, for a given  $\ell$  and  $s$  the multiplicity (statistical weight) is written as:

$$\omega = \omega_\ell \omega_s = (2\ell + 1)(2s + 1) = \hat{\ell} \hat{s}$$

**Remarks:**

i- For single electron,  $\omega$  will gives the maximum number of electrons fills the states  $|n \ell m_\ell s m_s\rangle$ :

$$\omega = \omega_\ell \omega_s = (2\ell + 1)(2 \times \frac{1}{2} + 1) = 2\hat{\ell}$$

$\ell$	Term	$\omega$
0	S	2
1	P	6
2	D	10
3	F	14

ii- For a given  $n$ , maximum number of electrons:

$$\omega = 2 \sum_{\ell=0}^{n-1} (2\ell + 1) = 2(\sum 2\ell + \sum 1) = 2 \left\{ 2 \frac{n(n-1)}{2} + n \right\} = 2n^2$$

iii-  $\omega$  could be also written in a simpler form as:

$$\omega = \binom{2\hat{\ell}}{N} = \frac{(2\hat{\ell})!}{N!(2\hat{\ell} - N)!}$$

$\ell$	Term	$\omega$
0	S	$\binom{2}{1} = \frac{2!}{1!(2-1)!} = 2$
1	P	$\binom{6}{1} = \frac{6!}{1!(6-1)!} = 6$
2	D	$\binom{10}{1} = \frac{10!}{1!(10-1)!} = 10$
3	F	$\binom{14}{1} = \frac{14!}{1!(14-1)!} = 14$

iv- In general, for **uncoupled** states  $|\ell_1 s_1\rangle, |\ell_2 s_2\rangle, \dots, |\ell_n s_n\rangle$ , we have:

$$\omega = \prod_{i=1}^n \hat{\ell}_i \hat{s}_i = \prod_{i=1}^n \binom{2\hat{\ell}_i}{N_i}$$

Term	$\omega$
ns n's	$\binom{2}{1} \binom{2}{1} = 4$
ns <sup>2*</sup>	$\binom{2}{2} = \frac{2!}{2!(2-2)!} = 1$
ns n'p	$\binom{2}{1} \binom{6}{1} = 12$
np n'p	$\binom{6}{1} \binom{6}{1} = 36$
np <sup>2*</sup>	$\binom{6}{2} = \frac{6!}{2!(6-2)!} = 15$

\*Due to Pauli's exclusion principle, we have to be very careful for calculating  $\omega$  using  $\hat{\ell} \hat{s}$  formula. We will come to this problem very soon.

**In summary:** for the states  $(n\ell n\ell')$  we have to use  $\omega(n\ell n\ell') = 2\hat{\ell} 2\hat{\ell}'$ , and for the states  $(n\ell^2)$ , we have to use  $\omega(n\ell^2) = (2\ell + 1)(4\ell + 1)$

**LS-coupling:**  $\{(s_1 s_2)S, (\ell_1 \ell_2)L\}$  term symbol  $^{(2S+1)}L$ ,

$S = (s_1 + s_2), (s_1 + s_2) - 1, \dots, |s_1 - s_2|$ , and  $L = (\ell_1 + \ell_2), (\ell_1 + \ell_2) - 1, \dots, |\ell_1 - \ell_2|$

**Example 1:** for the state np n'p: Here we have:  $\left\{ \left( \frac{1}{2} \frac{1}{2} \right) S, (11)L \right\} \Rightarrow S = 0, 1, \quad L = \begin{Bmatrix} 0 & 1 & 2 \\ \downarrow & \downarrow & \downarrow \\ S & P & D \end{Bmatrix}$

**Table: LS Coupling of two inequivalent p-electrons  $np n'p$**

S	L	Spectral term	Multiplicity $\hat{S} \hat{L}$
0	0	<sup>1</sup> S	1
	1	<sup>1</sup> P	3
	2	<sup>1</sup> D	5
1	0	<sup>3</sup> S	3
	1	<sup>3</sup> P	9
	2	<sup>3</sup> D	15
Total			36

**Table: LS Coupling of three inequivalent p-electrons  $np\ n'\ p\ n''\ p$**

		$np\ n'\ p$ (Parent states)					$np\ n'\ p\ n''\ p$	
S	L	Spectral term	$\hat{S}\ \hat{L}$	S'	L'	Spectral term	$\hat{S}\ \hat{L}$	
0	0	$^1S$	1	$\frac{1}{2}$	1	$^2P$	6	
	1	$^1P$	3			$^2S, ^2P, ^2D$	2+6+10	
	2	$^1D$	5			$^2P, ^2D, ^2F$	6+10+14	
1	0	$^3S$	3	$\frac{1}{2}, \frac{3}{2}$	1	$^2P, ^4P$	6+12	
	1	$^3P$	9			$^2S, ^2P, ^2D, ^4S, ^4P, ^4D$	2+6+10+4+12+20	
	2	$^3D$	15			$^2P, ^2D, ^2F, ^4P, ^4D, ^4F$	6+10+14+12+20+28	
Total			36				216	

**Example 2:** for the state  $n\ell^2$  we have  $\left\{\left(\frac{1}{2}\ \frac{1}{2}\right)S, (\ell\ell)L\right\} \Rightarrow S = 0, 1, \quad L = \ell + \ell, \ell + \ell - 1, \dots, 0$ . In this case “L+S should be even”.

**Table: LS Coupling of two equivalent s-electrons  $ns^2$**

S	L	Spectral term	Multiplicity $\hat{S}\ \hat{L}$
0	0	$^1S$	1
1	0	$^3S$	3 (forbidden)
Total			1

**Table: LS Coupling of two equivalent p-electrons  $np^2$**

S	L	Spectral term	Multiplicity $\hat{S}\ \hat{L}$
0	0	$^1S$	1
	1		3 (forbidden)
	2	$^1D$	5
1	0		3 (forbidden)
	1	$^3P$	9
	2		15 (forbidden)
Total			15

**Table: LS Coupling of two equivalent p-electrons + one p-electrons  $np^2\ n'\ p,$**

		$np^2$ (Parent states)		$np^2\ n'\ p,$	
S	L	Spectral term	Multiplicity $\hat{S}\ \hat{L}$	Spectral term	$\hat{S}\ \hat{L}$
0	0	$^1S$	1	$^2P$	6
	1		3 (forbidden)	$^2P, ^2D, ^2F$	6+10+14
	2	$^1D$	5		
1	0		3 (forbidden)	$^2S, ^2P, ^2D, ^4S, ^4P, ^4D$	2+6+10+4+12+20
	1	$^3P$	9		
	2		15 (forbidden)		
Total			15		90

**LSJ-coupling (Intermediate coupling):**  $\{(s_1 s_2)S, (\ell_1 \ell_2)L\} J$  term symbol  $^{(2S+1)}L_J$

The Russell-Saunders **LSJ**-model has been more successful in accounting for atomic spectra of all but the heavier atoms. The model assumes that, the electrostatic interaction, including exchange forces, between two electrons dominates the spin-orbit interaction. In this case, the orbital momenta and the spins of the two electrons couple separately to form

$$\vec{L} = \vec{L}_1 + \vec{L}_2, \text{ and } \vec{S} = \vec{S}_1 + \vec{S}_2$$

The total angular momentum is given, as before, by

$$\vec{J} = \vec{L} + \vec{S}$$

For two inequivalent p-electrons we have:  $l = 2, 1, \text{ or } 0$  and  $s = 1 \text{ or } 0$ .

For each  $l$  and  $s$ , the  $j$ -values are :  $(l + s), (l + s) - 1, \dots, |l - s|$

and for each  $j$  value there are  $(2j+1)$  values of  $m_j$ . The combinations are given in the table below.

It will be observed that, although the number of states is once again 36 in a weak magnetic field, their energies are not the same as those in the  $j$ - $j$  coupling scheme (will be discussed ).

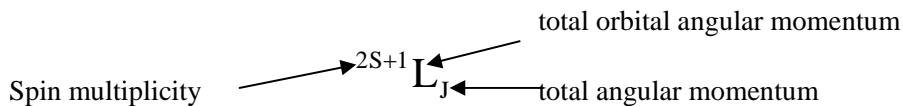
$$S = (s_1 + s_2), (s_1 + s_2) - 1, \dots, |s_1 - s_2|,$$

$$L = (\ell_1 + \ell_2), (\ell_1 + \ell_2) - 1, \dots, |\ell_1 - \ell_2|, \text{ and}$$

$$J = (L + S), (L + S) - 1, \dots, |L - S|,$$

The term symbol has the following information:

- 1.) Multiplicity
- 2.) Total angular momentum,  $\vec{J}$
- 3.) Total orbital angular momentum,  $\vec{L}$



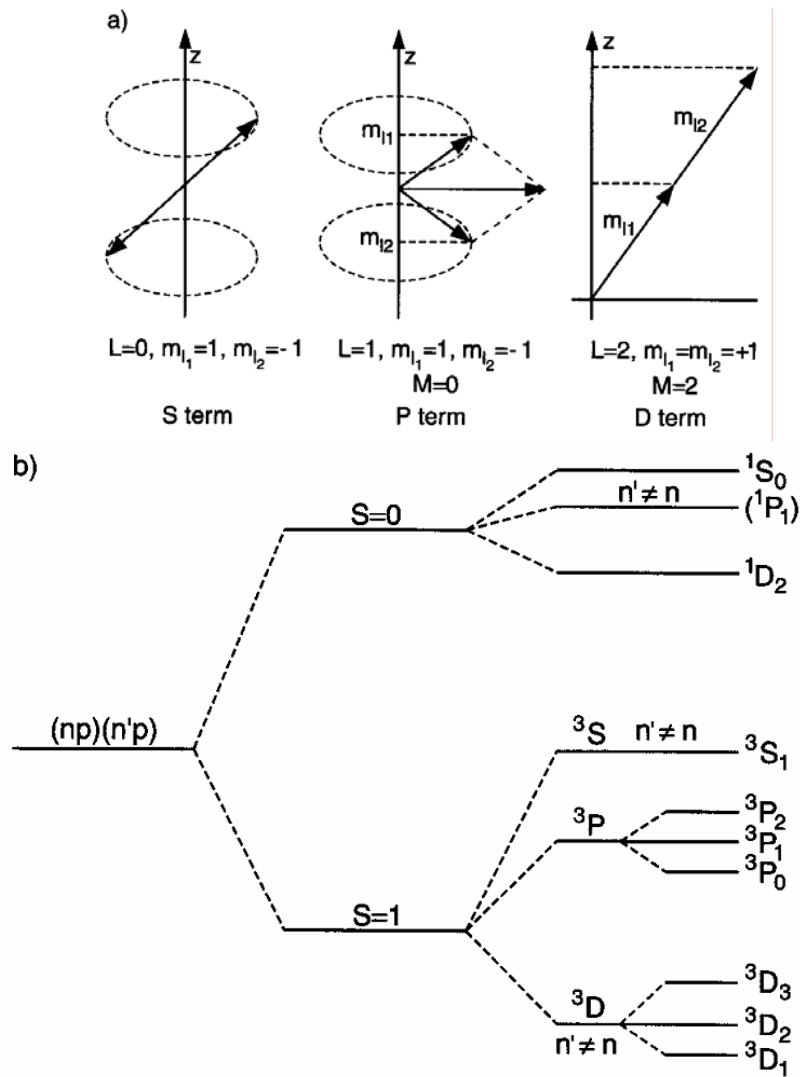
The orbital angular momentum is given as letter symbol.

L	0	1	2	3	4	5	etc...
symbol	S	P	D	F	G	H	etc...

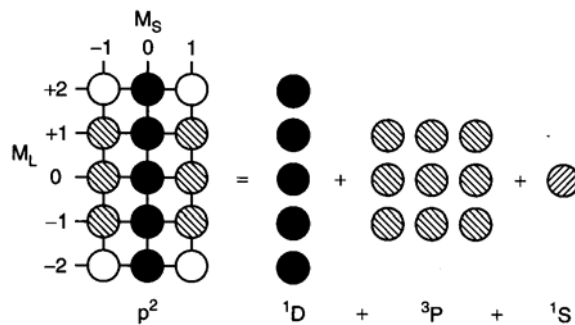
**Example:** for the state  $np n'p$ : Here we have  $\left\{ \left( \frac{1}{2} \frac{1}{2} \right) S, (11)L \right\} \Rightarrow S = 0, 1, L = 0, 1, 2$

**Table : Russell-Saunders coupling of two inequivalent p-electrons  $np n'p$**

S	L	J	Spectral term	Multiplicity $\sum \hat{J}_i = \hat{S} \hat{L}$
0	0	0	$^1S_0$	1
	1	1	$^1P_1$	3
	2	2	$^1D_2$	5
1	0	1	$^3S_1$	3
	1	0,1,2	$^3P_{0,1,2}$	1+3+5
	2	1,2,3	$^3D_{1,2,3}$	3+5+7
Total				36



**Fig. 6.34.** (a) Vector model of the  $p^2$ -configuration. (b) Term diagram. The blue levels are only possible for  $n_1 \neq n_2$



**Fig. 6.35.** Slater diagram of all levels ( $M_L, M_S$ ) for a  $p^2$ -configuration of equivalent electrons ( $n_1 = n_2$ ). The white circles are not observed because of the Pauli principle

The white circles indicate states that are forbidden by the Pauli's exclusion principle.

**j-j-coupling:**  $\{(\ell_1 s_1) j_1, (\ell_2 s_2) j_2\} J$  term symbol  $(j_1, j_2)_J$

So far, we have considered only LS-coupling and LSJ-coupling conditions, in which the electrostatic interactions between electrons are much stronger than the interaction between the spin of an electron and its own orbital motion. With increasing Z, the spin-orbit interactions become increasingly more important; in the limit in which these interactions become much stronger than the Coulomb terms, the coupling conditions approach pure jj coupling.

In the jj-coupling scheme, basis functions are formed by first coupling the spin of each electron to its own orbital angular momentum, and then coupling together the various resultants  $j_1$  in some arbitrary order to obtain the total angular momentum J:

This model assumes that the spin-orbital interaction dominates the electrostatic interactions between the particles. Thus, we write for each particle

$$\vec{J}_1 = \vec{L}_1 + \vec{S}_1 \quad \text{and} \quad \vec{J}_2 = \vec{L}_2 + \vec{S}_2$$

The total angular momentum is obtained by combining  $\vec{J}_1$  and  $\vec{J}_2$ :

$$\vec{J} = \vec{J}_1 + \vec{J}_2$$

and

$$j_i = (\ell_i + s_i), (\ell_i + s_i) - 1, \dots, |\ell_i - s_i|, \quad \text{and} \quad J = (j_1 + j_2), (j_1 + j_2) - 1, \dots, |j_1 - j_2|$$

**Example 4:** for the state  $np \ n'p$ : Here we have  $\left\{ \left(1 \frac{1}{2}\right) j_1, \left(1 \frac{1}{2}\right) j_2 \right\} \Rightarrow j_1 = \frac{1}{2}, \frac{3}{2}, \quad j_2 = \frac{1}{2}, \frac{3}{2}$

**Table: j-j Coupling of two inequivalent p-electrons  $np \ n'p$**

$j_1$	$j_2$	J	Spectral term	Multiplicity $\sum \hat{J}_i = \hat{J}_1 \hat{J}_2$
$\frac{1}{2}$	$\frac{1}{2}$	0,1	$\left(\frac{1}{2}, \frac{1}{2}\right)_{0,1}$	1+3
	$\frac{3}{2}$	1,2	$\left(\frac{1}{2}, \frac{3}{2}\right)_{1,2}$	3+5
$\frac{3}{2}$	$\frac{1}{2}$	1,2	$\left(\frac{3}{2}, \frac{1}{2}\right)_{1,2}$	3+5
	$\frac{3}{2}$	0,1,2,3	$\left(\frac{3}{2}, \frac{3}{2}\right)_{0,1,2,3}$	1+3+5+7
Total				36

In a weak magnetic field, each state of a given j will split into  $(2j+1)$  states corresponding to the allowed values of  $m_j$ .

Although the j-j coupling is used extensively for the description of the nuclear states observed in nuclear spectroscopy, it is not appropriate for many atomic systems because of the strong electrostatic and other interactions between the two electrons.

The rules for finding the states for two equivalent electrons are:

- 1- when  $j_1 \neq j_2$ , the value of J in  $(j_1, j_2)_J$  is found by the rules for the coupling of angular momenta.
- 2- When  $j_1 = j_2 = j$ , the allowed values of J in j are given by :  $J = 2j - 1, 2j - 3, \dots$

**Angular Momentum; Russell-Saunders coupling vs. *jj*-coupling; Term Symbols**

1. Calculate the allowed values of  $j$  for a  $d$  electron.

$$j = l + s, l + s - 1, \dots, |l - s|$$

For a  $d$  electron,  $l = 2$ ,  $s = 1/2$ . Therefore,  $j = \frac{5}{2}, \frac{3}{2}$

2. The quantum number  $L$  represents the total orbital angular momentum, and describes  $l-l$  coupling of the orbital angular momentum of two or more electrons. Determine the values of  $L$  for two  $d$  electrons. What are the corresponding letter symbols? *Hint*: The quantum number  $L$  may have values between the sum of the  $l$  values of the individual electrons and the absolute value of the difference of these numbers.  $L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$

The value of  $l$  for  $d$  electrons is 2. Therefore,

$$L = 2 + 2, 2 + 2 - 1, 2 + 2 - 2, 2 + 2 - 3, |2 - 2|$$

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

The value of  $L$  determines the letter symbol as follows,  $L = 0$  for S;  $L = 1$  for P;  $L = 2$  for D;  $L = 3$  for F;  $L = 4$  for G; etc. Therefore, the letter symbols corresponding to  $L = 4, 3, 2, 1, 0$  are G, F, D, P, and S respectively.

3. The quantum number  $S$  represents the total spin angular momentum, and describes the  $s-s$  coupling of the spin angular momentum of two or more electrons. Determine the values of  $S$  for two  $d$  electrons.

For two electrons

$$S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} - \frac{1}{2}$$

$$S = 1, 0$$

4. The quantum number  $J$  represents the total angular momentum, and describes the Russell-Saunders coupling between  $L$  and  $S$ . Determine the values of  $J$  for two  $d$  electrons. *Hint*: the allowed values of  $J$  are given by  $J = L + S, L + S - 1, \dots, |L - S|$

$$L = 4, S = 0, J = 4$$

$$L = 4, S = 1, J = 5, 4, 3$$

$$L = 3, S = 0, J = 3$$

$$L = 3, S = 1, J = 4, 3, 2$$

$$L = 2, S = 0, J = 2$$

$$L = 2, S = 1, J = 3, 2, 1$$

$$L = 1, S = 0, J = 1$$

$$L = 1, S = 1, J = 2, 1, 0$$

$$L = 0, S = 0, J = 0$$

$$L = 0, S = 1, J = 0, 1$$

5. Write the complete term symbols for the following states

- (a)  $L = 4, S = 1, J = 5;$
- (b)  $L = 2, S = 0, J = 2;$
- (c)  $L = 0, S = 0, J = 0$

The format for the term symbols is  $^{2S+1}X_J$ . The value of  $L$  determines the letter symbol  $X$  as follows,  $L = 0$  for S;  $L = 1$  for P;  $L = 2$  for D;  $L = 3$  for F;  $L = 4$  for G; etc. This leads to the following term symbols:

- (a)  ${}^3G_5$
- (b)  ${}^1D_2$
- (c)  ${}^1S_0$

6. Determine the electronic configuration for an atom with the term symbol  ${}^4S_{3/2}$ .

The value of the quantum number  $S$  can be determined from the multiplicity.

$$2S + 1 = 4$$

$$S = \frac{3}{2} = M_S$$

This implies that there are three unpaired electrons. The S letter symbol gives  $L = M_L = 0$ . This indicates that there is one electron in each of the  $p$  orbitals because  $M_L = (+1) + 0 + (-1) = 0$ . The configuration is  $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$

7. List the quantum numbers  $L$ ,  $S$ , and  $J$  for the following terms symbols:

- (a)  ${}^4G_{5/2}$
- (b)  ${}^3P_2$
- (c)  ${}^2D_{3/2}$ .

The format for the term symbols is  $^{2S+1}X_J$ , where  $S$  is the spin quantum number,  $(2S + 1)$  is the multiplicity, and  $J$  is the total angular momentum quantum number. The value of  $L$  determines the letter symbol  $X$  as follows,  $L = 0$  for S;  $L = 1$  for P;  $L = 2$  for D;  $L = 3$  for F;  $L = 4$  for G; etc.

$$(a) \quad L = 4; S = \frac{4-1}{2} = \frac{3}{2}; J = \frac{5}{2}$$

$$(b) \quad L = 1; S = \frac{3-1}{2} = 1; J = 2$$

$$(c) \quad L = 2; S = \frac{2-1}{2} = \frac{1}{2}; J = \frac{3}{2}$$

8. Derive the ground state term symbol for the following configuration  $(5s)^1(4d)^4$ , if given that  $J = 1/2$ .

$$M_L = L = 0 + (+2) + (+1) + 0 + (-1) = +2$$

$$M_S = S = \left(+\frac{1}{2}\right) + \left(+\frac{1}{2}\right) + \left(+\frac{1}{2}\right) + \left(+\frac{1}{2}\right) + \left(+\frac{1}{2}\right) = \frac{5}{2}$$

$$2S + 1 = 2\left(\frac{5}{2}\right) + 1 = 6$$

The term symbol is  ${}^6D_{1/2}$ . Note that all 5 electrons are unpaired.



9. Give the term symbol for Li:  $1s^2 2s^1$ .

$S = \frac{1}{2}, L = 0, J = \frac{1}{2}$  so the term is  $^2S_{1/2}$ . Note that we are only considering the unpaired electron.

10. Find the total angular momentum states ( $L, M_L$ ) for two electrons, one  $p$ -type and one  $d$ -type.

The quantum number  $L$  may have values between  $2 + 1 = 3$  and  $2 - 1 = 1$ .

$L = 3, M_L = 3, 2, 1, 0, -1, -2, -3$  (7 states)

$L = 2, M_L = 2, 1, 0, -1, -2$  (5 states)

$L = 1, M_L = 1, 0, -1$  (3 states)

The total number of states is  $7 + 5 + 3 = 15$ .

11- When spin-orbit coupling is large, Russell-Saunders coupling fails and  $jj$ -coupling must be used. It involves first coupling the individual spin and orbital momenta of the electrons into individual  $j$  values. Then, the quantum number  $J$  may have values between the sum of the  $j$  values of the individual electrons and the absolute value of the difference of these numbers.

$J = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$ . If there are more than 2 electrons, then  $j_1$  is first coupled to  $j_2$  to find a  $J_{12}$ . Then the total angular momentum  $J$  is found by coupling  $j_3$  to  $J_{12}$ .

Find all possible values of  $J$  for  $j_1 = 1, j_2 = \frac{1}{2}, j_3 = \frac{1}{2}$ .

First, add  $j_1$  and  $j_2$  to obtain  $J_{12} = \frac{3}{2}, \frac{1}{2}$ . Then add  $j_3 = \frac{1}{2}$  to the  $J_{12} = \frac{3}{2}$  state to obtain  $J = 2, 1$ ;

and add  $j_3 = \frac{1}{2}$  to the  $J_{12} = \frac{1}{2}$  state to obtain  $J = 1, 0$ . Therefore,  $J = 2, 1, 1, 0$ . Note that there are two states with  $J = 1$ .

**Not complete**

Possible quantum numbers for levels resulting from a  $np^2$  electron configuration with  $n_1=n_2=n$

L	S	$m_{\ell_1}$	$m_{\ell_2}$	$m_{s_1}$	$m_{s_2}$	$M_S$	$M_J$	Spectral term	Multiplicity $\hat{S} \hat{L}$
0	0	0	0	$\alpha$	$\beta$	0	0	$^1S_0$	1
2	0	0	-1	$\alpha$	$\alpha$	+1	0	$^1D_2$	5
1	1	1 1 0 1 0	0 -1 0 -1 -1	$\alpha$ $\alpha$ $\alpha$ $\beta$ $\beta$				$^3P_{0,1,2}$	3 (forbidden) 9 15 (forbidden)
Total									15