

What about when we have 2 valence  $e^-$  in same orbital?

$$CI (1s^2 2s^2) 2p^2 \Rightarrow l_1=1 \quad l_2=1 \Rightarrow L=2, 1, 0$$

$$s_1=1/2 \quad s_2=1/2 \Rightarrow S=1, 0$$

$$2s+1 = 3, 1$$

Possible terms are:

<u>L</u>	<u>S</u>	<u>J</u>	<u>Terms</u>
0	0	0	$^1S_0$
1	0	1	$^1P_1$
2	0	2	$^1D_2$
0	1	1	$^3S_1$
1	1	2, 1, 0	$^3P_2, ^3P_1, ^3P_0$
2	1	3, 2, 1	$^3D_3, ^3D_2, ^3D_1$

However - since these 2  $e^-$  are in SAME SHELL we must use Pauli's exclusion principle to see which terms are allowed

For each  $e^-$   $l=1 \Rightarrow m_l = -1, 0, +1$  and  $m_s = \pm 1/2$

so there are  $3 \times 2 = 6$  possible one  $e^-$  states

For 2  $e^-$ , there are  $\binom{6}{2} = \frac{6!}{2!(6-2)!} = \frac{6 \cdot 5}{2} = 15$  unique  $2 e^-$  states

What are they and which terms do they correspond to?

Let's make a table of possible  $m_l$  &  $m_s$

$m_s =$	$m_l$			$M_L$	$M_S$	State Number
	-1	0	+1			
	↑↓			-2	0	1
		↑↓		0	0	2
			↑↓	+2	0	3
	↑	↑		-1	+1	4
	↑	↓		-1	0	5
	↓	↑		-1	0	6
	↓	↓		-1	-1	7
	↑		↑	0	+1	8
	↑	↓	↑	0	0	9
	↓	↑	↓	0	0	10
	↓	↓	↑	0	-1	11
		↑	↓	+1	+1	12
		↑	↑	+1	0	13
		↓	↑	+1	0	14
		↓	↓	+1	-1	15

These are the 15 states!

Now let's make a table that adds up all the  $M_L$ 's and  $M_S$ 's:

$M_L \backslash M_S$	1	0	-1
+2	0	1	0
+1	1	2	1
0	1	3	1
-1	1	2	1
-2	0	1	0

Now let's check for terms in this table.  
For instance

$${}^3D_J \Rightarrow L=2 \Rightarrow M_L=2 \text{ should appear in } S=1 \Rightarrow M_S=1 \text{ our table}$$

It does NOT! Therefore  ${}^3D_J$  term is disallowed by Pauli's exclusion principle.

Let's try  $^1D \Rightarrow L=2 \Rightarrow M_L = -2, -1, 0, 1, 2$   
 $S=0 \Rightarrow M_S = 0$

Let's subtract those 5 states from our table

$M_L \backslash M_S$	1	0	-1
+2	0	0	0
+1	1	1	1
0	1	2	1
-1	1	1	1
-2	0	0	0

$\Rightarrow$  A  $^1D$  term exists!

Let's try  $^3P \Rightarrow L=1 \Rightarrow M_L = -1, 0, +1$   
 $S=1 \Rightarrow M_S = -1, 0, +1$

There are 9 combinations of  $M_L$  and  $M_S$  - let's subtract those:

$M_L \backslash M_S$	1	0	-1
+2	0	0	0
+1	0	0	0
0	0	1	0
-1	0	0	0
-2	0	0	0

$\Rightarrow$  The  $^3P_J$  terms exist!

The one remaining state has  $M_L=0$  and  $M_S=0$   
 There is only one term which has those as the only projections  $\Rightarrow L=0$  and  $S=0$   
 $2S+1=1$

$\Rightarrow$  A  $^1S$  term.

So the allowed terms for CI  $(1s^2 2s^2) 2p^2$  are:

$^1D$ ,  $^3P_J$ , and  $^1S$

The rest are NOT allowed by Pauli exclusion principle!