Application to the periodic table
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1 Periodic table

The Pauli principle produces any two electrons being in the same state (i.e., having the set of (n, l, m_l, m_s).

For fixed n, $l = n$-1, n-2, …, 2, 1
$m_l = l$, l-1, …., -l (2l +1).

Therefore there are n^2 states for a given n.

$$\sum_{l=0}^{n-1}(2\,l+1)\ //\ \mathrm{Simplify}$$

$$n^2$$

There are two values for ms (= ±1/2).
Thus, corresponding to any value of n, there are $2n^2$ states.

K shell

n	l	m	s	m_s	
1	0	0	1/2	±1/2	$(1s)^2$

L shell

n	l	m	s	m_s	
2	0	0	1/2	±1/2	$(2s)^2$
2	1	1,0,-1	1/2	±1/2	$(2p)^6$

M shell

n	l	m	s	m_s	
3	0	0	1/2	±1/2	$(3s)^2$
3	1	1,0,-1	1/2	±1/2	$(3p)^6$
3	2	2,1,0,-1,-2	1/2	±1/2	$(3d)^{10}$

N shell

n	l	m	s	m_s	
4	0	0	1/2	±1/2	$(4s)^2$
4	1	1,0,-1	1/2	±1/2	$(4p)^6$
4	2	2,1,0,-1,-2	1/2	±1/2	$(4d)^{10}$
4	3	3,2,1,0,-1,-2,-3	1/2	±1/2	$(4f)^{14}$

$(1s)^2|(2s)^2(2p)^6|(3s)^2(3p)^6(3d)^{10}|(4s)^2(4p)^6(4d)^{10}(4f)^{14}|(5s)^2(5p)^6\ ((5d)^{10}$….

Atoms with filled n shells have a total angular momentum and a total spin of zero. Electrons exterior these closed shells are called valence electrons.

H	$(1s)$
He	$(1s)^2$
Li	$(1s)^2 \vert (2s)^1$
Ba	$(1s)^2 \vert (2s)^2$
B	$(1s)^2 \vert (2s)^2(2p)^1$
C	$(1s)^2 \vert (2s)^2(2p)^2$
N	$(1s)^2 \vert (2s)^2(2p)^3$
O	$(1s)^2 \vert (2s)^2(2p)^4$
F	$(1s)^2 \vert (2s)^2(2p)^5$
Ne	$(1s)^2 \vert (2s)^2(2p)^6 \vert$
Na	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^1$
Mg	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2$
Al	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^1$
Si	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^2$
P	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^3$
S	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^4$
Cl	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^5$
Ar	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6$
K	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^1$
Ca	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^2$
Sr	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^3$
Ti	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^4$
V	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^5$
Cr	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^6$
Mn	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^7$
Fe	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^8$
Co	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^9$
Ni	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^{10} \vert$
Cu	$(1s)^2 \vert (2s)^2(2p)^6 \vert (3s)^2(3p)^6(3d)^{10} \vert (4s)^1$

2 Hund's rule

2.1 Symmetry of wave functions

Landau:
The Hamiltonian H of the system (in the absence of a magnetic field) does not contain the spin operators, and hence, when it is applied to the wave function, it has no effect on the spin variables. The wave function of the system of particles can be written in the form of product,

$$|\psi\rangle = |\psi_{space}\rangle |\chi_{spin}\rangle$$

where $|\psi_{space}\rangle$ depends only on the coordinate of the particles and $|\chi_{spin}\rangle$ only on their spins

$|\psi\rangle = |\psi_{space}\rangle|\chi_{spin}\rangle$ should be anti-symmetric since electrons are Fermions.

2.2 Hund's rule

Electron states in the atom

(n, l, m), s = 1/2

For a given l, the number m takes $2l+1$ values. The number s is restricted to only two values ±1/2. Hence there are altogether $2(2l+1)$ different states with the same n and l.

There states are said to be equivalent.

According to Pauli's principle, there can be only one electron in each such state. Thus at most $2(2l+1)$ electrons in an atom can simultaneously have the same n and l.

Hund's rule is known concerning the relative position of levels with the same configuration but different L and S.

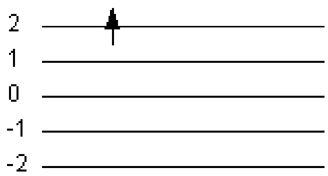
(1) The maximum values of the total spin S allowed by the exclusion principle.
(2) The maximum values of the total orbital angular momentum L consistent with this value of S.
(3) $J = |L - S|$ for less than half full.
(4) $J = L + S$ for more than half full.

The electron configuration $(3d)^n$ (l = 2, n = 1 - 10)

A d shell corresponds to l = 2, with five values of ml. Multiplying this by 2 for the spin states gives a total of 10. Then the configuration $(3d)^{10}$ represents a full shell. It is non-degenerate, and the state is $^1S_0$. This is a general rule for a full shell. It follows because each of electrons must have a different pair of m_l and m_s values.

$(3d)^1$: Ti^{3+}, V^{4+}

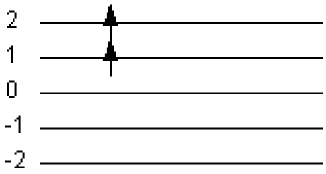
$^2D_{3/2}$ (ground state)



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

$(3d)^2$: V^{3+}

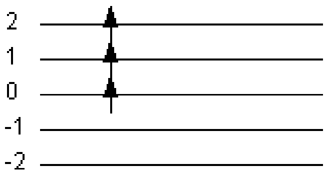
$^3F_2$



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

$(3d)^3$: Cr^{3+}, V^{2+}

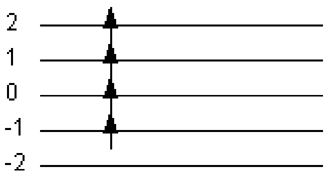
$^4F_{3/2}$



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

$(3d)^4$: Cr^{2+}, Mn^{3+}

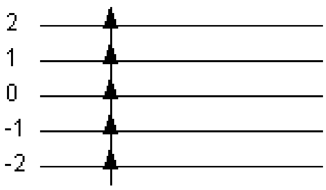
$^5D_0$



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

$(3d)^5$: Fe^{3+}, Mn^{2+}

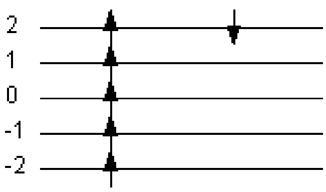
$^6S_{5/2}$



$L = 0$, $S = 5/2$, $J = 5/2$

$(3d)^6$: Fe^{2+}

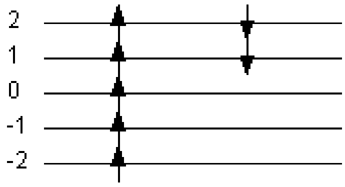
$^5D_4$



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

$(3d)^7$: Co^{2+}

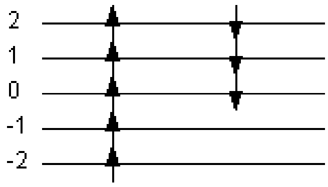
$^4F_{9/2}$



$L = 3$, $S = 3/2$, $J = 9/2$

$(3d)^8$: Ni^{2+}

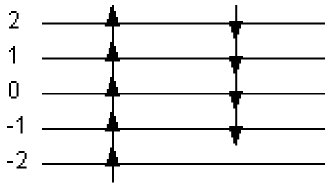
$^3F_4$



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

$(3d)^9$: Cu^{2+}

$^2D_{5/2}$



$L = 2$, $S = 1/2$, $J = 5/2$

$(3d)^9$

This configuration represents a set of electrons one short of a full shell. Since a full shell has zero angular momentum (both orbital and spin), it follows that if one electron is removed from a full shell, the spin angular momentum of the remainder are minus those of the one that was removed. So the *L*, *S*, and *J* values of remainder are the same as if there were only one electron in the shell.

$(3d)^{10}$

A d shell corresponds to $l = 2$, with five values of m_l. Multiplying this by two for the spin states gives 10. Thus the configuration $(3d)^{10}$ represents a full shell. $L = 0$. $S = 0$. $J = 0$.

3 Ground state (anti-symmetric state)

3.1 $(2p)^2$ electron configuration

We can apply the above consideration to the $(2p)^2$ electron configuration: each electron has l =1 orbital angular momentum ($l = 1$) and spin angular momentum (s =1/2).

For orbital angular momentum: D_1 x D_1

$$\begin{array}{|c|c|}\hline 1&1\\\hline\end{array}\,,\ \begin{array}{|c|c|}\hline 1&2\\\hline\end{array}\,,\ \begin{array}{|c|c|}\hline 1&3\\\hline\end{array}\,,\ \begin{array}{|c|c|}\hline 2&2\\\hline\end{array}\,,\ \begin{array}{|c|c|}\hline 2&3\\\hline\end{array}\,,\ \begin{array}{|c|c|}\hline 3&3\\\hline\end{array}\quad (L = 2 \text{ and } L = 0)$$

$$\begin{array}{|c|}\hline 1\\\hline 2\\\hline\end{array}\,,\ \begin{array}{|c|}\hline 1\\\hline 3\\\hline\end{array}\,,\ \begin{array}{|c|}\hline 2\\\hline 3\\\hline\end{array}\quad (L = 1)$$

For spin angular momentum $D_{1/2}$x$D_{1/2}$

$$\begin{array}{|c|c|}\hline 1&1\\\hline\end{array}\,,\ \begin{array}{|c|c|}\hline 1&2\\\hline\end{array}\,,\ \begin{array}{|c|c|}\hline 2&2\\\hline\end{array}\quad (S = 1)$$

$$\begin{array}{|c|}\hline 1\\\hline 2\\\hline\end{array}\quad (S = 0)$$

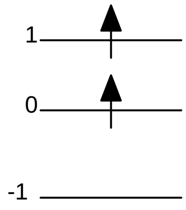
Therefore we have the following combination:

L	S	J	$2J$+1	Electron configuration
2 (*s*)	1 (*s*)	3,2,1	7,5,3	^{3}D
2 (*s*)	0 (*as*)	2	5	^{1}D
1 (*as*)	1 (*s*)	2,1,0	5,3,1	^{3}P
1 (*as*)	0 (*as*)	1	3	^{1}P
0 (*s*)	1 (*s*)	1	3	^{3}S
0 (*s*)	0 (*as*)	0	1	^{1}S

as: anti-symmetric state, *s*: symmetric state, *m*: mixed state.

The total wave function should be anti-symmetric under particle exchange. From the above Table,

((Hund's rule))
The ground state is $^3P_0$:
L = 1 (antisymmetric), S = 1 (symmetric); $J = |L-S| = 0$



3.2 $(2p)^3$ electron configuration

For orbital angular momentum

$D_1 x D_1 x D_1 = D_3 + 2D_2 + 3D_1 + D_0 \rightarrow L = 3, 2, 1$, and 0.

For spin angular momentum

$D_{1/2} x D_{1/2} x D_{1/2} = D_{3/2} + 2D_{1/2} \quad \rightarrow S = 3/2$ and 1/2.

The corresponding total angular momentum J is given by

$J = L+S, L+S-1, \ldots\ldots, |L-S|$

for each combination of L and S.

L	S	J	$2J+1$	Electron configuration
3(*s*)	3/2(*s*)	9/2	10	^4F
		7/2	8	
		5/2	6	
		3/2	4	
3(*s*)	1/2(*m*)	7/2	8	^2F
		5/2	6	
2(*m*)	3/2(*s*)	7/2	8	^4D
		5/2	6	
		3/2	4	
		1/2	2	
2(*m*)	1/2(*m*)	5/2	6	^2D
		3/2	4	
1(*s*)	3/2(*s*)	5/2	6	^4P
		3/2	4	
		1/2	2	
1(*s*)	1/2(*m*)	3/2	4	^2P
		1/2	2	
0(*as*)	3/2(*s*)	3/2	4	^4S
0(*as*)	1/2(*m*)	1/2	2	^2S

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as: anti-symmetric state, *s*: symmetric state, *m*: mixed state.

((Note))

<u>Anti-symmetric (L = 0)</u>

$$\begin{array}{|c|}\hline 1\\\hline 2\\\hline 3\\\hline\end{array}$$

m=0

<u>Symmetric (L = 3, 1)</u>

$$\underset{m=3}{\begin{array}{|c|c|c|}\hline 1&1&1\\\hline\end{array}},\quad \underset{m=2}{\begin{array}{|c|c|c|}\hline 1&1&2\\\hline\end{array}},\quad \underset{m=1}{\begin{array}{|c|c|c|}\hline 1&1&3\\\hline\end{array}},\quad \underset{m=1}{\begin{array}{|c|c|c|}\hline 1&2&2\\\hline\end{array}}$$

$$\underset{\mathrm{m}=0}{\begin{array}{|c|c|c|}\hline 1&2&3\\\hline\end{array}},\quad \underset{m=-1}{\begin{array}{|c|c|c|}\hline 1&3&3\\\hline\end{array}},\quad \underset{m=0}{\begin{array}{|c|c|c|}\hline 2&2&2\\\hline\end{array}},\quad \underset{m=-1}{\begin{array}{|c|c|c|}\hline 2&2&3\\\hline\end{array}},$$

$$\underset{m=-2}{\begin{array}{|c|c|c|}\hline 2&3&3\\\hline\end{array}},\quad \underset{m=-3}{\begin{array}{|c|c|c|}\hline 3&3&3\\\hline\end{array}},$$

<u>Mixed symmetry (L = 1, 2)</u>

$$\underset{m=2}{\begin{array}{|c|c|}\hline 1&1\\\hline 2\\\cline{1-1}\end{array}},\quad \underset{m=1}{\begin{array}{|c|c|}\hline 1&1\\\hline 3\\\cline{1-1}\end{array}},\quad \underset{m=1}{\begin{array}{|c|c|}\hline 1&2\\\hline 2\\\cline{1-1}\end{array}},\quad \underset{m=-1}{\begin{array}{|c|c|}\hline 1&3\\\hline 3\\\cline{1-1}\end{array}},\quad \underset{m=0}{\begin{array}{|c|c|}\hline 1&2\\\hline 3\\\cline{1-1}\end{array}}$$

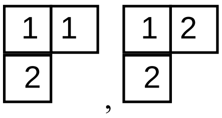
$$\underset{m=0}{\begin{array}{|c|c|}\hline 1&3\\\hline 2\\\cline{1-1}\end{array}},\quad \underset{m=-1}{\begin{array}{|c|c|}\hline 2&2\\\hline 3\\\cline{1-1}\end{array}},\quad \underset{m=-2}{\begin{array}{|c|c|}\hline 2&3\\\hline 3\\\cline{1-1}\end{array}}$$

For spin angular momentum

S = 3/2, m = 3/2, 1/2, -1/2, -3/2 (symmetric states)

$$\underset{m=3/2}{\begin{array}{|c|c|c|}\hline 1&1&1\\\hline\end{array}},\quad \underset{m=1/2}{\begin{array}{|c|c|c|}\hline 1&1&2\\\hline\end{array}},\quad \underset{m=-1/2}{\begin{array}{|c|c|c|}\hline 1&2&2\\\hline\end{array}},\quad \underset{m=-3/2}{\begin{array}{|c|c|c|}\hline 2&2&2\\\hline\end{array}}$$

S= 1/2 (mixed states)

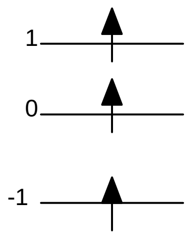


m=1/2 m=-1/2

Hund's rule

The ground state is given by L = 0, S = 3/2, and J = 3/2.

$^4S_{3/2}$



The possibility is that L = 0 (anti-symmetric) and S = 3/2 (symmetric), and J = 3/2. The ground state is $^3S_{3/2}$. Thus the total wave function is anti-symmetric under the particle exchange;

$$|\psi\rangle = |\psi_{space}\rangle|\chi_{spin}\rangle$$

Problem

1. Calculate the degeneracy, and list the possible $^{2S+1}L_J$ values for each of the following electronic configurations. (a) 2s2p and (b) 2p3p. For each configuration, verify that the sum of the number of states of each $^{2S+1}L_J$ combination is equal to the degeneracy of the configuration.

(a)

2s electron: n = 2, l = 0, s = 1/2 (1x2 = 2 states)

2p electron: n = 2, l = 1, s = 1/2 (3x2 = 6 states)

For spin angular momentum

$D_{1/2}xD_{1/2} = D_1+D_0$

S = 1 (symmetric), S = 0 (anti-symmetric)

For orbital angular momemtum

$D_1xD_0 = D_1$

$L = 1$

For total angular momentum

L	S	J	$2J+1$	Electron configuration
1	1	2,1,0	5,3,1	^3P
1	0	1	3	^1P
0	1	1	3	^3S
0	0	0	1	^1S

(b)
2p electron: $n = 2$, $l = 1$, $s = 1/2$ (3x2 = 6 states)
3p electron: $n = 3$, $l = 1$, $s = 1/2$ (3x2 = 6 states)

For spin angular momentum
$D_{1/2}xD_{1/2} = D_1+D_0$
S = 1 (symmetric), S = 0 (anti-symmetric)

For orbital angular momemtum
$D_1xD_1 = D_2 + D_1 + D_0$
$L = 2, 1, 0$

For total angular momentum

L	S	J	$2J+1$	Electron configuration
2	1	3,2,1	5,3,1	^3D
2	0	2	3	^1D
1	1	2,1,0	5,3,1	^3P
1	0	1	3	^1P
0	1	1	3	^3S
0	0	0	1	^1S

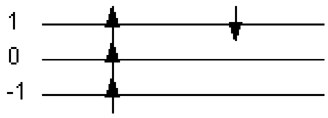
2. The electronic configuration of the ground state of nitrogen is $(1s)^2(2s)^2(2p)^3$. (a) What is the degeneracy of this electronic configuration? (b) List the permitted products of single-electron states for the electrons in the 2p shell in order of decreasing m_l value. (c) What is the possible $^{2s+1}L_j$ values for the electronic configuration? (d) Which is the lowest energy?

See the text above.

3. What are the possible states for the ground configuration of O^8 which includes four electrons in its outermost shell? Check that the $^3P_2$ grpund state is included in your list.

The electron colnfiguration of O: $(1s)^2(2s)^2(2p)^4$

From the Hund's rule, the ground state is $^3P_2$.



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

For spin angular momentum

$D_{1/2} x D_{1/2} x\ D_{1/2} x D_{1/2} = D_2 + 3D_1 + 2D_0 \rightarrow S = 2$, 1, and 0.

For orbital angular momentum

$D_1 x D_1 x\ D_1 x D_1 \rightarrow L = 4$, 3, 2,1,and 0.

The corresponding J values are given by the sequence,

L	*S*	*J*	Electron configuration
4	2	6,5,4,3,2	^5G
4	1	5,4,3	^3G
4	0	4	^1G
3	2	5,4,3,2,1	^5F
3	1	4,3,2	^3F
3	0	3	^1F
2	2	4,3,2,1,0	^5D
2	1	3,2,1	^3D
2	0	2	^1D
1	2	3,2,1	^5P
1	1	2,1,0	^3P
1	0	1	^1P
0	2	2	^5S

0	1	1	^3S
0	0	0	^1S

Green denotes the Hund's law.