Addition of Angular Momentum

For many electron atoms: the total angular momentum is the sum of the angular momentum of each of the electrons.

Let's examine a 2 e^- system: e^- #1 is in state $(n_1, l_1, m_{l_1}, m_{s_1})$

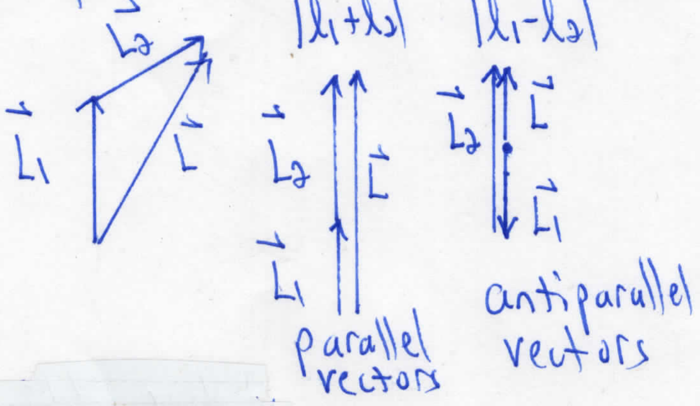
e^- #2 is in state $(n_2, l_2, m_{l_2}, m_{s_2})$

The total Orbital angular momentum = $\vec{L} = \vec{L}_1 + \vec{L}_2$

The total Spin angular momentum = $\vec{S} = \vec{S}_1 + \vec{S}_2$

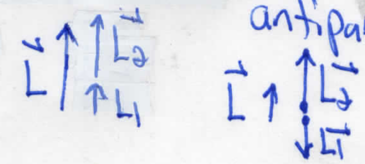
The Total angular momentum = $\vec{J} = \vec{L} + \vec{S}$

The permitted values of L: L = ranges from $\underbrace{|l_1+l_2|}_{\text{maximum}}$ to $\underbrace{|l_1-l_2|}_{\text{minimum}}$



maximum value when $\vec{L}_1, \vec{L}_2$ are parallel

minimum value when $\vec{L}_1, \vec{L}_2$ are antiparallel



Permitted values of S: S = ranges from $|s_1+s_2|$ to $|s_1-s_2|$

Permitted values of J: J = ranges from $|L+S|$ to $|L-S|$

Permitted values of M_L = ranges from $-L$ to L

Permitted values of M_S = ranges from $-S$ to S

Permitted values of M_J = ranges from $-J$ to J

For the z-component of $\vec{L}$:

$$L_z = L_{z1} + L_{z2} \Rightarrow M_L = m_{\ell 1} + m_{\ell 2}$$

For the z-component of $\vec{S}$:

$$S_z = S_{z1} + S_{z2} \Rightarrow M_S = m_{s1} + m_{s2}$$

Let's examine Helium: ${}^2He$ $\quad m_\ell = 0 \; \underline{\uparrow\downarrow} \; 1s \quad (\ell = 0)$

e^- #1: $\ell_1 = 0, \; s_1 = 1/2$

e^- #2: $\ell_2 = 0, \; s_2 = 1/2$

Allowed values of $L = |\ell_1 + \ell_2|$ to $|\ell_1 - \ell_2| = 0$ to $0 = 0$

Allowed values of S:

$$S = |s_1 + s_2| \text{ to } |s_1 - s_2| = |\tfrac{1}{2} + \tfrac{1}{2}| \text{ to } |\tfrac{1}{2} - \tfrac{1}{2}| = 1 \text{ to } 0$$

$$\Rightarrow S = 0, 1$$

Allowed values of J: $\quad J = |L + S|$ to $|L - S|$

for $S = 0$: $J = |0+0|$ to $|0-0| = 0$ to $0 = 0$

for $S = 1$: $J = |0+1|$ to $|0-1| = 1$ to $1 = 1$

$$\Rightarrow J = 0, 1$$

The quantum states for Helium, (L, S, J), are then $(0,0,0)$ and $(0,1,1)$

The multiplicity of a state is $(2S+1)$

Thus, the $(0,0,0)$ state is a singlet state: $2\cdot 0+1=1$

the $(0,1,1)$ state is a triplet state: $2\cdot 1+1=3$

Spectroscopic Notation: $L = 0 \quad 1 \quad 2 \quad 3$

State $= S \quad P \quad D \quad F$

In spectroscopic notation, one writes the $(0,0,0)$ state as

$$(0,0,0) = \underbrace{{}^{1}}_{2S+1=1}\underbrace{S}_{L=0}\underbrace{{}_{0}}_{J=0}$$

"one S zero state"

$$(0,1,1) = \underbrace{{}^{3}}_{2S+1=3}\underbrace{S}_{L=0}\underbrace{{}_{1}}_{J=1}$$

"three S one state"

To see if these states obey the Pauli Exclusion principle, lets make a table of all the possible combinations of $(m_{l1}, m_{s1}, m_{l2}, m_{s2})$ states

m_{l1}	m_{s1}	m_{l2}	m_{s2}	M_L	M_S	M_J
0	$+\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	0
0	$-\frac{1}{2}$	0	$+\frac{1}{2}$	0	0	0
0	$+\frac{1}{2}$	0	$+\frac{1}{2}$	0	1	1
0	$-\frac{1}{2}$	0	$-\frac{1}{2}$	0	-1	-1

$m_l=0$ ↑↓

$m_l=0$ ↑↑

violates Pauli

Notice that the last two rows in the table violate the Pauli Exclusion Principle since both electrons have the same quantum #'s ($m_{\ell_1}, m_{s_1}, m_{\ell_2}, m_{s_2}$). Thus, we cannot have any states with $M_J = 1$ or $J = 1$ since M_J = ranges from $-J$ to J = $-1, 0, 1$.

Thus $J = 1$ requires an $M_J = 1$ state.

Thus, the $(0,1,1) = {}^3S_1$ state is not allowed by the Pauli Exclusion Principle

The only state allowed for the $1s^2$ state of helium is the ${}^1S_0$ state.

Let's examine Carbon: $1s^2 2s^2 2p^2$

It has two 2p valence electrons (where $\ell = 1$ for p-states)

e^- #1 : $\ell_1 = 1$, $s_1 = 1/2$

e^- #2 : $\ell_2 = 1$, $s_2 = 1/2$

$\Rightarrow L = |\ell_1 + \ell_2|$ to $|\ell_1 - \ell_2| = |1+1|$ to $|1-1| = 2, 1, 0$

$S = |s_1 + s_2|$ to $|s_1 - s_2| = |\frac{1}{2} + \frac{1}{2}|$ to $|\frac{1}{2} - \frac{1}{2}| = 1, 0$

$J = |L+S|$ to $|L-S|$

$$\left.\begin{array}{l} \text{maximum } |L+S| = 2+1 = 3 \\ \text{minimum } |L-S| = 0-0 = 0 \end{array}\right\} \Rightarrow J = \underbrace{0,1,2,3}$$

ranges from maximum to minimum values in integer steps

The (L, S, J) quantum states are then:

when $L = 0$: $(0,0,0)$, $(0,1,1)$

$\downarrow$ $^1S_0$ $\quad$ $\downarrow$ $^3S_1$

$\overset{L+S}{}$ $\overset{L-S}{}$
$J = |1+1|$ to $|1-1|$
$= 2,1,0$

When $L = 1$: $(1,0,1)$, $(1,1,2)$, $(1,1,1)$, $(1,1,0)$

$\downarrow$ $^1P_1$ $\quad$ $\downarrow$ $^3P_2$ $\quad$ $\downarrow$ $^3P_1$ $\quad$ $\downarrow$ $^3P_0$

$J = |2+1|$ to $|2-1|$
$= 3,2,1$

When $L = 2$: $(2,0,2)$, $(2,1,3)$, $(2,1,2)$, $(2,1,1)$

$\downarrow$ $^1D_2$ $\quad$ $\downarrow$ $^3D_3$ $\quad$ $\downarrow$ $^3D_2$ $\quad$ $\downarrow$ $^3D_1$

To see which states above are forbidden due to the Pauli Exclusion Principle, let's make a table of all possible combinations of $(m_{\ell 1}, m_{s1}, m_{\ell 2}, m_{s2})$

Note: since $l_1 = 1$ for electron #1, then

$m_{l1} = -1, 0, 1$. Similarly, $m_{l2} = -1, 0, 1$.

$m_{s1} = -\frac{1}{2}, \frac{1}{2}$ $\qquad$ $m_{s2} = -\frac{1}{2}, \frac{1}{2}$

Quantum states for electron #1 : (m_{l1}, m_{s1})

(m_{l1}, m_{s1})	State
$(0, \frac{1}{2})$	$\equiv A$
$(0, -\frac{1}{2})$	$\equiv B$
$(1, \frac{1}{2})$	$\equiv C$
$(1, -\frac{1}{2})$	$\equiv D$
$(-1, \frac{1}{2})$	$\equiv E$
$(-1, -\frac{1}{2})$	$\equiv F$

if electron #2 is indistinguishable from electron #1, then

$$\underset{e^-\#1}{A}\,\underset{e^-\#2}{B} = \underset{e^-\#1}{B}\,\underset{e^-\#2}{A}$$

State $AB = (m_{l1}, m_{s1}, m_{l2}, m_{s2}) = (0, \frac{1}{2}, 0, -\frac{1}{2})$

$BA = (m_{l1}, m_{s1}, m_{l2}, m_{s2}) = (0, -\frac{1}{2}, 0, \frac{1}{2})$

$AB = BA$ for indistinguishable electrons

State AA cannot exist due to Pauli Exclusion

$AA = (0, \frac{1}{2}, 0, \frac{1}{2}) \Rightarrow$ both electrons have the same quantum #

Then, all the possible cumbinations of states is :

AB BC CD DE EF

AC BD CE DF

AD BE CF

AE BF

AF

there are 15 possible states

m_{ℓ_1}	m_{s_1}	m_{ℓ_2}	m_{s_2}	M_L	M_S	M_J	
0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0	0	$\rightarrow {}^1S_0$
0	$\frac{1}{2}$	1	$\frac{1}{2}$	1	1	2	$\rightarrow {}^3P_2$
0	$\frac{1}{2}$	1	$-\frac{1}{2}$	1	0	1	
0	$\frac{1}{2}$	-1	$\frac{1}{2}$	-1	1	0	
0	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	0	-1	
0	$-\frac{1}{2}$	1	$\frac{1}{2}$	1	0	1	
0	$-\frac{1}{2}$	1	$-\frac{1}{2}$	1	-1	0	
0	$-\frac{1}{2}$	-1	$\frac{1}{2}$	-1	0	-1	
0	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	-1	-1	-2	$\rightarrow {}^3P_2$
1	$\frac{1}{2}$	1	$-\frac{1}{2}$	2	0	2	$\rightarrow {}^1D_2$
1	$\frac{1}{2}$	-1	$\frac{1}{2}$	0	1	1	
1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	0	0	0	
1	$-\frac{1}{2}$	-1	$\frac{1}{2}$	0	0	0	
1	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	0	-1	-1	
-1	$\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	0	-2	$\rightarrow {}^1D_2$

One can see some of the states in the table. We can immediately rule out the $^3D_3$, $^3D_2$, $^3D_1$ states (on page 5)

Since $L = 2$, $S = 1$ $\Rightarrow$ $M_L = -2, -1, 0, 1, 2$
$M_S = -1, 0, 1$

need two spin up electrons

the possible m_ℓ values for the two electrons

$m_\ell = -1$ ———

$m_\ell = 0$ ———

$m_\ell = 1$ —↑ ↑—

Violates Pauli Exclusion

$$M_L = m_{\ell_1} + m_{\ell_2} = 1 + 1 = 2$$
$$M_S = m_{s_1} + m_{s_2} = \tfrac{1}{2} + \tfrac{1}{2} = 1$$

But this state violates the Pauli Exclusion Principle.

Thus, 5 of the 15 states belong to the $^1D_2$ which does not violate Pauli Exclusion

$L = 2$, $S = 0$ $\Rightarrow$ $M_L = -2, -1, 0, 1, 2$
$M_S = 0$

need a spin up and spin down pair of electrons

$m_\ell = -1$ ———

$m_\ell = 0$ ———

$m_\ell = 1$ —↑ ↓—

$$M_L = 1 + 1 = 2$$
$$M_S = \tfrac{1}{2} - \tfrac{1}{2} = 0$$

At first glance, the $^3S_1$, $^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$
states do not violate Pauli Exclusion

$^3S_1$

$m_\ell = -1$ ↑

$= 0$

$= 1$ ↑

OK

$M_L = -1 + 1 = 0$

$M_S = \frac{1}{2} + \frac{1}{2} = 1$

$S = 1,\ M_S = -1, 0, 1$

$L = 0,\ M_L = 0$

two spin up electrons

$^3P_2$

$m_\ell = -1$

$m_\ell = 0$ ↑

$m_\ell = 1$ ↑

$M_L = 0 + 1 = 1$

$M_S = \frac{1}{2} + \frac{1}{2} = 1$

$S = 1,\ M_S = -1, 0, 1$

$L = 1,\ M_L = -1, 0, 1$

two spin up electrons

$^1P_1$

$m_\ell = -1$

$m_\ell = 0$ ↓

$m_\ell = 1$ ↑

$M_L = 1 + 0 = 1$

$M_S = \frac{1}{2} - \frac{1}{2} = 0$

$S = 0,\ M_S = 0$

$L = 1;\ M_L = -1, 0, 1$

pair of spin up & down electron

Note that each state with quantum number J can split into M_J states when a magnetic field is applied. Thus, when $J = 2 \rightarrow M_J = -2, -1, 0, 1, 2$

↳ it splits into $(2J+1) = 5$ states

Thus,

$^1S_0$ has $(2J+1) = 2\cdot 0+1 = 1$ state

$^3S_1$ has $(2J+1) = 2\cdot 1+1 = 3$ states

$^1P_1$ has $(2J+1) = 2\cdot 1+1 = 3$ states

$^3P_0$ has $2\cdot 0+1 = 1$ states

$^3P_1$ has $2\cdot 1+1 = 3$ "

$^3P_2$ has $2\cdot 2+1 = 5$ "

$^1D_2$ has $2\cdot 2+1 = 5$ "

$^3D_3$, $^3D_2$, $^3D_1$ are not allowed (violate Pauli)

Thus, there are 21 states, but the table only lists 15 $\Rightarrow$ Some of these states are still not allowed by Pauli Exclusion. In the next Lecture, we will see which ones using symmetry arguments. We will just use the process of elimination to see which states violate Pauli Exclusion.

In the table on page 7, there are two cases where $M_J = +2$. The only two states with $M_J = +2$ (where $J=2$) is

$$^1D_2, {}^3P_2 \Rightarrow 10 \text{ states}$$

If the $^3P_2$ state is ok, then the $^3P_0$ and $^3P_1$ states must be ok (they all have $L=1$, $S=1$)

$$^3P_0, {}^3P_1 \Rightarrow 4 \text{ states}$$

Since there are only 15 possible state, that leaves the

$$^1S_0 \Rightarrow 1 \text{ state}$$

since the $^3S_1$ and $^1P_1$ both have 3 states. These states must violate Pauli Exclusion.

The allowed states for carbon are then

$$^1S_0, {}^3P_0, {}^3P_1, {}^3P_2, {}^1D_2$$

We can find which of these states is the ground state by using Hund's Rule:

Hund's Rule: Electrons in a subshell remain unpaired (that is, have parallel spins) whenever possible.

$\Rightarrow$ the origin lies in the mutual repulsion of electrons $\rightarrow$ the farther apart the electrons are, the lower the energy of the atom.

The ground state (L, S, J) values are found through:

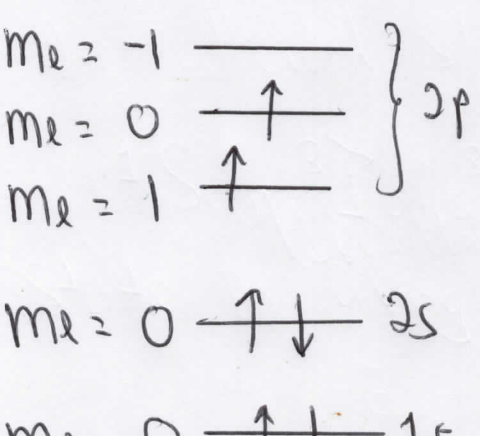
$$S = M_{S,max}$$

$$L = M_{L,max}$$

$$J = |L - S| \text{ for } \leq \text{ half filled subshell}$$

$$J = |L + S| \text{ for } > \text{ half filled subshell}$$

For carbon: $1s^2 2s^2 2p^2$



$$M_{S,max} = \overset{1s}{\left(\tfrac{1}{2} - \tfrac{1}{2}\right)} + \overset{2s}{\left(\tfrac{1}{2} - \tfrac{1}{2}\right)} + \overset{2p}{\left(\tfrac{1}{2} + \tfrac{1}{2}\right)}$$
$$= 1$$

$\Rightarrow S = 1$

$$M_{L,max} = \overset{1s}{(0 + 0)} + \overset{2s}{(0 + 0)} + \overset{2p}{(1 + 0)}$$
$$= 1$$

$\Rightarrow L = 1$

since the 2p-subshell is less than half filled,

$$J = |L - S| = |1 - 1| = 0$$

The ground state is

$$(L, S, J) = (1, 1, 0) = {}^3P_0 \text{ State}$$

Let's find the grund state of:

Ⓐ Nitrogen: $1s^2 2s^2 2p^3$

$$\left.\begin{array}{l} m_l = -1 \ \underline{\ \uparrow\ } \\ m_l = 0 \ \underline{\ \uparrow\ } \\ m_l = 1 \ \underline{\ \uparrow\ } \end{array}\right\} 2p$$

$$m_l = 0 \ \underline{\ \uparrow\downarrow\ } \ 2s$$

$$m_l = 0 \ \underline{\ \uparrow\downarrow\ } \ 1s$$

$$M_{S,max} = \overset{1s}{0} + \overset{2s}{0} + \overset{2p}{\left(\tfrac{1}{2} + \tfrac{1}{2} + \tfrac{1}{2}\right)} = 3/2$$

$$\Rightarrow S = 3/2$$

$$M_{L,max} = \overset{1s}{0} + \overset{2s}{0} + \overset{2p}{(1 + 0 - 1)} = 0$$

$$\Rightarrow L = 0$$

since the 2p-subshell is half filled:

$$J = |L - S| = |0 - 3/2| = 3/2$$

Nitrogen Ground State is

$$(L, S, J) = (0, 3/2, 3/2) = {}^4S_{3/2}$$

(B) Oxygen: $1s^2 2s^2 2p^4$

$m_\ell = -1$ ↑
$m_\ell = 0$ ↑
$m_\ell = 1$ ↑↓ } 2p

$m_\ell = 0$ ↑↓ 2s

$m_\ell = 0$ ↑↓ 1s

$$M_{S,max} = 0 + 0 + \overbrace{\left(\tfrac{1}{2} - \tfrac{1}{2} + \tfrac{1}{2} + \tfrac{1}{2}\right)}^{2p} = 1$$

$$\Rightarrow S = 1$$

$$M_{L,max} = 0 + 0 + (1 + 1 + 0 - 1) = 1$$

$$\Rightarrow L = 1$$

Since the p-subshell is more than half-filled:

$$J = |L + S| = |1 + 1| = 2$$

Oxygen ground state: $(L, S, J) = (1, 1, 2) = {}^3P_2$

(C) Gadolinium: $[Xe]\, 6s^2 4f^7 5d^1$

$m_\ell = -2$
$m_\ell = -1$
$m_\ell = 0$
$m_\ell = 1$
$m_\ell = 2$ ↑ } 5d

$m_\ell = -3$ ↑
$m_\ell = -2$ ↑
$m_\ell = -1$ ↑
$m_\ell = 0$ ↑
$m_\ell = 1$ ↑
$m_\ell = 2$ ↑
$m_\ell = 3$ ↑ } 4f

$m_\ell = 0$ ↑↓ 6s

$$M_{S,max} = \overset{6s}{0} + \overset{4f}{7\left(\tfrac{1}{2}\right)} + \overset{5d}{1\left(\tfrac{1}{2}\right)} = 4$$

$$\Rightarrow S = 4$$

$$M_{L,max} = \overset{6s}{0} + \overset{4f}{0} + \overset{5d}{2} = 2$$

$$\Rightarrow L = 2$$

Since the 4f-subshell is half-filled,

$$J = |L - S| = |2 - 4| = 2$$

Ground state is

$(L, S, J) = (2, 4, 2) = {}^9D_2$