1.1 Hund’s rules

Use the Hund’s rules to determine the ground state for the following atoms:

Carbon: $1s^2\ 2s^2\ 2p^2$

Oxygen: $1s^2\ 2s^2\ 2p^4$

1.1 Hund’s rules - Solution

Carbon: $1s^2\ 2s^2\ 2p^2$
Only the 2p subshell is partially occupied

m	$+1$	0	-1
m_s	$\uparrow$	$\uparrow$	

Maximize M_S
$M_S = +1 \rightarrow S = 1$

Maximize M_L
$M_L = +1 \rightarrow L = 1$

subshell less than half-filled → $J = L - S = 0$

Oxygen: $1s^2\ 2s^2\ 2p^4$
Only the 2p subshell is partially occupied

m	$+1$	0	-1
m_s	$\uparrow\ \downarrow$	$\uparrow$	$\uparrow$

Maximize M_S
$M_S = +1 \rightarrow S = 1$

Maximize M_L
$M_L = +1 \rightarrow L = 1$

subshell more than half-filled → $J = L + S = 2$

1.2 Energy spectrum of oxygen

In the previous exercise we have found the ground state of carbon and oxygen.

Now, we want to determine the excited states of oxygen, in the situation where:
- the 1s shell and the 2s subshell are full;
- the occupation of the 2p orbitals is modified, but not the number of 2p electrons.

For the moment, neglect the spin-orbit coupling.

Explain qualitatively the energy sequence

Hints for the procedure:
- consider a $2p^2$ filling, equivalent to the $2p^4$ filling (easier to visualize);
- consider all the possible combinations of m and m_s , compatibly with the Pauli principle, giving rise to (M_L, M_S) microstates;
- group them to identify the pairs of L and S values;
- write the spectroscopic terms.

1.2 Energy spectrum of oxygen - Solution

m	1	0	-1	M_L	M_S
m_s	↑	↑		$+1$	$+1$
	↑		↑	0	$+1$
		↑	↑	-1	$+1$
	↓	↓		$+1$	-1
	↓		↓	0	-1
		↓	↓	-1	-1
	↑	↓		$+1$	0
	↑		↓	0	0
		↑	↓	-1	0
	↓	↑		$+1$	0
	↓		↑	0	0
		↓	↑	-1	0
	↑ ↓			$+2$	0
		↑ ↓		0	0
			↑ ↓	-2	0

Equivalent

M_L \ M_S	$+1$	0	-1
$+2$		$(+1^{\uparrow},+1^{\downarrow})$	
$+1$	$(+1^{\uparrow},0^{\uparrow})$	$(+1^{\uparrow},0^{\downarrow})$ $(+1^{\downarrow},0^{\uparrow})$	$(+1^{\downarrow},0^{\downarrow})$
0	$(+1^{\uparrow},-1^{\uparrow})$	$(+1^{\uparrow},-1^{\downarrow})$ $(+1^{\downarrow},-1^{\uparrow})$ $(0^{\uparrow},0^{\downarrow})$	$(+1^{\downarrow},-1^{\downarrow})$
-1	$(0^{\uparrow},-1^{\uparrow})$	$(0^{\uparrow},-1^{\downarrow})$ $(0^{\downarrow},-1^{\uparrow})$	$(0^{\downarrow},-1^{\downarrow})$
-2		$(-1^{\uparrow},-1^{\downarrow})$	

1.2 Energy spectrum of oxygen - Solution

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

Overall, there are 15 (micro)states.
The table above reports the multiplicity of each state.
For example there are 2 states with $M_L = -1$ and $M_S = 0$.

The maximum M_L is ± 2. These M_L are projections of a $L = 2$ state, together with $M_L = \pm 1$ and $M_L = 0$. All these states have $M_S = 0$, so the first configuration that we can identify is $L = 2, S = 0$.

We remove these 5 states from the table, to find the other ones.

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

The maximum M_L now is ± 1. These M_L are projections of a $L = 1$ state, together with $M_L = 0$. For all of them $M_S = +1, 0, -1$, corresponding to $S = 1$.

The identified configuration is $L = 1, S = 1$.

We remove these 9 states from the table.

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

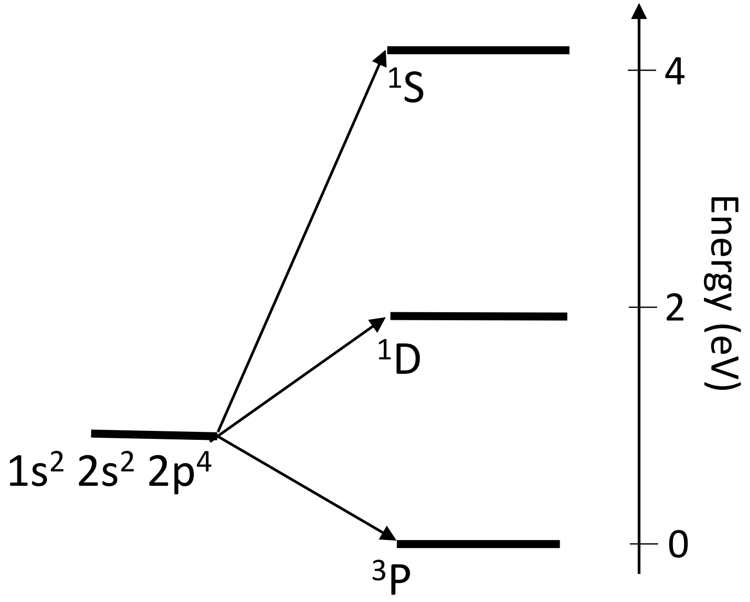
There is only one state left, with $M_L = 0$ and $M_S = 0$. The configuration is $L = 0, S = 0$

1.2 Energy spectrum of oxygen - Solution

To summarize, we have three terms:
$S = 0\,,\, L = 2$
$S = 0\,,\, L = 0$
$S = 1\,,\, L = 1$

This is valid for both carbon and oxygen.
From the Hund's first and second rule: the ground term is $S = 1\,,\, L = 1$. In spectroscopic notation ${}^{2S+1}\mathrm{X}$ ($L = 1 \rightarrow \mathrm{X} = \mathrm{P}$ and $2S + 1 = 3$): ${}^{3}\mathrm{P}$

The other terms:
$S = 0\,,\, L = 2$ ($L = 2 \rightarrow \mathrm{X} = \mathrm{D}$ and $2S + 1 = 1$): ${}^{1}\mathrm{D}$
$S = 0\,,\, L = 0$ ($L = 0 \rightarrow \mathrm{X} = \mathrm{S}$ and $2S + 1 = 1$): ${}^{1}\mathrm{S}$



Qualitative explanation of energy order:
- from the Hund's first and second rule, we know that $S = 1\,,\, L = 1$ is the ground term;
- the $L = 0$, $S = 0$ term is the highest in energy, since it has both low spin and low orbital angular momentum.

You can apply the same procedure to find the configurations for Ti [Ar] $4s^2\ 3d^2$ shown in the lecture.

1.3 Spin-orbit coupling and third Hund’s rule

The spin-orbit coupling (SOC) lifts the degeneracy of states with same S and L, but different J.

a) Demonstrate that

$$\langle L,S,J,M|\boldsymbol{L}\cdot\boldsymbol{S}|L,S,J,M\rangle=\frac{1}{2}[J(J+1)-L(L+1)-S(S+1)]$$

where $|L,S,J,M\rangle$ is the angular part of the many-electron wave function.

b) We want to demonstrate the relation between λ, the SOC factor for a many-electron system, and the one-electron SOC parameter ζ_{nl}.

We can write that (i occupied states):

$$\langle R_{nl},L,M_L,S,M_S|\textstyle\sum_i \xi_{nl}\,\boldsymbol{l}_i\cdot\boldsymbol{s}_i|R_{nl},L,M_L,S,M_S\rangle=\lambda\,M_L M_S$$

and equivalently that:

$$\langle R_{nl},L,M_L,S,M_S|\textstyle\sum_i \xi_{nl}\,\boldsymbol{l}_i\cdot\boldsymbol{s}_i|R_{nl},L,M_L,S,M_S\rangle=\zeta_{nl}\displaystyle\sum_i m_i\,m_{s\,i}$$

Consider the ground term of a system with a subshell **less** than half-filled, characterized by L and S according to Hund’s rules (if it helps, as example you can use carbon).

Using the two previous relations, show that $\lambda=\frac{\zeta_{nl}}{2S}$

Consider now the ground term of a system with a subshell **more** than half-filled, characterized by L and S according to Hund’s rules (as example you can use oxygen).

Show that $\lambda=-\frac{\zeta_{nl}}{2S}$

c) Use these results to find the expressions of $\Delta E_{SO}=\lambda\boldsymbol{L}\cdot\boldsymbol{S}$ for the two cases.

Deduce that for a subshell less then half-filled the state with minimum J has the lowest energy, while for a subshell more than half-filled the maximum J has the lowest energy.

1.3 Spin-orbit coupling and third Hund’s rule - Solution

a) $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$

$$\boldsymbol{J}^2 = \boldsymbol{L}^2 + \boldsymbol{S}^2 + 2\,\boldsymbol{L}\cdot\boldsymbol{S} \quad \rightarrow \quad \boldsymbol{L}\cdot\boldsymbol{S} = \frac{1}{2}(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2)$$

$$\left\langle L,S,J,M \middle| \frac{1}{2}(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2) \middle| L,S,J,M \right\rangle =$$

$= \frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$ (in principle in units of $\hbar^2$)

b) From the expressions given, we deduce that (i occupied states)

$$\lambda\, M_L M_S = \zeta_{nl} \sum_i m_i\, m_{s\,i}$$

For the **less** than half-filled subshell, according to the Hund’s rules:
$\sum m = M_L = L$ and $\sum m_s = M_S = S \rightarrow$

$$\lambda\, L\, S = \zeta_{nl} \frac{1}{2} \sum m = \zeta_{nl} \frac{1}{2} L \qquad \rightarrow \lambda = \frac{\zeta_{nl}}{2S}$$

For the **more** than half-filled subshell :

$$\lambda\, L\, S = \zeta_{nl} \left[\frac{1}{2} \sum_{-l}^{l} m - \frac{1}{2} \sum m \right] = -\zeta_{nl} \frac{1}{2} L \qquad \rightarrow \lambda = -\frac{\zeta_{nl}}{2S}$$

We notice that the sign of λ changes as we go from a less than half-filled to a more than half-filled subshell.

c) The ground term is a multiplet with J that can assume the following values: $J = |L - S|, \ldots L + S$

Subshell **less** then half-filled:

$$\Delta E_{SO} = \lambda \boldsymbol{L}\cdot\boldsymbol{S} = +\frac{\zeta_{nl}}{2S}\frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$$

This expression has the maximum negative value (energetically favored) for the minimum J
→ the SOC makes the state with $J = |L - S|$ the ground state

For carbon this corresponds to : $L = 1,\ S = 1,\ J = 0.$
States with $J = 1, 2$ are higher in energy

Subshell **more** then half-filled:

$$\Delta E_{SO} = \lambda \boldsymbol{L}\cdot\boldsymbol{S} = -\frac{\zeta_{nl}}{2S}\frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$$

This expression has the maximum negative value for the maximum J
→ the SOC makes the state with $J = L + S$ the ground state

For carbon this corresponds to : $L = 1,\ S = 1,\ J = 2.$
States with $J = 0, 1$ are higher in energy.

1.4 Spin-orbit coupling in oxygen

We want to evaluate the effect of the spin-orbit coupling on the terms of oxygen found previously.
Does it act on all the terms?
Calculate the energy splitting ΔE_{SO} for the states where the SOC lifts the degeneracy.

Hints:
- use the relation demonstrated in the previous exercise
- estimate the value of ζ for the 2p electrons of oxygen (Z=8) from the graph given in the lecture, express λ as a function of ζ, and provide the energy values in meV.

1.4 Spin-orbit coupling in oxygen- Solution

The SOC acts only on states where both L and S are non-zero. Therefore it leaves unperturbed the multiplet $^1\mathrm{D}$ ($L=2, S=0$), that remains 5-fold degenerated. With $J=2$, the symbol can be written as $^1\mathrm{D}_2$.
The other state is the singlet $^1\mathrm{S}$ ($L=0, S=0$), $^1\mathrm{S}_0$.

The SOC acts on the multiplet with $S=1$, $L=1$, $^3\mathrm{P}$.
The possible values of J are: $J = |L-S|, \ldots\ L+S = 0, 1, 2$

The subshell is more than half-filled, therefore $\lambda = -\frac{\zeta_{2p}}{2S}$:

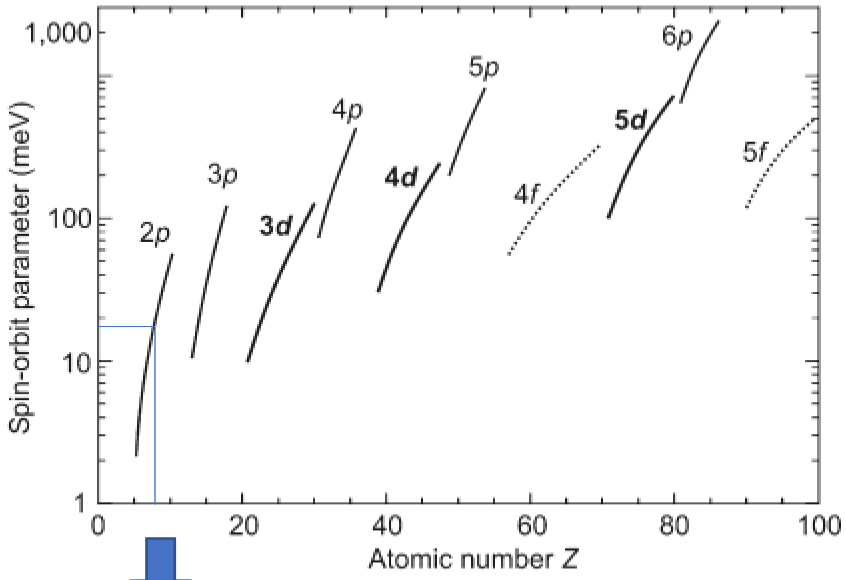
$$\Delta E_{SO} = \lambda \boldsymbol{L}\cdot\boldsymbol{S} = -\frac{\zeta_{2p}}{4S}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

$$J=0 \rightarrow \Delta E_{SO} = \quad -\frac{\zeta_{2p}}{4}\,[0-2-2] = \zeta_{2p}$$

$$J=1 \rightarrow \Delta E_{SO} = \quad -\frac{\zeta_{2p}}{4}\,[2-2-2] = \frac{\zeta_{2p}}{2}$$

$$J=2 \rightarrow \Delta E_{SO} = \quad -\frac{\zeta_{2p}}{4}\,[6-2-2] = -\frac{\zeta_{2p}}{2}$$

As already deduced in the previous exercise, we find that the state with maximum J is energetically favorable for a more than half-filled shell once the SOC is switched on.



$\zeta_{2p} \approx 18$ meV