Contents: Spectroscopic Terms and Selection Rules

Let us look at carbon (C) atom in the ground-state configuration ($1s^2\ 2s^2\ 2p^2$). In this configuration, *1s* and *2s* electrons make up the closed shell and the *2s* subshell, respectively. Thus, the only electrons that can contribute to nonzero values of *L*, *S* and *J* are the two *2p* electrons. Without considering the Pauli exclusion principle, we have 15 distinct possible states for a given p^2 configuration :

$l_1=l_2=1,\ s_1 = s_2 = \frac{1}{2}$. See "Atoms & Molecules," by M. Karplus and R.N. Porter (W.A. Benjamin, Inc., 1970), chapter 4.

Thus, a term symbol that characterizes the entire quantum state of a given atom had been proposed and is represented by the following symbol :

$$n\ {}^{2S+1}L_J \quad \ldots\ldots. (27)$$

(i) L represents the total orbital angular-momentum quantum number :

L =	0	1	2	3	4	5
	S	P	D	F	G	H

Spectroscopic Terms and Selection Rules

(ii) The superscript denotes the multiplicity of the state, which is the number of different possible orientations of $\boldsymbol{L}$ and $\boldsymbol{S}$ (thus, the number of different possible values of $\boldsymbol{J}$ vector).

Recall $J = L+S, L+S-1, \ldots\ldots\ldots, |L-S|$ .... (26)

when $S=0$, $J=L$ only, the multiplicity = 1 (singlet state)
when $S=\frac{1}{2}$, $J= L\pm\frac{1}{2}$, the multiplicity = 2 (doublet state)
when $S=1$, $J=L+1$, L or $L-1$, the multiplicity = 3 (triplet state)

$\therefore$ Multiplicity $(\Omega) = 2S + 1$

(iii) The total angular-momentum quantum number J is used as a subscript.

Example

(ex 1) the ground state of Na : $3\ ^2S_{1/2}$

the first excited state of Na : $3\ ^2P_{1/2}$

Find the possible quantum numbers, **n**, l, j and m_j of the outer electron.

* for $3\ ^2S_{1/2}$; $n = 3$, $l = 0$, $j = ½$, $m_j = \pm\frac{1}{2}$

* for $3\ ^2P_{1/2}$; $l = 1$, Eq. (26) $\longrightarrow j = \frac{3}{2}$ or $\frac{1}{2}$ $\longrightarrow$ $\therefore$ two possible j values.

$$(i)\ n = 3,\ l = 1,\ j = \frac{3}{2},\ m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \quad (Eq.(17))$$

$$or \quad (ii)\ n = 3,\ l = 1,\ j = \frac{1}{2},\ m_j = -\frac{1}{2}, +\frac{1}{2}$$

* We use capital letters for L and J since this state would involve more than one state.

(ex 2) Is it possible for a $2\ ^2P_{5/2}$ state to exist ?

$$L = 1 \rightarrow \therefore\ J = \frac{1}{2}, \frac{3}{2} \rightarrow \therefore\ J = \frac{5}{2}$$ is impossible !

(10) Hund Rules

It is known that there could be 5 distinct possible states for a given p^2 configuration of carbon atom ($1s^2\ 2s^2\ 2p^2$).

They are : $^3P_{2,1,0}$ $\quad ^1D_2$ $\quad ^1S_0$

Hund's Rule:

Then, it is necessary to find their relative energy in order to choose which term characterizes the ground state. This can be done by a set of simple rules, called **Hund's rules.**

> **(a)** The terms are ordered according to their S values, the term with maximum S being most stable and the stability decreasing with decreasing S. Thus, the ground state has maximum spin multiplicity.
> **(b)** For a given value of S, the state with maximum L is most stable.
> **(c)** For given S and L, the minimum J value is most stable if there is an open shell that is less than half-full and the maximum J is most stable if the subshell is more than half-full.

* Rules (a) and (b) arise from the electron-electron interaction, while rule (c) is a consequence of the spin-orbit (magnetic) interaction (See Page 14 of this chapter).
* In the above rules, S and L can be effectively replaced by their z component quantum numbers, M_S and M_L, respectively.

Various energy state of Corban

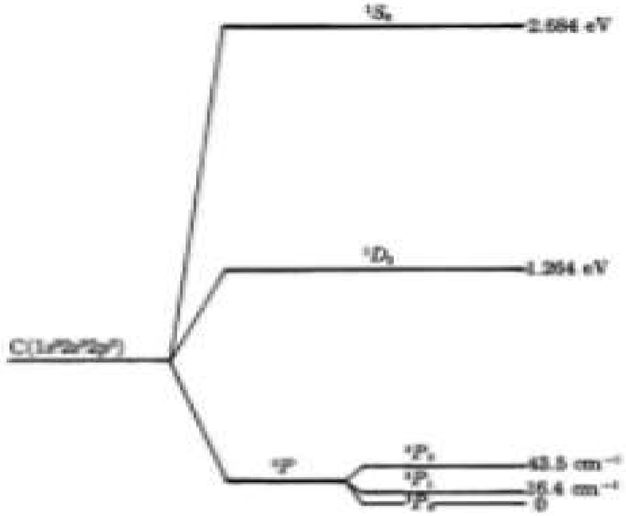

Fig. 4.11. Term splitting in the ground-state ($1s^2 2s^2 2p^2$) configuration of carbon.

Here

$M_L = m_{l1} + m_{l2} + \cdots\cdots$

$M_S = m_{s1} + m_{s2} + \cdots\cdots$

and $J = L+S,\ L+S-1,\ \cdots\cdots\ |L-S|$.

Table 4.5 Ground-state configuration and terms for first- and second-row elements

H	He	Li	Be	B	C	N	O	F	Ne
$1s$	$1s^2$	$2s$	$2s^2$	$2p$	$2p^2$	$2p^3$	$2p^4$	$2p^5$	$2p^6$
$^2S_{1/2}$	$^1S_0$	$^2S_{1/2}$	$^1S_0$	$^2P_{1/2}$	$^3P_0$	$^4S_{3/2}$	$^3P_2$	$^2P_{3/2}$	$^1S_0$

Table 4.6 *Assignment of electrons in the ground-state configuration according to Hund's rules*

m	B	C	N	O	F	Ne
+1	↑	↑	↑	↑↓	↑↓	↑↓
0		↑	↑	↑	↑↓	↑↓
−1			↑	↑	↑	↑↓
M_S	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0
M_L	1	1	0	1	1	0

Example

$M_L = m_{l1} + m_{l2} + \cdots$, $M_S = m_{s1} + m_{s2} + \cdots$, and $J = L+S, L+S-1, \cdots |L-S|$

where M_L and M_S are the quantum numbers for the z component of the total orbital and spin angular momentum, respectively. We further have the relations :

* $M_s = S, S-1, S-2, \ldots\ldots, -S$ ($2S+1$ values of M_S for a given S)
* $M_L = L, L-1, L-2, \ldots\ldots, -L$ ($2L+1$ values of M_L for a given L)

((Example))

Oxygen atom has $2s^2 2p^4$ electronic configuration outside the filled 1s shell. Find the term symbol for its ground-electronic state ?

(i) According to the Rule (a), the maximum S or M_S (i.e., parallel spins) is preferred.

$M_S = ½ + ½ + ½ - ½ = 1$. (See the bottom Table in the previous page.)

$\therefore$ $S = 1$. $\rightarrow$ $\therefore$ $\Omega = 2S+1 = 3$

(ii) p-orbital $\leftrightarrow$ $l = 1$ $\rightarrow$ The possible value of $m_l = 0, \pm 1$

According to the Rule (b), the maximum L or M_L is preferred.

$M_L = (+1)+(0)+(-1)+(+1) = 1$. (See the bottom Table in the previous page.)

$\therefore$ $L = 1$ $\rightarrow$ $\therefore$ P symbol

(iii) $J = L+S, L+S-1, \cdots |L-S|$.

$\therefore$ possible $J = 2, 1, 0$

$2p^4$ configuration $\leftrightarrow$ more than half-full. $\rightarrow$ $\therefore$ maximum J is preferred (Rule (c)).

$\therefore$ J = 2. $\rightarrow$ ${}^3P_2$

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