STUDY MATERIAL

Dumkal College
Basantapur,Dumkal

Topic: Extra nuclear structure of atom: Elementary idea of Microstates

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Microstates

The electronic configuration of an atom, ion or molecule is not a complete description of arrangement of electrons in a subshell of an atom. For a given electronic configuration, there are several ways of arrangement of electrons in a subshell. For example, for p^2-electronic configuration, there are 15 ways in which electrons can be arranged. Similarly for d^2-configuration, there are 45 ways of arrangement of electrons. The different ways in which the electrons can be arranged in the orbitals of a subshell are called microstates of the configuration. Microstates are also called as atomic states.

$$\text{Number of microstates} = \frac{N!}{x!\,(N-x)!}$$

$${}^{10}C_2 = \frac{10 \times 9}{1 \times 2} = 45$$

where

$N = 2(2l+1)$ = twice the number of orbitals.

x = number of electrons.

For example microstates for p^2-configuration $= \frac{6!}{2!(6-2)!}$

$$= \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1 \times 4 \times 3 \times 2 \times 1}$$

$$= 15$$

The fifteen microstates for p^2-configuration are shown in the following table :

	m_l	+1	0	−1	M_S	M_L
1		↑↓			0	+2
2			↑↓		0	0
3				↑↓	0	−2
4		↑	↓		0	+1
5		↓	↑		0	+1
6		↑		↓	0	0
7		↓		↑	0	0
8			↑	↓	0	−1
9			↓	↑	0	−1
10		↑	↑		+1	+1
11		↑		↑	+1	0
12			↑	↑	+1	−1
13		↓	↓		−1	+1
14		↓		↓	−1	0
15			↓	↓	−1	−1

Spectroscopic Terms : If the inter electronic repulsions are very small *i.e.* negligible, then the microstates of a given electronic configuration have the same energy. But atoms and molecules are compact, therefore, the inter-electronic repulsions are really strong and can not be ignored. As a result, microstates which correspond to different relative spatial arrangement of electrons have different energies. If the microstates that have the same energy are grouped together when inter-electronic repulsions are taken into account, the spectroscopically different energy levels are obtained and these energy levels are called **terms** or **atomic states.** These terms are characterized by symbols S and L. Thus,

$$\text{Atomic state} = {}^{2S+1}L$$

The values of L correspond to atomic states described as S, P, D, F, ... which are parallel to the values of l for s, p, d, f ..... orbitals.

The atomic states or terms are very important in the interpretation of spectra of coordination compounds.

Term Symbols : The term symbol for a particular atomic state or term is written as :

$$^{2S+1}_{J}L$$

A term symbol provides three informations :

1. The letter S, P, D, F, G, H or I indicates the total angular momentum quantum number, L.
2. The left superscript in the term symbol represents the spin multiplicity of the term.

3. The right subscript in the term symbol provides the value of the total angular momentum quantum number, J.

Equivalent and Non-Equivalent Electrons

The two or more electrons are referred to equivalent if they have the same value of n and of l. Thus, the electrons in a given d or f subshell are equivalent. For example, two $2p$ electrons in the ground state of the carbon atom are equivalent because $n_1 = n_2 = 2$ and $l_1 = l_2 = 1$. Similarly, the two $3d$ electrons in the ground state of Ti^{2+} or V^{3+} ion are equivalent because $n_1 = n_2 = 3$ and $l_1 = l_2 = 2$. On the other hand, the two electrons are said to be non-equivalent if they have either $n_1 \neq n_2$ or $l_1 \neq l_2$ or both $n_1 \neq n_2$ and $l_1 \neq l_2$. For example, the two electrons in the excited state of the Be atom, $1s^1 2s^1$ are non-equivalent because $n_1 \neq n_2$ ($n_1 = 1$, $n_2 = 2$) and $l_1 = l_2 = 0$. Similarly, the two electrons in the excited state of the carbon atom, $1s^2 2s^2 2p^1 3p^1$ are also non-equivalent because $n_1 \neq n_2$ ($n_1 = 2$, $n_2 = 3$) and $l_1 = l_2 = 1$. Similarly the two electrons in the configurations $2s^1 2p^1$ and $3p^1 3d^1$ are also non-equivalent because $n_1 = n_2 (= 2)$ and $l_1 \neq l_2$ ($l_1 = 0$, $l_2 = 1$) for $2s^1 2p^1$ configuration and $n_1 = n_2 (= 3)$ and $l_1 \neq l_2$ ($l_1 = 1$, $l_2 = 2$) for $3p^1 3d^1$ configuration.

Number of Microstates for a Given Spectroscopic Term

A spectroscopic term may be associated with two or more microstates. The number of microstates for a given spectroscopic term is given by the relation :

$$\text{Number of microstates} = (2S + 1)\,(2L + 1)$$

This relationship is illustrated using the following spectroscopic terms :

Term	L	$2S + 1$	Number of microstates $(2S + 1)\,(2L + 1)$
^1S	0	1	$1 \times (2 \times 0 + 1) = 1$
^3P	1	3	$3 \times (2 \times 1 + 1) = 9$
^1D	2	1	$1 \times (2 \times 2 + 1) = 5$
^3F	3	3	$3 \times (2 \times 3 + 1) = 1$
^1G	4	1	$1 \times (2 \times 4 + 1) = 9$

How to Derive Term Symbols

The following steps are used to derive the term symbols for a given electronic configuration :

(1) Write the electronic configurations and ignore the inner closed shell.

(2) Couple the spins to find the values of S according to the series

$$S = |s_1 + s_2|,\ |s_1 + s_2 - 1|,\ \ldots\ldots,\ |s_1 - s_2|$$

(3) Couple the orbital angular momenta to find the values of L according to the series :

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, \ldots\ldots, |l_1 - l_2|$$

(4) Couple L and S to find the values of J according to the Clebsch-Gordan series :

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

(5) Express the term symbol, $^{2S+1}L_J$.

(6) Find the total number of microstates and verify them by sum up the microstates calculated for each spectroscopic term. If the number of microstates calculated from the electronic configuration is equal to the total number of microstates calculated from the spectroscopic terms, then the derived term symbols are correct.

Let us derive the term symbols for electronic configurations having one or two unpaired electrons in the partly filled subshells. The term symbols for the electronic configurations having three or more unpaired electrons is lengthy and complicated and therefore, beyond the scope.

(I) Term Symbols for atoms or ions having only one unpaired electron :

(a) For Na atom : The electronic configuration of Na atom is $[Ne]3s^1$. Ignoring the inner closed shell, we get,

$$S = s = \frac{1}{2} \text{ and } L = l = 0$$

For $L = 0$, the term is S

For $S = \frac{1}{2}$, $\quad 2S + 1 = 2 \times \frac{1}{2} + 1 = 2$

$$J = |L + S|, \ldots\ldots, |L - S|$$
$$= |0 + \frac{1}{2}|, \ldots\ldots |0 - \frac{1}{2}| = \frac{1}{2}$$

Thus, the term symbol for the sodium atom is ${}^2S_{1/2}$.

Verification : Number of microstates on the basis of electronic configuration is

$$= \frac{2!}{1!(2-1)!} = 2 \times 1 = 2$$

Number of microstates corrresponding to the derived term symbol is

$$= (2S + 1)\ (2L + 1) = 2 \times (2 \times 0 + 1) = 2$$

Since the number of microstates for the sodium atom is 2 by both the approaches. Thus, the derived term symbol is correct.

(b) For F atom : The electronic configuration of F is $[He]2s^2 2p^5$ which can be treated as $[Ne]2p^{-1}$, where the notation $2p^{-1}$ indicates the absence of a $2p$ electron. Thus $S = s = \frac{1}{2}$ and $L = l = 1$.

For $S = \frac{1}{2}$, $2S + 1 = 2$

For $L = 1$, the term is P

For $L = 1$ and $S = \frac{1}{2}$

$$J = |L + S|, \ldots\ldots, |L - S|$$
$$= |1 + \frac{1}{2}|, \ldots\ldots, |1 - \frac{1}{2}| = \frac{3}{2}, \frac{1}{2}$$

Thus, the spectroscopic term for the F atom is ${}^2P$ and the term symbols are ${}^2P_{3/2}$ and ${}^2P_{1/2}$.

Verification :

Number of microstates for $2p^5$ configuration $= \frac{6!}{5!\,1!} = 6$

Number of microstates for ^2P term $= 2 \times (2 \times 1 + 1)$

$= 6$

Since the number of microstaes calculated for $2p^5$ configuration and ^2P term are identical. Thus the derived term symbol is correct.

(ii) Term symbols for atoms having two valence electrons in excited electronic states, *i. e.*, the atoms having non-equivalent electrons :

In such electronic configurations having non-equivalent electrons, neither the Pauli exclusion principle nor the principle of indistinguishability restricts the L and S values for the term symbols. Thus, the term symbols obtained for the configurations having the non-equivalent electrons obey the Pauli's exclusion principle but no deviation. Some example illustrating the derivation of term symbols are given below :

(a) The excited state electronic configuration of Be is $1s^2 2s^1 2p^1$. In this case the $2s^1$ and $2p^1$ electrons are non-equivalent. Thus, for $2s^1 2p^1$ configuration.

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

(*i.e.*, the electrons may be parallel $S = 1$ or antiparallel, $S = 0$)

For $S = 1$, $2S + 1 = 2 \times 1 + 1 = 3$ and

For $S = 0$, $2S + 1 = 1$

$$L = | l_1 + l_2 |, \ldots\ldots, | l_1 - l_2 |$$
$$= | 0 + 1 |, \ldots\ldots, | 0 - 1 |$$
$$= 1, \text{ the term is } P$$

Thus, the spectroscopic terms corresponding to $S = 1$, $S = 0$ and $L = 1$ are ^3P and ^1P.

For $S = 1$ and $L = 1$

$$J = | 1 + 1 |, \ldots\ldots, | 1 - 1 |$$
$$= 2, 1, 0$$

Thus the term symbols for $S = 1$ and $L = 1$ are :

$$^3P_2, \ ^3P_1 \text{ and } ^3P_0$$

Now, for $S = 0$ and $L = 1$,

$$J = | 0 + 1 |, \ldots\ldots, | 0 - 1 |$$
$$= 1$$

Thus, the term symbol for $S = 0$ and $L = 1$ is $^1P_1$. Hence, the total possible term symbols for $s^1 p^1$ configuration are $^3P_2$, $^3P_1$, $^3P_0$ and $^1P_1$.

Verification :

Number of microstates for $2s^1 2p^1$ configuration

$$= \frac{2!}{1!\ 1!} \times \frac{6!}{1!\ 5!}$$
$$= 12$$

Number of microstates for ^3P and ^1P terms are calculated as follows :

Spectroscopic term	Number of microstates $(2S+1)(2L+1)$
^3P	$3\times(2\times1+1)=9$
^1P	$1\times(2\times1+1)=3$
	Total no. of microstates = 12

Since the number of microstates for $2s^1 2p^1$ configuration and, ^3P and ^1P terms are identical (= 12). Thus, the derived spectroscopic terms are correct.

(b) For the carbon atom in excited state :

The ground state electronic configuration of the carbon atom is $1s^2 2s^2 2p^2$. If one of the $2p$ electron is promoted to a $3p$ orbital, then the excited state electronic configuration of carbon becomes $1s^2 2s^2 2p^1 3p^1$ in which the p electrons are non-equivalent. For $2p^1 3p^1$ configuration.

$$S = \left|\frac{1}{2}+\frac{1}{2}\right|, \ldots\ldots, \left|\frac{1}{2}-\frac{1}{2}\right|$$

$$= 1, 0$$

For $S = 0$, $2S+1 = 2\times0+1 = 1$

and for $S = 1$, $2S+1 = 2\times1+1 = 3$

$$L = |l_1 + l_2|, \ldots\ldots, |l_1 - l_2|$$

$$= |1+1|, \ldots\ldots, |1-1|$$

$= 2, 1, 0$, the corresponding terms are D, P and S respectively

Thus, the spectroscopic terms or states for $S = 1$ and $S = 0$ are

$$^3D, \ ^3P, \ ^3S, \ ^1D, \ ^1P, \ ^1S$$

For $L = 2$ and $S = 1$

$$J = |2+1|, \ldots\ldots, |2-1|$$

$$= 3, 2, 1$$

Thus, the term symbols for $L = 2$ and $S = 1$ are

$$^3D_3, \ ^3D_2, \ ^3D_1$$

For $L = 2$ and $S = 0$

$$J = |2+0|, \ldots\ldots, |2-0|$$

$$= 2$$

Thus, the term symbol for $L = 2$ and $S = 0$ is

$$^1D_2$$

For $L = 1$ and $S = 1$,

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

$$= 2, 1, 0$$

Thus, the term symbols for $L = 1$ and $S = 1$ are $^3P_2$, $^3P_1$ and $^3P_0$.

For $L = 1$ and $S = 0$,

$$J = |1+0|, \ldots\ldots, |1-0|$$
$$= 1$$

Thus, the term symbol for $L = 1$ and $S = 0$ is ${}^1P_1$.

For $L = 0$ and $S = 1$

$$J = |0+1|, \ldots\ldots, |0-1|$$
$$= 1$$

Thus, the term symbol for $L = 0$ and $S = 1$ is ${}^3S_1$

For $L = 0$ and $S = 0$.

$$J = 0$$

Thus, for $L = 0$ and $S = 0$, the term symbol is ${}^1S_0$.

Hence, the possible term symbols for $2p^1 3p^1$ configuration are ${}^3D_3$, ${}^3D_2$, ${}^3D_1$, ${}^1D_2$, ${}^3P_2$, ${}^3P_1$, ${}^3P_0$, ${}^1P_1$, ${}^3S_1$ and ${}^1S_0$.

Verification :

Number of microstates for a given electronic configuration is $= \frac{6!}{1!\ 5!} \cdot \frac{6!}{1!\ 5!} = 36$

Number of microstates for a given term $= (2S+1)\ (2L+1)$

Number of microstates for the spectroscopic terms are calculated in the following table :

Spectroscopic term	**Number of microstates** $(2S+1)\ (2L+1)$
${}^3D$	$3 \times (2 \times 2 + 1) = 3 \times 5 = 15$
${}^3P$	$3 \times (2 \times 1 + 1) = 3 \times 3 = 9$
${}^3S$	$3 \times (2 \times 0 + 1) = 3 \times 1 = 3$
${}^1D$	$1 \times (2 \times 2 + 1) = 1 \times 5 = 5$
${}^1D$	$1 \times (2 \times 1 + 1) = 1 \times 3 = 3$
${}^1S'$	$1 \times (2 \times 0 + 1) = 1 \times 1 = 1$
	Total no. of microstates = 36

Since the number of microstates calculated for the $2p^1 3p^1$ and for the spectroscopic terms ${}^3D$, ${}^3P$, ${}^3S$, ${}^1D$, ${}^1P$ and ${}^1S$ are identical. Thus, the derived terms symbols are correct.

(c) Term Symbols for a $3p^1 3d^1$ configuration :

For the $3p^1 3d^1$ configuration,

$$S = \left|\frac{1}{2}+\frac{1}{2}\right|, \ldots\ldots, \left|\frac{1}{2}-\frac{1}{2}\right|$$
$$= 1, 0$$

The number of microstates calculated for the ^3F, ^3D, ^3P, ^1F, ^1D and ^1P are calculated in the following table :

Spectroscopic term	Number of microstates $(2S+1)(2L+1)$
^3F	$3\times(2\times3+1)=21$
^3D	$3\times(2\times2+1)=15$
^3P	$3\times(2\times1+1)=9$
^1F	$1\times(2\times3+1)=7$
^1D	$1\times(2\times2+1)=5$
^1P	$1\times(2\times1+1)=3$
	Total no. of microstates = 60

Since the number of microstates for $2p^1 3d^1$ configuration and for ^3F, ^3D, ^3P, ^1F, ^1D and ^1P terms is identical (= 60). Thus the derived spectroscopic terms are allowed.

(d) The term symbols for $1s^1\,2s^1$ configuartion :

For $1s^1 2s^1$ configuration, the two s electrons are non-equivalent.

$$S = \left|\frac{1}{2}+\frac{1}{2}\right|, \ldots\ldots, \left|\frac{1}{2}-\frac{1}{2}\right|$$

$$= 1, 0$$

For $S = 1$, $\quad 2S+1 = 3$ and

For $S = 0$, $\quad 2S+1 = 1$

$$L = |\, l_1 + l_2 \,|, \ldots\ldots, |\, l_1 - l_2 \,|$$

$$= |\, 0+0 \,|, \ \ldots\ldots, |\, 0-0 \,|$$

$= 0$, the corresponding term is S

Thus, for $S = 1$ and $S = 0$, the spectroscopic terms are ^3S and ^1S respectively.

For $L = 0$ and $S = 1$, $J = 1$

Thus, the term symbol for $L = 0$ and $S = 1$ is $^3S_1$

For $L = 0$ and $S = 0$, $J = 0$

Thus the spectroscpic term is $^1S_0$

Hence, the term symbols for $S = 1$ and $S = 0$ are $^3S_1$ and $^1S_0$

Verification :

Number of microstates for $1s^1 2s^1$ configuration $= \dfrac{2!}{1!\ 1!} \times \dfrac{2!}{1!\,1!}$

$= 4$

Number of microstates for ^3S and ^1S terms are calculated as follows :

Spectroscopic term	Number of microstates $(2S+1)(2L+1)$
^3S	$3\times(2\times0+1)=3$
^1S	$1\times(2\times0+1)=1$
	Total no. of microstates = 4

Since the number of microstates for $1s^1 2s^1$ configuration and ^3S and ^1S terms are identical. Thus the derived term symbols for $1s^1 2s^1$ configuration are correct.

(iii) The term symbols for atoms or ions having equivalent electrons in the ground state :

For a system containing two equivalent electrons, the Pauli's exclusion principle restricts the icrostates that can occur in the configuration and consequently it affects the terms that can occur. This due to the reason that $n_1 = n_2$ and $l_1 = l_2$ and we can not simultaneously choose $m_{l_1} = m_{l_2}$ and $= m_{s_2}$. Secondly if the values of all the four quantum numbers, n, l, m_l and m_s for each of the two ectrons are exchanged, the initial situation is identical in every

Ground State Term : Hund's Rule

The terms derived for an electronic configuration have different energies. For example, the p^2-electronic configuration gives rise to three terms that are 3_P, 1_D and 1_S. These three terms have different energies. These terms represent three states with different amount of inter-electronic repulsions. The ground state term (lowest energy) can be determined by using the Hund's rules.

1. For a given configuration, the ground state term (term of lowest energy) is that which has highest spin multiplicity. The ground state, therefore, have the highest number of unpaired electrons and this gives rise to minimum repulsion and high exchange energy. For example, the ground state term for p^2-configuration is $3p$.
2. If the two states have the same spin multiplicity, the state with highest value of L will be the ground state. For example, for d^2-configuration, the terms are 3_F, 3_P, 1_S, 1_D and 1_G. 3_F and 3_P both have same spin multiplicity but 3_F has higher value of L. Thus, 3_F has lower energy than 3_P. Hence 3_F is the ground state.

3. For a given electronic configuration, if spin multiplicities are same and the values of L are also same for two atomic states, then the state having lowest J value will be of lowest energy if the subshell is less than half filled, and the state having highest value of J will be of lowest energy if the subshell is more than half filled.

If the subshell is exactly half filled, it has only one value of J. This law is applicable when spin-orbit coupling is taken into account.

To Identify the Ground State Term and Ground State Term Symbol for Atoms

Following steps are used to identify the ground state:

(1) Identify the microstate that has the highest value of S.

(2) Find out the spin multiplicity $(2S + 1)$.

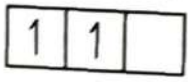
(3) Determine the maximum possible value of $M_L\ (= \Sigma m_i)$ or L.

(4) Select maximum value of J for more than half filled subshell and minimum value of J for less than half filled subshell.

Examples :

(i) p^2-Configuration :

m_l $\quad +1 \quad 0 \quad -1$



$L = M_L = +1 + 0 = +1$, P state

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

Spin multiplicity $= 2S + 1 = 2 \times 1 + 1 = 3$

$\therefore$ Ground state term $= {}^3P$

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

$= 1 + 1, \ldots\ldots 1 - 1$

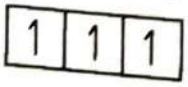
$= 2, 1, 0$

Since p-subshell is less than half filled.

$\therefore$ Ground state term symbol $= {}^3P_0$

(ii) p^3- Configuration :

m_l $\quad +1 \quad 0 \quad -1$



$L = M_L = +1 + 0 - 1 = 0$, $\quad S$ state

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$$2S+1=2\times\frac{3}{2}+1=4$$

$\therefore$ Ground state term $= {}^4S$

For $L=0$, and $S=\frac{3}{2}$

$$J=\left|0+\frac{3}{2}\right|.....\left|0-\frac{3}{2}\right|$$

$$=3/2$$

$\therefore$ Ground state term symbol $= {}^4S_{3/2}$

(iii) For d^2-Configuration (Ti^{2+} or V^{3+} ion) :

m_l +2 +1 0 −1 −2 $\qquad M_L = 2 + 1 = 3$, F state

1	1			

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

$2S+1=2\times1+1=3$

Ground state term $= 3_F$

$$J=|L+S|,.....|L-S|$$
$$=3+1,.....|3-1|$$
$$=4,3,2$$

Since d-orbital is less than half filled, lowest value of J will give the ground state term. Therefore, ground state term symbol $= {}^3F_2$. The d^n and d^{10-n} configurations give identical terms (Table 5.2).

Table 5.2 : Terms for d^n Configurations

Electronic Configuration	Ground State Term	Other Terms with Same Spin Multiplicity as that of Ground State
d^1, d^9	2_D	—
d^2, d^8	3_F	$3_P, 1_G, 1_D, 1_S$
d^3, d^7	4_F	$4_P, 2_P, 2_D, 2_F, 2_G, 2_H$
d^4, d^6	5_D	$3_P, 3_D, 3_F, 3_G, 3_H,$ $1_S, 1_D, 1_F, 1_G, 1_I$
d^5	6_S	$4_P, 4_D, 4_F, 4_G, 2_S, 2_P,$ $2_D, 2_F, 2_G, 2_H, 2_I$
d^{10}	1_S	—

Model Questions on Microstates

1. Determine the total number of microstates and ground state term symbol (R-S term) for a d^2-system.
2. Determine the ground state term for V^{3+}.
3. What do you mean by microstate?
4. Deduce ground state term symbol for atom having atomic number 22.
5. The different possible energy states for d^2-configuration are ^3F, ^3P, ^1G, ^1D and ^1S. predict the ground state term with necessary arguments
6. State Hund's rules and hence find out the ground state term for carbon atom.

References

1. Kumar Ajay (2016), "Coordination chemistry" 4th Edition.
2. Ramanee D. Wijesekera, "Coordination compounds, Bonding, Structure & Nomenclature.