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- **Spectroscopic term symbol**
  - **Energy ordering of terms**

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Spectroscopic term symbol:

- **Term** : A term is an energy level of an atomic system specified by an electronic configuration of an atom/ ion in the complexes .
- Partially field shell generates inter-electronic repulsion and spin orbit coupling.

How terms are generated ?

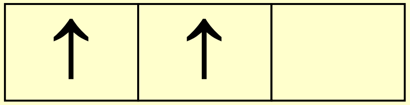
Electronic configuration → (Inter Electronic repulsion) → Terms → (Spin orbit coupling) → State → (External Magnetic Field states are populated) → Microstates

Spectroscopic Term symbol :

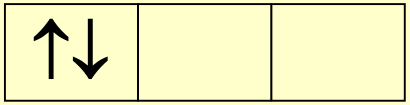
Spin multiplicity → $^{(2S+1)}L_J$ ←

L = 0	S term
L = 1	P term
L = 2	D term
L = 3	F term

- Two p orbital electrons spin (s) can be written as if they interact ----



$S = ½+½= 1$



$S = ½- ½= 0$

This coupling also called as spin – spin coupling

- Allowed L values – It is total orbital angular momentum, generated due to coupling of orbital angular momentum of two electrons.

$L = (l_1+l_2),\quad (l_1+l_2-1),\quad (l_1+l_2-2),\quad ---|l_1-l_2|$

L	0	1	2	3	4	5	6	7
Term symbol =	S	P	D	F	G	H	I	K

iii) The coupling of orbital angular momentum (L) with spin angular momentum (S) is called L- S coupling .]

This coupling gives total angular momentum quantum number J ,Which is determined as :

$J = L+S, \quad L+S-1, \quad L+S-2 \ , \ --- \quad |L-S|$

Maximum ... Minimum

Ground state term symbol for :

i) . Atom

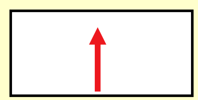
ii). ion

iii). complex

Problem 1. : Determine the ground state term symbol for H atom

$_1H = 1s^1$

l= 0



L = 0

↓

^2S

Spin multiplicity = 2S + 1

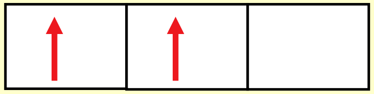
= 2x1/2 + 1

= 2

Problem 2. : Determine the ground state term symbol for Carbon atom

$_6C = 1s^2 2s^2 2p^2$

l= 1 0 -1



Spin multiplicity = 2S + 1

= 2x1 + 1

= 3

L = 1

↓

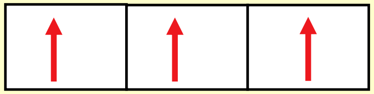
^3P

Problem 3. : Determine the ground state term symbol for Nitrogen atom

$_7N = 1s^2 2s^2 2p^3$

↓

l= 1 0 -1



Spin multiplicity = 2S + 1

= 2x3/2 + 1

= 4

L = 1 +0 −1

L = 0

^4S

Problem 4. : Determine the ground state term symbol for Chlorine atom

$_{17}Cl = 1s^2 2s^2 2p^6 3s^2 3p^5$

l= 1	0	-1
↑↓	↑↓	↑

Spin multiplicity = 2S + 1

= 2x1/2 + 1

= 2

L = 1+1+ +0 +0 −1

L = 1

^2P

Problem 5 : Determine the ground state term symbol for O^{--} ion

$_8O = 1s^2 2s^2 2p4$

$O^{--} = 1s^2 2s^2 2p^6$

l= 1	0	-1
↑↓	↑↓	↑↓

Spin multiplicity = 2S + 1

= 2x0 + 1

= 1

L = 1+1+ +0 +0 −1−1

L = 0

^1S

Problem 6 : Determine the ground state term symbol for Ti, and Ti^{3+}

$_{22}Ti = 1s^2 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^2$

$\ell =$ 2	1	0	-1	-2
↑	↑			

$L = \Sigma\, l_i$

$= 2+1$

$L = 3$

^3F

Spin multiplicity = 2S + 1

= 2x1 + 1

= 3

$Ti^{3+} = 1s^2 2s^2 2p^6\ 3s^2 3p^6 3d^1$

$\ell =$ 2	1	0	-1	-2
↑				

$L = \Sigma\, l_i$

$= 2$

^2D

Spin multiplicity = 2S + 1

= 2x1/2 + 1

= 2

Problem 6 : Determine the ground state term symbol for Cu and Cu^{2+} ion

$_{29}Cu = 1s^2 2s^2 2p^6\ 3s^2 3p^6 4s^1 3d^{10}$

$\ell =$ 2	1	0	-1	-2		L= 0
↑↓	↑↓	↑↓	↑↓	↑↓		↑

$L = \Sigma\ l_i$

$= 2+2+1+1+0 -1-1-2-2 +0$

L = 0

^{2}**S**

Spin multiplicity = 2S + 1

= 2x1/2 + 1

= 2

$Cu^{2+} = 1s^2 2s^2 2p^6\ 3s^2 3p^6 3d^9$

$\ell =$ 2	1	0	-1	-2
↑↓	↑↓	↑↓	↑↓	↑

Spin multiplicity = 2S + 1

= 2x1/2 + 1

= 2

$L = \Sigma\ l_i$

$= 2+2+1+1+0 -1-1-2$

L = 2

^{2}**D**

Apply L–S cuplinfg scheme ofn the terms to get sub elergy level s

Electronic Configuration → Terms —Spin orbit coupling→ Sub level

Term symbol = $^{2S+1}L_J$

Apply this scheme

J = |L+S|, L+S–1, L+S–2 . . . | L–S |

Examples : ^3F_J —L– S→ ?

Apply L– S coupling Scheme on ^3F term

$$^3F \xrightarrow{L - S\ coupling}$$

Solution

^3F

L= 3

2S +1 = 3

2S = 3–1

2S = 2

S = 2/2

S = 1

J = L+S	J = L+S –1	J = L–S
= 3+1	= 3+1–1	= 3– 1
= 4	= 3	= 2
$^3F_4$	$^3F_3$	$^3F_2$

$$^3F \xrightarrow{L - S\ coupling} {}^3F_4\ ,\ {}^3F_3\ ,\ {}^3F_2$$

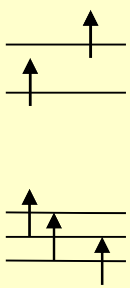
^3F has three subleve

What is difference between Spin of electron (s) and Magnetic spin (M_s) ?

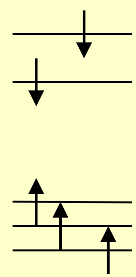
Yes , the Spin of electron (s) and Magnetic spin (M_s) are distinguishable

Ex : Identify the Spin 'S' and Magnetic spin M_S of the following configuration :

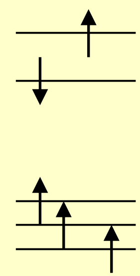
d^5



$S = 5/2$, $M_S = 5/2$



$S = 5/2$, $M_S = 1/2$



$S = 5/2$, $M_S = 3/2$

1 - Singlet

2 - Doublet

3 - Triplet

4 - Quartet

5 - Quintet

6 - sextet

Significance of Spin multiplicity

- Spin multiplicity = 2S + 1
- Possible ways of representation of electrons spin orientation in respective orbital
- Example:
- $d^1 \rightarrow {}^2D$
- One electron can be represented in two different distinguishable ways in d orbital

↑					U
↓					D

d^2 → ^3F

Two electron can be represented three different distinguishable ways in d orbital

↑	↑				U U
↓	↓				D D
↑	↓				U D

d^3 → ^4F

↑	↑	↑			U U U
↓	↓	↓			D D D
↑	↑	↓			U U D
↑	↓	↓			U D D

d^4 → ^5D

↑	↑	↑	↑		U U U U
↓	↓	↓	↓		D D D D
↑	↑	↑	↓		U U U D
↑	↑	↓	↓		U U D D
↑	↓	↓	↓		U D D D

d^5 → ^6S

↑	↑	↑	↑	↑	U U U U U
↓	↓	↓	↓	↓	D D D D D
↑	↑	↑	↑	↓	U U U U D
↑	↑	↑	↓	↓	U U U D D
↑	↑	↓	↓	↓	U U D D D
↑	↓	↓	↓	↓	U D D D D

Total terms for d^1 to d^{10} configuration :

Configurations	Spectroscopic term symbols
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1D, ^1G, ^1S
d^3, d^7	^4F, ^4P, ^{2}(P, 2xD, F, G, H)
d^4, d^6	^5D, ^{3}(2xP, D, 2xF, G, H), ^{1}(2xS, 2xD, F, 2xG, I)
d^5	^6S, ^{4}(P,D, F, G), ^{2}(S, P, 2xD, 2xF, 2xG, H , I) , ^1S

Energy ordering of terms:

- When once the number of terms are known for the given configuration, it is important to arrange them in the increasing order of their energy. This energy sequencing of terms is based on the minimization of repulsive energies . According to Hund's Rule: given by

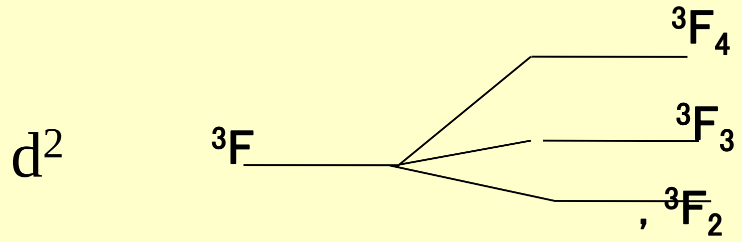
Hund's rules :

1. Highest spin multiplicity has lower energy.

2. If the two of terms has highest spin multiplicity, then the terms of larger 'L' will be lower energy .

3. The lowest level is that with minimum values of J, if the shell is less then half field. e.g. for d^2 = $^3F_2 < ^3F_3 < ^3F_4$.

4. The lowest level is that with Maximum values of J, if the shell is more then half field. e.g. for d^8 = $^3F_4 < ^3F_3 < ^3F_2$.



Problem : Apply Hund's rule and arrange the following terms increasing order of energy

i). ^{4}F, ^{4}P, ^{2}P, ^{2}D, ^{2}G, ^{2}F, ^{2}H, ^{1}I

ii) ^{3}P, ^{3}D, ^{3}F, ^{3}G, ^{3}H, ^{1}S, ^{1}D, ^{1}F, ^{1}G, ^{1}I , ^{5}D

THE END