SP-1(A):TERM SYMBOLS

Addition of angular momentum vectors L and S of individual valence electron.

LS (RS=Russel-Saunder coupling)

Rules for determining ground state Term Symbol:

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

Where;

S = Σm_s (max) = Total spin –Maximum spin multiplicity- Hund's Rule

L = Σm_l (max) =Maximize the orbital angular momentum =Total orbital angular momentum.

Notation: L = 0, 1, 2, 3, 4, 5, 6 ……

S, P, D, F, D, H ……..

Calculate J

J = L+S, L+S-1, ……. |L-S| = Total angular momentum quantum number

(i) J = **Max** if the shell is more than half filled and **Min** if less than half filled.

(ii) When the two states have same L value, the one having greater S value will have less energy.

(iii) When the two states have same S value, then the one having greater L value will have less energy.

(iv) For orbital having less than half filled , the energy order is

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

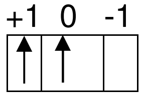
EXAMPLES

Ground state symbols for some selected (configurations)atoms and ions

1. **Carbon , p^2**

2p

+1 0 -1



L = +1+ 0 = 1; Term= P

S = ½ + ½ = 1; **2S+1**=3

J = L+S; (L+S)-1;……. ..|L-S| = 2, 1, 0

The configuration is less than half filled .Hence, **J** must be **minimum**.

J = 0 must be the ground state.

The term symbol = $^{3}\mathbf{P}_{0}$

2. Nitrogen, p^3

$2p^3$

+1 0 -1

↑	↑	↑

L = +1 0 -1= 0

S = ½ + ½ + ½ = 3/2; **2S +1** = 4

J = 3/2 , ½

Term = $^{4}\mathbf{S}_{3/2}$

3. Na , $3s^1$

Na = [Ne] $3s^1$

L=0

S= ½ ; **2S+1** = 2 x ½ + 1 = 2

J = L + S … to|L-S| = ½

Term symbol for **Na** = $^{2}\mathbf{S}_{½}$

4. d^1 - States

m_l = 2 1 0 –1 –2

↑				

L = 2

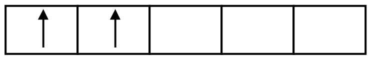
S = ½ ; **2S+1** = 2 x ½ + 1 = 2

J = L+S …..|.L-S| = 5/2 , 3/2 , ½

Term symbol is $^{2}\mathbf{D}_{½}$

5. d^2 – States (V^{3+})

m_l = 2 1 0 –1 –2



L = 2+1 = 3

S = ½ + ½ = 1 ; **2S+1** = 2(1) + 1 = 3

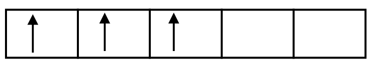
J = L+S; (L+S)-1;……….L-S = 4 , 3 , 2

= L+S = 2 (Less than half filled)

Term symbol is ^{3}**F$_2$**

6. d^3 - States

m_l = 2 1 0 –1 –2



L = 2 + 1 + 0 = 3

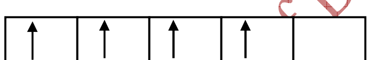
S = ½ + ½ + ½ = 3/2 ; **2S+1** = 2 x 3/2 + 1 = 4

J = L+S ……..L-S = (3 + 3/2) ………. to (3-3/2) = 9/2 , 7/2 , 5/2 , 3/2 .

Term symbol for is ^{4}**F$_{3/2}$**

7. d^4 - States

m_l = 2 1 0 –1 –2



L = 2 + 1 + 0 – 1 = 2

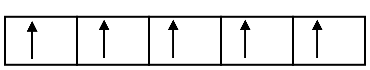
S = ½ + ½ + ½ + ½ = 2 ; 2S+1 = 2 x 2 + 1 = 5

J = L+S to L-S = 4, 3

Term symbol for is ^{5}**D$_0$**

8. d^5 - States

m_l = 2 1 0 –1 –2



L= 2 + 1 + 0 – 1 – 2 = 0

S = ½ + ½ + ½ + ½ + ½ = 5/2; **2S+1** = 2 x 5/2 + 1 = 6 ;

J = (L+S) , (L+S-1)………..(L-S) = 5/2 , 3/2 , ½ = 5/2 (J_{max} , Half filled- Highest)

Term symbol for $\mathbf{d^5}$ is $\mathbf{^6S_{5/2}}$

9. $\mathbf{d^8}$ - States

m_l = 2 1 0 –1 –2

↑↓	↑↓	↑↓	↑	↑

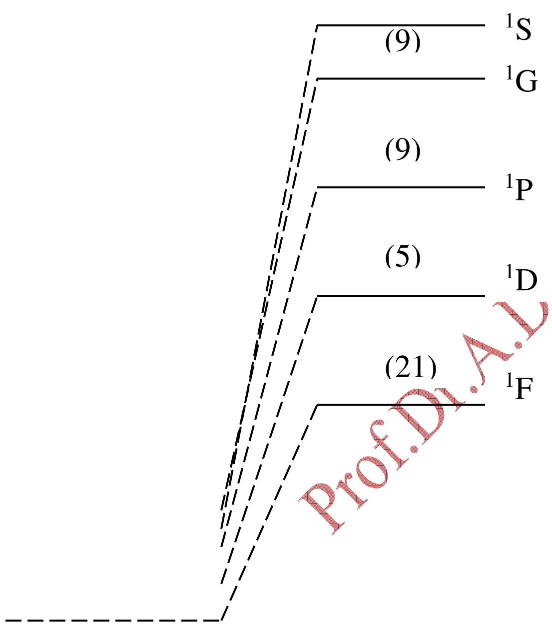
L = 2+1 = 3

S = ½ + ½ = 1 ; 2S+1 = 2(1) + 1 = 3

J = L+S … L-S = 3+1 to 3-1 = 4 , 3 , 2 (more than half filled)

Term symbol for $\mathbf{^3F_4}$

Similarly, $\mathbf{d^6}$ = ^{5}D; d^7 = ^{4}F; $\mathbf{d^8}$ = ^{3}F; $\mathbf{d^9}$ = ^{2}D



The term arising from the electron interaction* (J+S to J-S) *in the d^2* (*Ground state-$^3F_2$*) *ion.

The degeneracy of each term is indicated in parenthesis

Free ion terms for various d^n (Oh) ions.

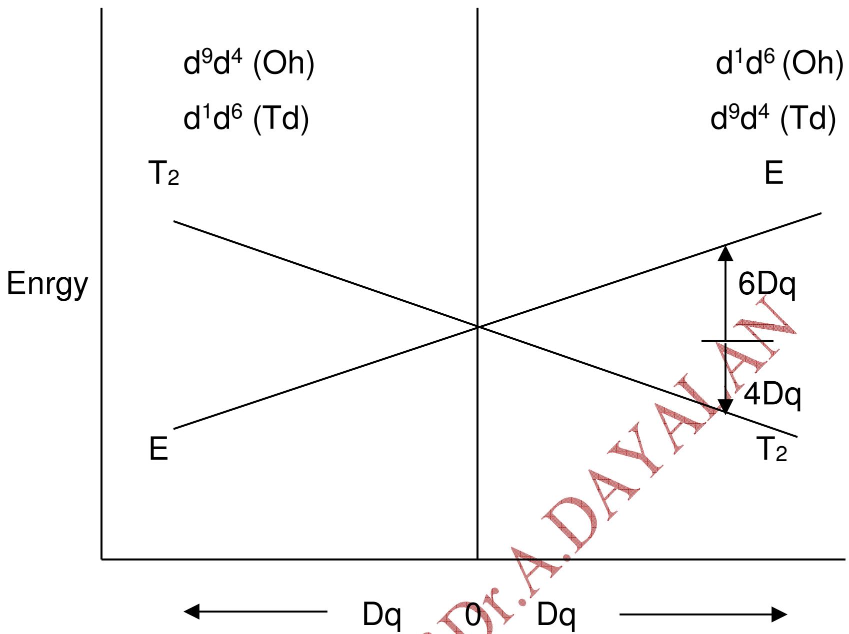
d^n	Terms
d^1 d^9	^{2}D
d^2 d^8	^{3}F ^{3}P ^{1}G ^{1}D ^{1}S
d^3 d^7	^{4}F ^{4}P ^{2}H ^{2}G ^{2}F ^{2}D ^{2}D ^{2}P
d^4 d^6	^{5}D ^{3}H ^{3}G ^{3}F ^{3}F ^{3}D ^{3}P ^{1}I ^{1}G ^{1}G ^{1}F ^{1}D ^{1}D ^{1}S ^{1}S
d^5	^{6}S ^{4}G ^{4}F ^{4}D ^{4}P ^{2}I ^{2}H ^{2}G ^{2}G ^{2}F ^{2}F ^{2}D ^{2}D ^{2}P ^{2}S

Ground State term symbol for some atoms

S = $^3P_2$; **Cl** = $^2P_{3/2}$; **Si** = $^3P_0$; **Ti** = $^3F_2$; **Cr** = $^7S_3$; **Ni** = $^3F_4$

ORGEL DIAGRAM

NB: All the d-d transitions are multiplicity and Laporte forbidden



LHS: d^9 & d^4 (Oh) & d^1d^6 (Td) complexes give only one line corresponding to the transition.

d^9(Oh) E ($t_{2g}^6\ e_g^3$) ⟶ T_2 ($t_{2g}^5\ e_g^4$)

e_g^3 can occur in two ways(E-doubly degenerate) as

$d_{(x^2-y^2)}$	d_{z^2}
2	1
1	2

t_{2g}^5 in three ways(T_2 triply degenerate) as

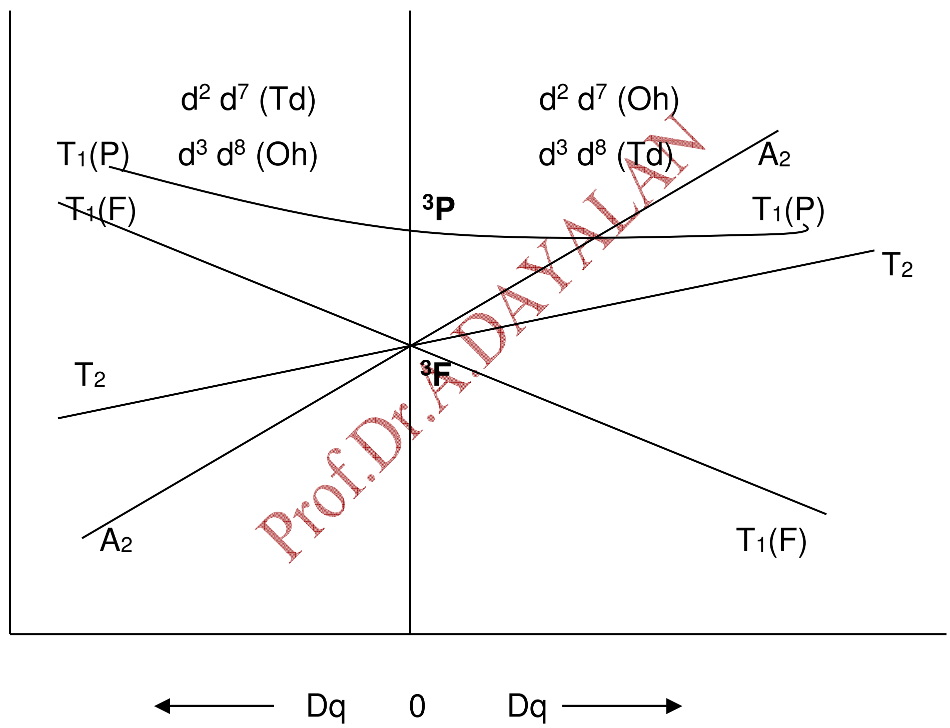
d_{xy}	d_{yz}	d_{zx}
2	1	1
1	2	1
1	1	2

RHS: Similarly,

d^9 & d^4 (Td) & $d^1 d^6$ (Oh) complexes give **only one line** corresponding to the transition.

d^9 (Td) T_2 (t_{2g}^5 e_g^4) ⟶ E (t_{2g}^6 e_g^3)

NB: Td complexes (no centre of symmetry) give **more intense bands** than the Oh complexes.



^{3}F gets splitted but not **^{3}P**

Spectra of V(III)- d^2 (Oh) –(*Two lines*)- RHS

T_{1g}(F) is the ground state.The possible transition are

$T_{1(g)}$F ⟶ $^3T_2$(F) (1700 cm^{-1})

$T_{(g)}$F ⟶ $^3T_1$(P) (2400 cm^{-1})

T_{1g}(F) ⟶ A_2g (Two electron transition impossible, low intensity)

Spectra of Ni(II)-d^8 -(Oh)– (*Three lines*)- LHS :

	Ligand	
	H_2O	NH_3
$^3A_{2g} \longrightarrow T_{2g}$	8500 cm^{-1}	10750 cm^{-1}
$^3A_{2g} \longrightarrow T_{1g}$ (F)	15400	17500
$^3A_{2g} \longrightarrow T_{1g}$ (P)	26000	28200
	Weak field ligand	Strong field ligand
	Low Dq	High Dq
	Low energy	High energy

Possible electronic arrangement for $t_{2g}^2 \longrightarrow t_{2g}^1\ eg^1$

But, the transition

$xy^1\ xz^1\ yz \longrightarrow xy\ zx^2\ yz$

T_{2g} (triplet) A_{2g} (singlet)

is multiplicity forbidden and may take place with low intensity.