Electronic Configuration:

According to Bohr's Theory, the position of the lines in hydrogen spectrum was explained interms of only a single quantum number n, called Principal quantum number. But, Bohr's theory was inadequate to explain the fine structure of hydrogen atom. The fine structure of hydrogen spectrum can be observed with spectroscope of high resolving power. The fine structure of spectral lines of other elements is often observed with spectroscopes of low resolving power. Further division of spectral lines occur if the substance is placed in a magnetic field or an electric fields. These are known as Zeeman effect and Stark effect respectively. Thus single quantum number is inadequate and additional quantum numbers are needed to specify in detail the energy levels of atomic electrons. To explain the energy levels in an atom four quantum numbers are necessary. The four quantum numbers are.

(a) Principal Quantum number (n)
(b) Azimuthal Quantum number (l)
(c) Magnetic Quantum number (ml)
(d) Spin Quantum number

(a) Principal Quantum number (n): The principal quantum number is designated by the letter 'n'. This quantum number denotes the energy level or the principal shell to which an electron belongs. The principal quantum number has only integral values.

(b) Azimuthal quantum number (l): An extension to Bohr's model of an atom is Sommerfeld's model of an atom. According to Sommerfeld's model electron moves round the nucleus in elliptical orbits. In circular orbits, the angular position of the electron from the nucleus changes during a revolution, whereas in case of elliptical orbits both the distance of the electron from the nucleus and angular position changes simultaneously. Hence the motion of a particle in an ellipse has two degrees of freedom and thus two quantum numbers are needed to represent the electronic motion.

To describe the motion of an electron another quantum number called Azimuthal quantum number is introduced and is denoted by the letter 'l'. This is also called as angular momentum quantum number or orbital quantum number or sometimes as subsidiary quantum numbers. This quantum number gives an idea of the shape of the orbital.

For a given value of n (Principal quantum number), l can have any value from 0 to (n-1)

For $n=1$, $l=0$ and for $n=2$, $l=0,1$

(c) Magnetic Quantum number (m_l): The lines of spectrum will further split in placed in strong magnetic field, the phenomenon is called as Zeeman effect. The spectral lines will also be split by an electric field, which is known as stark effect. This type of splitting of spectral lines in magnetic & electric field indicates that the energy levels are further subdivided by the field. Therefore an additional quantum number is needed to specify these energy levels.

The additional quantum number which is used to specify these energy sub levels is magnetic quantum number and is denoted by the letter 'm_l'. This quantum number corresponds to the component of the orbital angular momentum along a reference direction. This quantum gives an idea about the spatial orientation of the sub shells.

The possible values of m_l depend on the values of l, m_l can have the following values for a given value of l.

i.e. $m_l = 0, \pm1, \pm2, \pm3, \ldots\ldots, \pm l$.

∴ for $l=0$, $m_l=0$ and for $l=1$ $m_l=0, \pm1$ ~~etc~~.

(d) Spin Quantum number: Even the three quantum numbers n, l and m_l were found to be inadequate for explaining the multiplicity and fine structure of some spectral lines that could be observed with a spectroscope of high resolving power. For example, the doublet of a 'Na' D line cannot be explained using the three quantum numbers. Thus the idea of 'electron spin' was therefore advanced by Uhlenbeck and Goudsmith in 1925 to account for this. The fourth quantum number is spin quantum number used to explain the multiplicity of spectral lines. The spin quantum number can have only two values $+\frac{1}{2}$ and $-\frac{1}{2}$

Electronic Configuration: The description of electronic state of an atom in terms of the individual electrons constitute the electronic configuration.

The principal electronic shells in an atom are designated as K, L, M, N etc and corresponds to the principal quantum number $n=1, 2, 3, 4$ etc respectively. Each of these shells is associated with a group of quantum states & energy states. The maximum number of electrons for each principal quantum number 'n' can be given by $2n^2$

The filling up of orbitals with electrons takes place according to certain rules (i) Aufbau Principle (ii) Hund's rule of maximum multiplicity (iii) Pauli's exclusion principle.

Russel - Saunders terms and Coupling Schemes:

Term: A term is an energy level of anatomic system specified by an electronic configuration. Thus, a configuration give rise to several terms. A given configuration may have completely filled shells and partially filled or unfilled shells. The electrons in an unfilled shell of a free ion are subjected to two perturbations (i) interelectronic repulsions and (ii) spin-orbit coupling.

(i) Inter-electronic repulsion: The electrons in an unfilled shell repel each other and the energy of the configuration depends upon the way in which the electrons are arranged relative to each other. This inter electronic repulsion leads to splitting up of the degenerate configuration into many terms.

(ii) Spin-orbit coupling: Electron possess two types of angular ~~an~~ momenta. They are spin ~~angular~~ angular momentum and orbital angular momentum. These two angular momenta couple to cause a perturbation on the configurati

The perturbations due to interelectronic repulsions and spin-orbit coupling do not operate simultaneously. The perturbation due to interelectro repulsion being certainly larger than the spin orbit coupling, the terms ~~are~~ generated generated due to inter electronic repulsion are further split into levels or states. The states generated are further split into microstates by the application of magnetic or electric fields. The microstates are non-degenerate.

~~configuration~~

$$\text{configuration} \xrightarrow[\text{repulsion}]{\text{inter-electronic}} \text{Terms} \xrightarrow[\text{coupling}]{\text{Spin-orbit}} \text{states} \xrightarrow[\text{effect}]{\text{Zeeman}} \text{Microstates}$$

Formula for number of microstates:

An arrangement with specific m_l and m_s values for an electronic configuration is called a microstate. The formula for the number of microstates for equivalent ~~configurations~~ electrons with l^q configuration is

$$n = \frac{(4l+2)!}{q!\,(4l+2-q)!}$$

where n is number of microstates; l is orbital quantum number i.e. l=0, s

l=1 for p orbital, l=2 for d orbital etc.

q = number of electrons in a particular configuration.

For example the no of microstates possible for d^2 configuration

$$n = \frac{[4(2)+2]!}{2!\,[4(2)+2-2]!} = \frac{10!}{2!\,8!} = \frac{10\times 9}{2} = 45$$

The formula for calculating the number of microstates for a system with non-equivalent electrons ~~[illegible]~~ with configuration $l_i^p l_j^q$ is

$$n = \left\{\frac{(4l_i+2)!}{p!\,[4l_i+2-p]!}\right\}\left\{\frac{(4l_j+2)!}{q!\,[4l_j+2-q]!}\right\}$$

Where l_i, l_j are orbital quantum number, p and q are no of electrons in l_i and l_j orbitals respectively.

Orbital angular momentum:

As a particle moving in a straight path passes ~~[illegible]~~ linear momentum; the electron while circulating about the nucleus in an orbit would have orbital angular momentum.

$$\text{orbital angular momentum} = [l(l+1)]^{1/2}\frac{h}{2\pi}$$

With increasing value of l, the angular momentum also increases. Thus an electron in d-orbital ($l=2$) has higher angular momentum than the electron in a p-orbital.

'l' denotes the orbital angular momentum for a single electron. When there is more than one electron in sub shell or orbital, the energy states depend on the resultant orbital angular momentum quantum number (L) of ~~indivi~~ individual electrons. The total orbital angular momentum quantum number (L) can be defined as

$$L = l_1 + l_2 + l_3 + \dots = \sum_i l_i$$

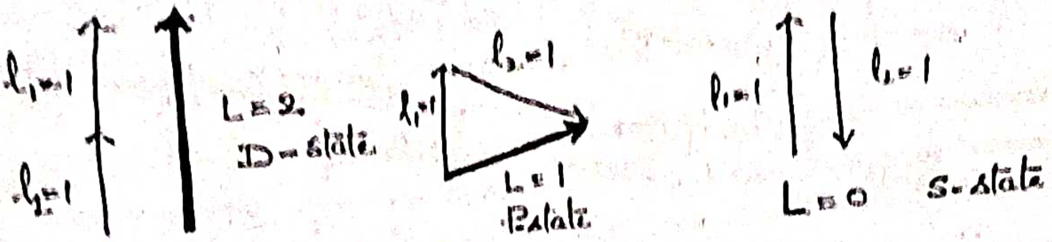
Thus for various values of L the term symbols are

When L =	0	1	2	3	4	5	6	7	8
Term Symbol X =	S	P	D	F	G	H	I	K	L

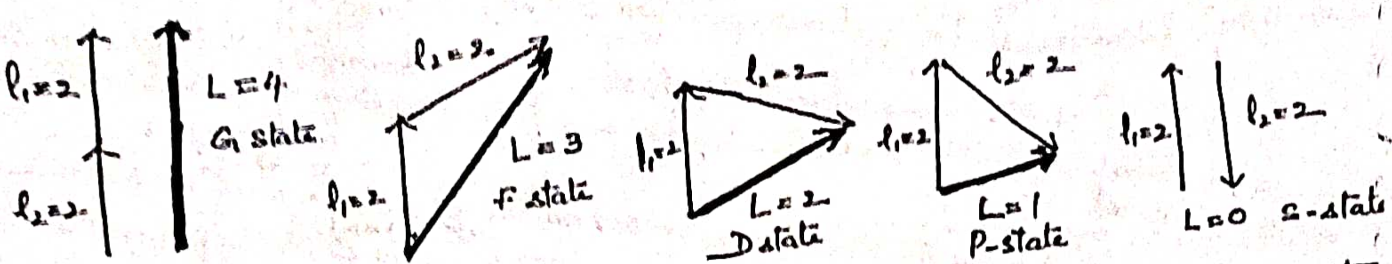
Vector coupling of orbital angular momenta:

The individual angular momenta of electrons undergo vector coupling. This vector coupling can be given as follows.

For example consider p^2 configuration; for p orbital $l_1=1$ and $l_2=1$ [∵ there are two electrons in p orbitals]. The interaction or coupling of $l_1=1$ and $l_2=1$ can be diagrammatically shown as follows.



Similarly for a d^2 configuration we have $l_1=2$, $l_2=2$. The vector coupling can be diagrammatically represented as follows.



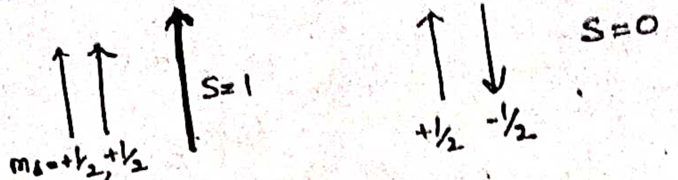
Simply, the total orbital angular momentum for equivalent two electron system can be written as

$$L = l_1+l_2,\ l_1+l_2-1,\ \text{-----}\ |l_1-l_2|$$

Spin angular Momentum:

For a single electron, the spin quantum number (M_s) has values of $+\frac{1}{2}$ or -. When there is more than one electron, the resultant spin angular momentum is obtained by the coupling of spin angular momentum of individual electrons.

For example when two electrons in a configuration couple with their spins, say as in p^2 configuration, we get:



Russell-Saunders Coupling or L-S coupling:

The coupling of total orbital angular momentum 'L' with total spin angular momentum 'S' to give a total angular momentum 'J' is known as Russell-Saunders coupling or L-S coupling. For lighter atoms, the coupling of orbital angular momentum of individual electrons, the coupling of s_i angular momentum of individual electrons will occur first and then of resultant orbital angular momentum and resultant spin angular momentum will occur i.e. L and S couple to give J

There $J = L+S,\ L+S-1,\ \dots\ |L-S|$

For p^2 configuration the coupling can be given as follows.

1. (i) $L=2$ $S=1$

$\therefore J = 2+1,\ 2+1-1, \dots 2-1$

$= 3,\ 2,\ 1$

(ii) $L=1$ $S=1$

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

$=2,1,0.$

i.e. A term can be written as ${}^{(2S+1)}X_J$. Where $(2S+1)$ is spin multiplicity and X is symbol written basing on L value.

$\therefore$ The term for $L=2$ $S=1$ is ${}^3D$ and Possible J values are 3,2,1.

i.e. The states are ${}^3D_3, {}^3D_2, {}^3D_1$.

Similarly for $L=1$ and $S=1$, the possible states are ${}^3P_2, {}^3P_1, {}^3P_0$

(iii) $L=0$ $S=1$

$\therefore J=1$

${}^3S_1$

p^2 configuration: The possible terms for p^2 configuration are ${}^3D, {}^1D, {}^3P, {}^1P, {}^3S$ and ${}^1S$.

The no. of microstates for p^2 configuration are $(n)=\frac{(4(1)+2)!}{2!(4(1)+2-2)!}=\frac{6!}{2!\,4!}=\frac{6\times5}{2}=15$

All the above terms are not allowed. The allowed terms should not violate Paulis Exclusion principle. According to Pauli's Exclusion principle each electron in an atom should have different set of four quantum numbers. The allowed terms are ^1D, ^3P and ^1S

Derivation of terms:

The term symbol can be given as $^{(2S+1)}X_J$

where S is total spin of the electrons and (2S+1) is the spin multiplicity. X assumes the letter according to L.

The components of L and S can have the following quantized values.

$M_L = L, L-1, \ldots\ldots, -(L-1), -L$ i.e. (2L+1) values.

$M_S = S, S-1, \ldots\ldots, -(S-1), -S$ i.e. (2S+1) values.

As there are (2L+1) values of M_L and (2S+1) values of M_S, the degeneracy or multiplicity of the term is given by (2L+1)(2S+1). The term will have

(2L+1) orbital degeneracy

(2S+1) – Spin degeneracy.

Therefore, each value of M_L occurs (2S+1) times, and each value of M_S, occurs (2L+1) times. The spectral terms can be worked as follows. A spectral term corresponds to a set of microstates.

Consider a system of p^1 configuration:

The possible arrangements of the electron can be written as follows with the help of m_l and m_s values for a p-electron.

For p^1 electron $l = 1$ and $m_l = +1, 0, -1$ and for one electron $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$.

With m_l and m_s values, the possible microstates can be given as follows.

$(1, +\frac{1}{2})$, $(1, -\frac{1}{2})$, $(0, \frac{1}{2})$, $(0, -\frac{1}{2})$, $(-1, \frac{1}{2})$, $(-1, -\frac{1}{2})$

or simply the above microstates can also be written as

$(\overset{+}{1})$, $(\overset{-}{1})$, $(\overset{+}{0})$, $(\overset{-}{0})$, $(\overset{+}{-1})$, $(\overset{-}{-1})$

The above electron arrangement can diagramatically be represented as

m_l =	+1	0	-1	M_L	M_S
	↑			1	+½
	↓			1	-½
		↑		0	+½
		↓		0	-½
			↑	-1	+½
			↓	-1	-½

A term representing all these microstates can be written by taking maximum value of L (or $M_L = L$ to $-L$) and the appropriate spin value, |S|. In this case, the maximum L value is 1 corresponding to the letter P for a term. Thus the term symbol for p^1 configuration can be written as follows

∵ $S = ½$ the multiplicity $(2S+1)$ is 2.

∴ The symbol is ^2P

The multiplicity of ^2P term is $[2(1)+1][2(½)+1] = 3 \times 2 = 6$. Therefore the term ^2P alone takes care of all possible arrangements.

Similarly the lone terms for other configurations such s^1, d^1, f^1 etc are as follows,

s^1 $M_L = 0$ $M_S = ½$ ^2S Total multiplicity $[2(0)+1][2(½)+1] = 2$

d^1 $M_L = 2$ $M_S = ½$ ^2D Total multiplicity $[2(2)+1][2(½)+1] = 10$

f^1 $M_L = 3$ $M_S = ½$ ^2F Total multiplicity $[2(3)+1][2(½)+1] = 14$

p^2 configuration

For systems having more than one electron the process of finding the appropriate terms becomes little difficult. The no of possible microstates for p^2 configuration are $\frac{[4(1)+2]!}{2![4(1)+2-2]!} = \frac{6!}{2!4!} = 15$. Even though 36 microstates are possible, only 15 are allowed microstates. The following six microstates which violate paulis Exclusion principle are not allowed.

ml	1	0	-1	M_L	M_S
	↑↑			2	1
		↑↑		0	1
			↑↑	-2	1
	↓↓			2	-1
		↓↓		0	-1
			↓↓	-2	-1

So out of 36 possible microstates 6 are not allowed basing on Pauli's Exclusion principle. Out of the remaining 30 possible microstates only 15 are meaningful because of the indistinguishability of the two electrons. The 15 allowed microstates of p^2 configuration can be given as follows.

ml	1	0	-1	M_L	M_S
				+1	+1,0,0,-1
				0	+1,0,0,-1
				-1	+1,0,0,-1

+1	0	-1	M_L	M_S
↑↓			2	0
	↑↓		0	0
		↑↓	-2	0

For $M_L=1$ the possible M_S values are +1, 0, 0, −1. This can be diagrammatically represented as follows.

m_l	+1	0	−1	M_L	M_S
	↑	↑		1	+1
	↑	↓		1	0
	↓	↑		1	0
	↓	↓		1	−1

The no of allowed microstates can be summarised as follows.

M_L / M_S	1	0	−1
2	-	1	-
1	1	2	1
0	1	3	1
−1	1	2	1
−2	-	1	-
Total	3	9	3

= 15 microstates (3+9+3)

From the above summarised table the spectral terms can be derived as follows.

A term can be deduced first by taking maximum value of M_L for L is equal to 2 and this is possible only if both the electrons are arranged in a box with $m_l=1$ and their spins are antiparallel so that Pauli's exclusion principle is not violated.

From maximum M_L value 2 it is possible to write $L=2$. For $M_L=2$ the possible M_S value is 0 (i.e. $S=0$)

$\therefore L=2 \quad S=0$.

M_L/M_S	0
2	1
1	1
0	1
-1	1
-2	1

5 microstates

L = 2
S = 0

Term is ^1D

The multiplicity associated with this term
$= [2L+1][2S+1] = [2(2)+1][2(0)+1] = 5$

Subtract the above table from the summarised microstates table and the resulting table is as follows.

M_L/M_S	1	0	-1
2	—	1	—
1	1	2	1
0	1	3	1
-1	1	2	1
-2	—	1	—

−

M_L/M_S	0
2	1
1	1
0	1
-1	1
-2	1

=

M_L/M_S	1	0	-1
1	1	1	1
0	1	2	1
-1	1	1	1
Total =	3	4	3

3+4+3 = 10 microstates

Here maximum $M_L = 1$ and $M_S = 1$
→ L = 1 and S = 1
∴ Term is ^3P

Multiplicity =
$[2(1)+1][2(1)+1]$
$= (3)(3) = 9$

The resulting table includes one additional microstate than the microstates corresponding to ^3P state. This additional microstate may correspond to some other state. The value L = 0 is possible only when the two electrons are present in $m_l = 0$ with antiparallel spins i.e. S = 0. After L = 2 and L = 1, the next ~~as~~ L value is 0.

i.e.

M_L/M_S	0
0	1

L = 0
S = 0
∴ Term is ^1S
Multiplicity = $[2(0)+1][2(0)+1]$
$= (1)(1) = 1$. i.e. only one microstate.

M_L/M_S	1	0	-1
+1	1	1	1
0	1	2	1
-1	1	1	1

−

M_L/M_S	0
0	1

=

M_L/M_S	1	0	-1
1	1	1	1
0	1	1	1
-1	1	1	1

9 microstates

All the microstates can be simply summarised as follows

Term	^1S	^1D	^3P
No of microstates	1	5	9

∴ Total = 1+5+9 = 15 microstates

∴ Only these three terms can account for all the 15 microstates.

d^2 configuration:

For a d^2 configuration the allowed term symbols and their microstates can be derived as follows. 45 microstates are possible for d^2 configuration. The terms are derived by a similar way followed for p^2 configuration. The allowed microstates with m_l and m_s values can be represented as follows.

↑↑ ↑↓ ↓↑ ↓↓

m_l	2	1	0	-1	-2	M_L	M_S
	●	●				3	+1, 0, 0, -1
	●		●			2	+1, 0, 0, -1
	●			●		1	+1, 0, 0, -1
	●				●	0	+1, 0, 0, -1
		●	●				+1, 0, 0, -1
		●		●		0	+1, 0, 0, -1
		●			●	-1	+1, 0, 0, -1
			●	●		-1	+1, 0, 0, -1
			●		●	-2	+1, 0, 0, -1
				●	●	-3	+1, 0, 0, -1
	↑↓					4	0
		↑↓				2	0
			↑↓			0	0
				↑↓		-2	0
					↑↓	-4	0

V^{+3} - $3d^2$ ✓

Ti^{+2} - $3d^2$

(45)

Allowed microstates can be summarised as follows.

M_L/M_S	1	0	-1
4	–	1	–
3	1	2	1
2	1	3	1
1	2	4	2
0	2	5	2
-1	2	4	2
-2	1	3	1
-3	1	2	1
-4	–	1	–
Total	10	25	10

= 45 microstates

Derivation of spectral terms for d^2 configuration from summary table can be given as follows.

Maximum M_L value is 4 which is possible for $L = 4$, this is possible only when the electrons are present in $m_l = 2$ with antiparallel spin i.e. $S = 0$.

M_L/M_S	0
4	1
3	1
2	1
1	1
0	1
-1	1
-2	1
-3	1
-4	1

Total 9 microstates

$L = 4$

$S = 0$

Term ^1G

Multiplicity $= [2(4)+1][2(0)+1] = 9$ microstates

The next maximum L value is 3 and maximum S value is 1

M_L/M_s	1	0	-1
3	1	1	1
2	1	1	1
1	1	1	1
0	1	1	1
-1	1	1	1
-2	1	1	1
-3	1	1	1
Total	7	7	7

= 21 microstates

L = 3
S = 1
Term is ^3F
Multiplicity = $[2(3)+1][2(1)+1] = 21$ microstates

Next possible L value is 2. This is possible only when the two electrons are present in $m_l = 1$ box with antiparallel spins i.e. S = 0.

M_L/M_s	0
2	1
1	1
0	1
-1	1
-2	1

5 microstates

L = 2
S = 0
∴ Term is ^1D
Multiplicity = $[2(2)+1][2(0)+1]$ = 5 microstates

Next possibility L = 1 S = 1

M_L/M_s	1	0	-1
1	1	1	1
0	1	1	1
-1	1	1	1
	3	3	3

L = 1 S = 1
∴ Term is ^3P
Multiplicity = $[2(1)+1][2(1)+1]$ = 9 microstates

L = 0 S = 0.

M_L/M_s	0
0	1

1 microstate

L = 0 S = 0
∴ Term is ^1S
Multiplicity = $[2(0)+1][2(0)+1]$ = 1 microstate

H/

Terms	^3F	^3P	^1G	^1D	^1S
No of microstates	21	9	9	5	1

Total = 45 microstates

Thus these five terms account for all the 45 microstates.

Spin-Orbit Coupling and Zeeman Splitting:

As electron has spin, it behaves as a tiny bar magnet with a magnetic moment m_s, which can be given as

$$m_s = g_e \gamma_e S$$

Where g_e is the electronic g factor
γ_e is gyromagnetic ratio

Electron also moves around the nucleus, it has orbital angular momentum, and the orbital magnetic moment is given by

$$m_l = \gamma_e l$$

It is well known that the bar magnets may attract each other or repel, depending on their orientation. Similarly, the orbital and spin magnetic moments may have either attractive or repulsive orientations. The attractive orientation leads to energetically favourable position and repulsive orientation leads to energetically unfavourable positions.

The energies of interaction are not continuous and are quantised quantum mechanically. Thus, The orbital and spin angular momenta cannot have any orientation but only certain permitted orientations. The total angular momentum vector j can be obtained from the vectorial sum of l and s for a single electron.

$$j = l+s, l+s-1, \ldots, l-s.$$

If an electron has no orbital angular momentum [i.e. for ns $l=0$] then there is no spin orbit coupling. In general there are two types of Spin-orbit coupling

(a) L-S coupling Scheme
(b) j-j coupling Scheme.

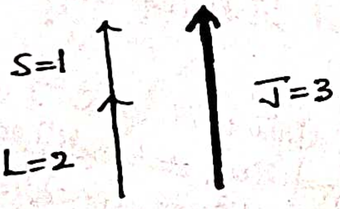
(a) L-S Coupling Scheme:

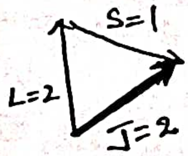
L-S coupling is the coupling of the total orbital angular momentum 'L' with the total spin angular momentum 's', to give a total angular momentum J. The total orbital angular momentum (L) is obtained by the coupling of the individual electronic orbital angular momenta and the total spin angular momentum is obtained by the coupling of individual electronic spin angular momenta. These two resultant momenta, L and S couple to give J.

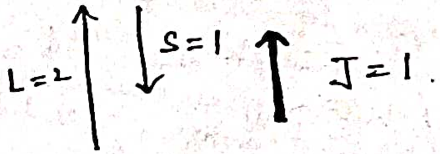
The L-S Coupling can be vectorially represented as follows.

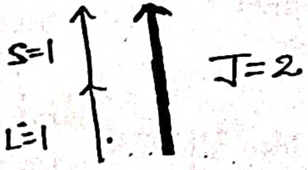
For p^2 configuration the following coupling Schemes are possible.

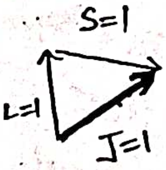
(a) S=1 L=2 J = 3, 2, 1 [^3D_J states]
= 1 J = 2, 1, 0 [^3P_J states]
= 0 J = 1 [^3S_J state]

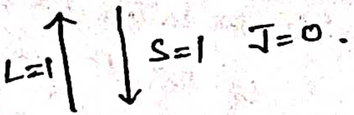


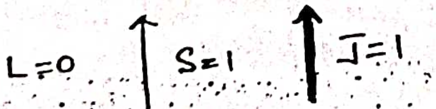




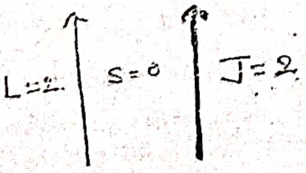


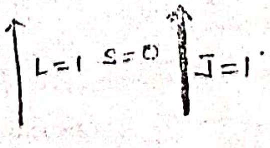






(b) S=0. L=2 J=2
=1 J=1
=0 J=0.





L=0 S=0 J=0.

(b) j-j Coupling Scheme:

This is second type of spin-orbit coupling and usually operates in case of atoms belonging to heavy elements. In this coupling scheme, the orbital angular momentum and spin angular momentum for a single electron couple to give j, the total angular momentum for a single electron. Then the j values of each electron may couple to give J. In heavy atoms or ions, the nuclear charge is high enough to force the coupling of l and s of individual electrons to give the resultant angular momentum j. This type of coupling of j_1, j_2 --- of individual electrons is known as j-j coupling.

Due to spin-orbit coupling different terms are possible for a given configuration. When once the number of terms are known for a configuration, it is important to arrange them in the order of their energy. The arrangement of terms in energy order is done by Hund's rule

(i) For a closed shell or a sub shell, the only allowed state is $^1S_0$

(ii) The lowest energy state will be of maximum multiplicity as it will be stabilised by the exchange energy.

(iii) With a given multiplicity, the state with largest L value will have the lowest energy. This holds for the ground state, but may break down for the excited states.

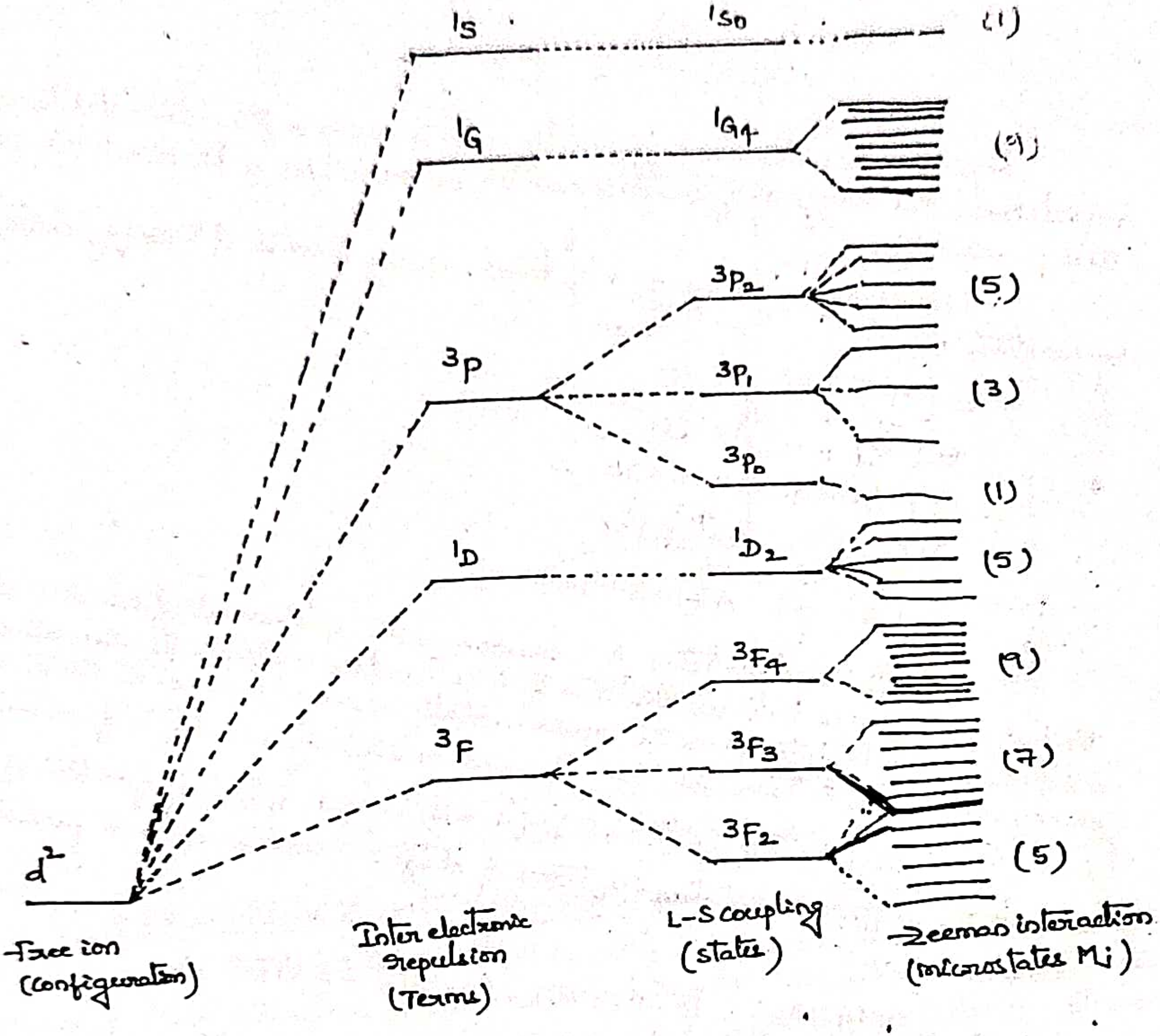
(iv) For less than half-filled subshell, the state with lowest J value will be the most stable state. With more than half filled subshell, the highest J value becomes the most stable state. The former are called normal multiplets, the latter are the inverted multiplets.

i.e. For d^2: $^3F_2 < {}^3F_3 < {}^3F_4$

d^8: $^3F_4 < {}^3F_3 < {}^3F_2$

Using Hund's rule, we can easily identify the ground state terms for any given configuration. When an atom is subjected to magnetic field each state corresponding to a term splits into several microstates and this splitting in a magnetic field is known as Zeeman splitting.

The complete profile of energy level splitting for d^2 configuration can be shown as follows.



Slater Condon Parameters:

A term is separated from the other terms by certain energy due to interelectronic repulsions of a configuration. Thus it is necessary to develop a theory of interelectronic repulsions with in a configuration that give the energies of terms above the ground term. The interelectronic repulsion energies can be calculated by solving the complicated integrals over the ~~electrons~~ orbitals occupied by electrons. The energies of terms can be expressed in terms of slater condon parameters [f_0, f_2, f_4] & Racah Parameters (A, B, C). These two parameters are related by the following equations.

$A = F_0 - 49F_4$
$B = F_2 - 5F_4$
$C = 35F_4$.

Racah parameters are generally used to express the inter-electronic repulsions. The energies of the terms can be expressed as a linear combination of these parameters.

For example, the energies of terms arising from a d^2-configuration can be written as

$$E(^3F) = A - 8B$$
$$E(^3P) = A + 7B$$
$$E(^1D) = A - 3B + 2C$$
$$E(^1G) = A + 4B + 2C$$
$$E(^1S) = A + 14B + 7C$$

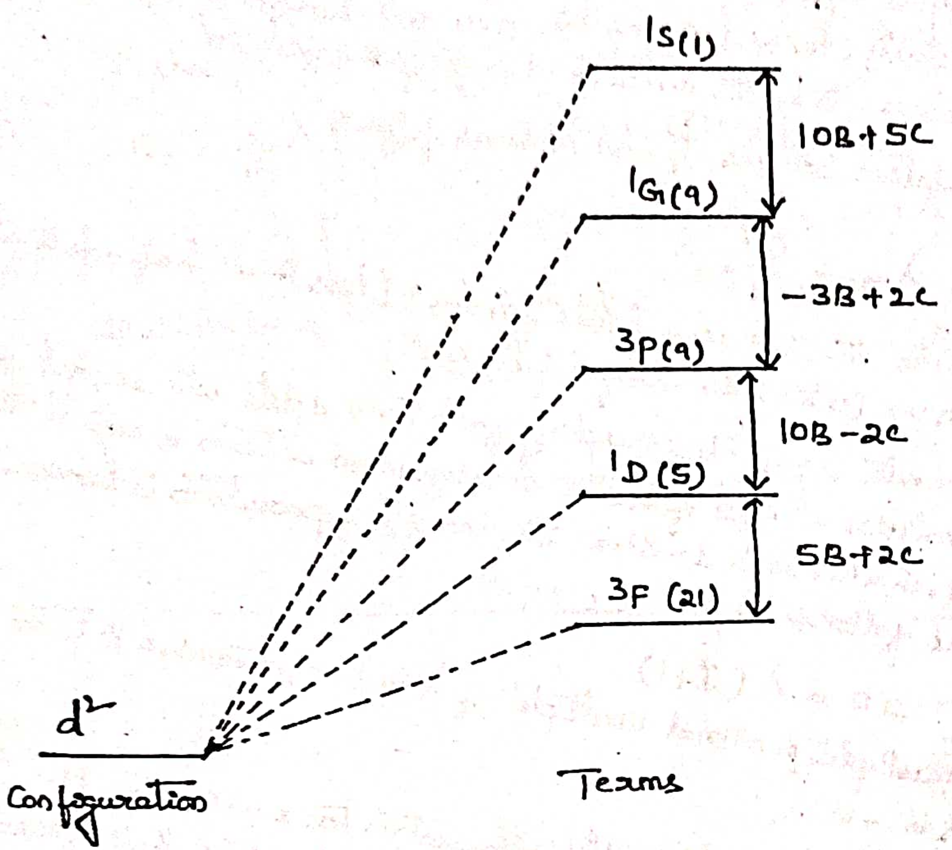
In all the above terms A is common and it gets cancelled while evaluating the energy difference between the terms of like & unlike multiplicity. The values of A, B and C can be calculated from the experimentally observed energies of the terms. The energy separation between the terms of same multiplicity is only a function of B.

$$\Delta E(^3P - ^3F) = (A+7B) - (A-8B) = 15B$$ which is function of only B

The energy difference between the terms of different multiplicities is function of B and C.

$$\Delta E(^1D \sim ^3F) = (A-3B+2C) - (A-8B) = 5B+2C$$
$$\Delta E(^3P \sim ^1D) = (A+7B) - (A-3B+2C) = 10B-2C$$
$$\Delta E(^1G \sim ^3P) = (A+4B+2C) - (A+7B) = -3B+2C$$
$$\Delta E(^1S \sim ^1G) = (A+14B+7C) - (A+4B+2C) = 10B+5C$$

The value of B increases with increase in the oxidation state of the metal ion. For example B value of V^{+2} is 765 cm^{-1} and for V^{+3} is 860 cm^{-1}. Thus, the magnitude of B is a direct measure of the extent of repulsive interaction between the electrons. The term separation mainly depends upon just B and C parameters only. This suggests that B and C are the main inter-electron repulsion parameters whose values can be obtained experimentally. The energy separation between the terms in d^2-configuration can be shown as follows.



Separation of terms of a d^2 configuration in B and C parameters. Values in parantheses indicate term degeneracy.

Term Separations due to Spin-Orbit coupling Parameters:

The two types of spin orbit coupling schemes are L-S and l-s coupling schemes. These interactions of spin and orbital angular momenta cause perturbation in a term. The two types of coupling schemes cause different magnitude of perturbation. The parameter ζ (zeta) is the single electron spin-orbit coupling constant and the parameter λ is the many-electron spin-orbit coupling constant. The magnitudes of both these parameters can be obtained from the multiplet splitting of the free ion's emission spectra.

The spin-orbit coupling ζ for one-electron can be calculated as follows.

$$\zeta_{n,l} = \left(\frac{e^2\hbar^2}{2m^2c^2a_0}\right)\left[\frac{Z^4}{n^3 l\left(l+\frac{1}{2}\right)(l+1)}\right]$$

From this equation it is clear that ζ depends upon n and l quantum numbers of the electron. m and e are the mass and charge of the electron and a_0 is the Bohr's radius. Z is the nuclear charge of the free ion.

The relation between ζ and λ is as follows

$$\lambda = \pm \zeta / 2S$$

where the +ve sign holds for n<5 (less than half-full shell) and the -ve sign for n>5 (more than half-full shell)

Due to spin-orbit coupling each term splits into several states specified by J values. The no of states arising from a term is equal to either (2S+1) or (2L+1) whichever is smaller. The energy separation between J and (J+1) can be given as follows.

$$\Delta E = \lambda (J+1)$$

The multiplet is normal multiplet if λ is +ve, otherwise it is an inverted multiplet if λ is -ve.

For example in d^2 and d^8 configuration terms are same but the multiplet is normal for d^2 ($\because \lambda$ is +ve as the configuration is less than half-filled) and is inverted for d^8 ($\because \lambda$ is -ve as more than half filled). The splitting pattern of terms for d^2 and d^8 can be given as follows.

The terms and states for d^2 configuration (Ground state) are

^3F (L=3 ; S=1) $\quad J = 3+1, 3+1-1, \ldots (3-1)$

$\qquad\qquad\qquad\qquad = 4, 3, 2.$

The energy order of these terms is $^3F_2 < {}^3F_3 < {}^3F_4$.

Whereas for d^8 configuration, the order is $^3F_4 < {}^3F_3 < {}^3F_2$

The following diagram represents energy separation between the levels obtained by the splitting of terms due to spin-orbit coupling in d^2 and d^8 configurations. λ is spin-orbit coupling parameter. The degeneracy of each level is shown in parantheses,

The energy, E_J of the level represented by J can be given by

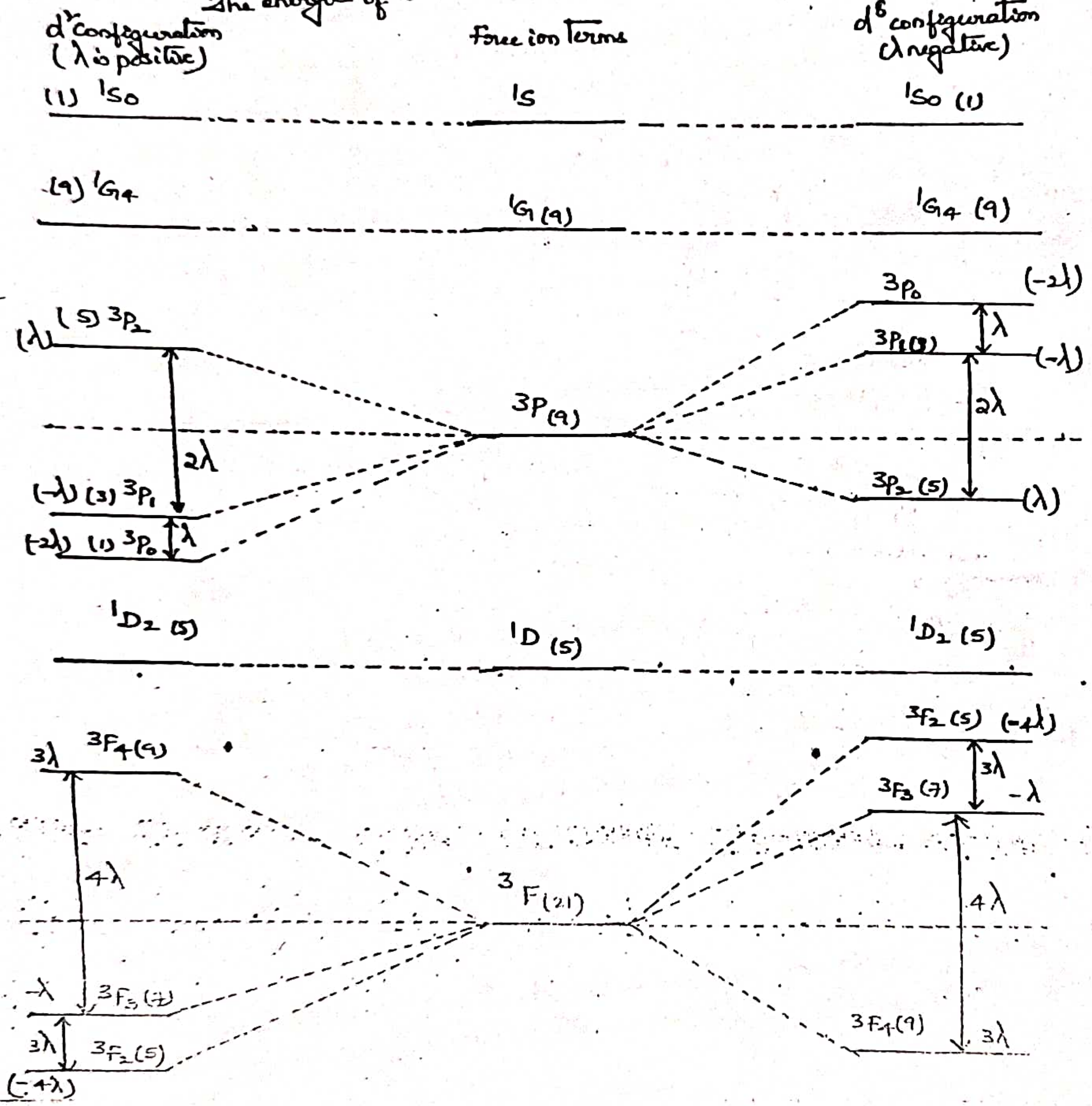
$$\therefore E_J = \left(\frac{1}{2}\right)\lambda\left[J(J+1) - L(L+1) - S(S+1)\right]$$

For example the energy of $^3F_2$ $(J=2, L=3, S=1)$ is

$$E_2 = \frac{1}{2}\lambda\left[2(2+1) - 3(3+1) - 1(1+1)\right]$$

$$= \frac{\lambda}{2}\left[6 - 12 - 2\right] = \frac{\lambda}{2}(-8) = -4\lambda$$

The energies of the levels are shown in diagram.



M. Srinivasa

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ELECTRONIC SPECTRA OF COMPLEXES

Introduction:

It is a well known fact that most of the transition metal complexes are coloured. For example $[Co(H_2O)_6]^{+2}$ is pink coloured and $[CoCl_4]^{-2}$ is blue coloured. The colour of the complexes is due to the electronic transitions between different energy levels. The electronic transition occurs due to absorption of radiant energy in the IR and visible UV-regions, while these energies give valuable information regarding the nature of bond

The electronic transitions in metal complexes are frequently referred to as d-d transitions. The colour of the complexes depend upon the magnitude of the spacing between the levels. The spacing depends upon the geometry of the complex, the nature of the ligands present and the oxidation state of the central metal atom.

The electronic spectra of different complexes usually include different no of absorptions. In order to determine the no of absorptions for a complex, it is necessary to develop an accurate energy level diagram.

Types of Electronic Spectra:

Generally four types of Electronic spectra are observed.

(1) Ligand field Spectra:

$t_{2g} - e_g^*$

This spectra occurs in the IR, visible and UV regions. Lower frequencies are not accessible experimentally; the higher frequencies though accessible, are overshadowed by the charge transfer and the intraligand transitions. Hence the study of d-d transitions is limited to the visible region of the spectrum. According to crystal field theory, these transitions are considered to be totally within the metal ion. Whereas some ligand contribution is included in ligand field theory & adjusted crystal field theory. According to molecular orbital theory, these transitions are due to excitation of the electron from t_{2g} level to e_g^* level belonging to the metal.

(2) Ligand to Metal charge transfer:

This occurs due to the transition of electron from MO located on the ligand to a non bonding & antibonding molecular orbital located on the metal atom. These charge transfer bonds cannot be explained by crystal field theory.

S. Dhilleswara Rao

(3) Metal to ligand charge transfer bands:

These occurs due to the transition of electron from an antibonding or nonbonding orbital on the metal atom to the antibonding orbital located on the ligand. These bands are generally observed for the metal ions in low oxidation states.

(4) The intraligand transitions:

The intraligand transitions are observed when an electron transition takes place from one ligand orbital to another orbital. These transitions are found in the UV region. For example, the aromatic heterocycles such as pyridine, bipyridyl and simple anionic ligands as NO_3^-, NO_2^- & SCN^- some additional charge transfer bands of free ligand in the region are observed. These transitions are of the type $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$

Selection Rules for Electronic Transitions:

All the electronic transitions are not possible. Some restrictions are imposed on the electronic transitions in terms of selection rules from the knowledge of quantum mechanics. These restrictions are known as selection rules.

(1) Spin Selection rule:

Spin selection rule states that transitions occur only between the levels with same spin multiplicity, which means that the number of unpaired electrons must be the same even after the transition.

The electromagnetic field of the incident radiation cannot change the relative orientations of the spins of the electrons in a complex. The antiparallel pair (↑↓) cannot be converted into to a parallel pair (↑↑); a singlet ($S=0$) cannot undergo a transition to a triplet ($S=1$). Therefore $\Delta S = 0$ for spin allowed transitions.

(2) Laporte Selection Rule:-

According to this rule transitions occur only between the levels with $\Delta l = \pm 1$ i.e. The transitions with in a given set of p or d orbitals are forbidden if the molecule or ion has a centre of symmetry.

In a centrosymmetric complex, ligand-field d-d transition are forbidden. Therefore the intensities of the forbidden transitions are weak. As tetrahedral complexes have no centre of symmetry, the Laporte rule is not applicable to them and therefore, the d-d transitions in them are strong.

The intensity of the absorption band is defined as

$$-\log\frac{I}{I_0} = \epsilon c l \text{ or } \log\frac{I_0}{I} = \epsilon c l.$$

where I/I_0 is the ratio of the intensities of emergent to incident radiation, c is molar concentration, ϵ is the molar extinction coefficient and l is the path length.

A Laporte-forbidden transition is usually stronger than a spin-forbidden transition.

Break down of the Selection Rules:

(1) Spin forbidden transitions: Certain spin forbidden transitions are observed for d^5 ion complexes having high pairing energy. The intensity of these transitions are very weak.

Spin forbidden transitions take place due to the spin-orbit angular momentum coupling. Because of spin-orbit coupling changes will occur in the energies of different states. As a result of slight mixing of two states, say a singlet state and a triplet state, the ground state becomes 99 percent singlet and one percent triplet and the excited state becomes 99 percent triplet and one percent singlet. The extent of mixing depends upon the difference in their energies and spin-orbit coupling constant. The spin-orbit coupling is greater for heavy atoms; consequently, the intensity of spin-forbidden bands increases with increasing atomic number.

(2) Laporte selection Rule: Break down of laporte selection rule occurs due to mixing of the orbitals on the metal ion or due to vibronic coupling. Thus if d and p orbital mix

$$\psi' = \psi(3d) + \alpha\,\psi(4P)$$

where α is the coefficient of mixing. This type of mixing produces temporary distortion in the field due to the ligand vibrations. Because of the ligand vibrations, the atom M is not at the centre of the symmetric field all the time during which the electron transition takes place.

In tetrahedral complexes, where there is no centre of symmetry, the mixing of d-p orbitals lead to more intense absorption bands than those for the octahedral complexes. The vibrational and electronic coupling, called the vibronic coupling remove the centre of ~~good~~ symmetry. If a forbidden band lies near an allowed band ~~[illegible]~~, the mixing of the fully allowed and forbidden energy states due to the vibronic coupling gives intense absorptions. This is called intensity stealing and depends upon the energy difference between the two states.

d-d transition spectra:

In order to understand the d-d transitions in the metal complexes, it is necessary to know (i) Russell-Saunders states for a d^n ion in order of increasing energies and (ii) group theory of quantum mechanics to find out the effect of an external field on these states.

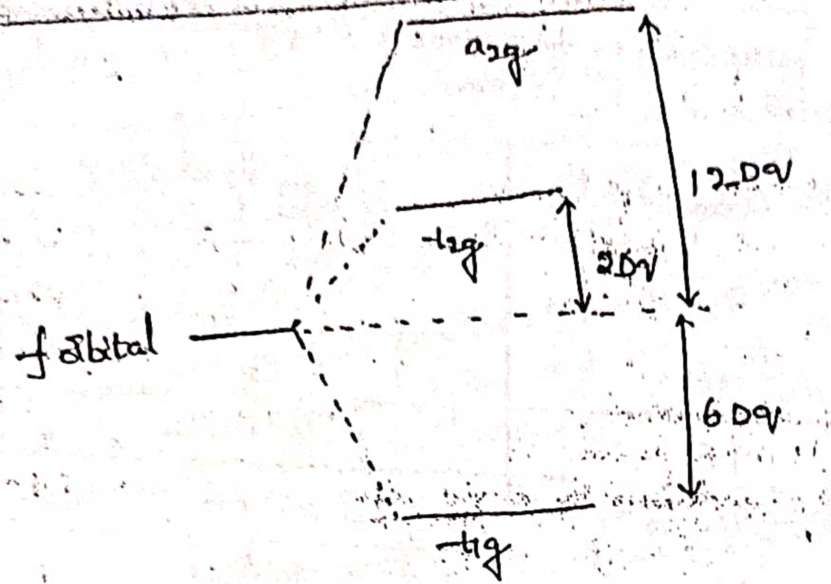
Splitting of orbitals in an octahedral field:

As 's' orbital is spherical and non degenerate it won't split into any state.

'p' orbitals also do not undergo any sought of splitting in an octahedral field as they interact with the field to the same extent.

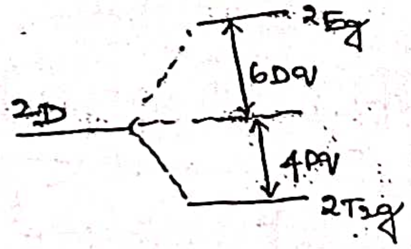
In an octahedral field the d-orbitals split into two groups; t_{2g} and e_g.

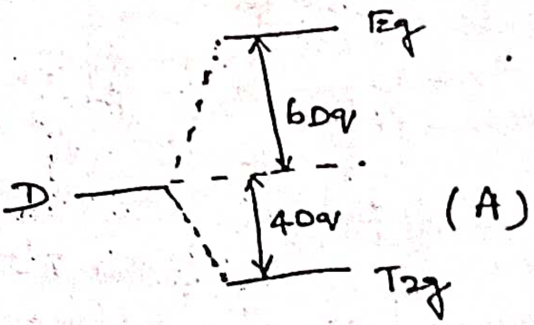
In an octahedral field the f-orbital splits into three groups — a triply degenerate t_{1g} group, a triply degenerate t_{2g} group and a singlet a_{2g} group.



Splitting of Russell-saunders states:

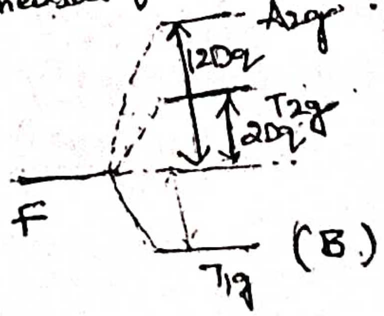
In the absence of an external field, d' configuration becomes ^2D. Which then breaks into two energy levels $^2T_{2g}$ (corresponding to t_{2g}) and ^2E_g (corresponding to e_g) in an external ligand field.





Splitting of the terms arising from d' configuration.

A d^2 configuration has two Russell-saunders states: a low energy 3F and the high energy 3p state. The F and P states behave similarly as f and P orbitals in an octahedral field. P state does not undergo splitting in an octahedral field.



Spectroscopic Ground State:

The spectroscopic ground states for various d^n configurations in weak octahedral field are given as follows.

configuration of the free ion	Ground state	Energy level diagram.
d^1	^2D	A
d^2	^3F	B
d^3	^4F	Inverted B
d^4	^5D	Inverted A
d^5	^6S	no splitting
d^6	^5D	A
d^7	^4F	B
d^8	^3F	Inverted B
d^9	^2D	Inverted A
d^{10}	^1S	no splitting

Splitting of the ground state terms in an octahedral field:

The splitting of the ground state terms can be given as follows.

Term	Components in octahedral field
S	A_{1g}
P	T_{1g}
D	$T_{2g} + E_g$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Orgel diagrams:

These diagrams were developed by Leslie Orgel in 1955. Orgel diagrams show how the energy levels of a transition metal atom split when it is placed in a ligand field. The vertical axis in an orgel diagram shows the energy and the horizontal axis shows the strength of the ligand field, with zero ligand field at the centre of the horizontal axis.

The splitting pattern for d^n configuration is same as d^{n+5} and the opposite of d^{10-n} which can be observed in an orgel diagram. These diagrams combinedly represent the splitting pattern in octahedral and tetrahedral fields.

Combined orgel diagram for d^1, d^4, d^6, d^9 octahedral and tetrahedral fields

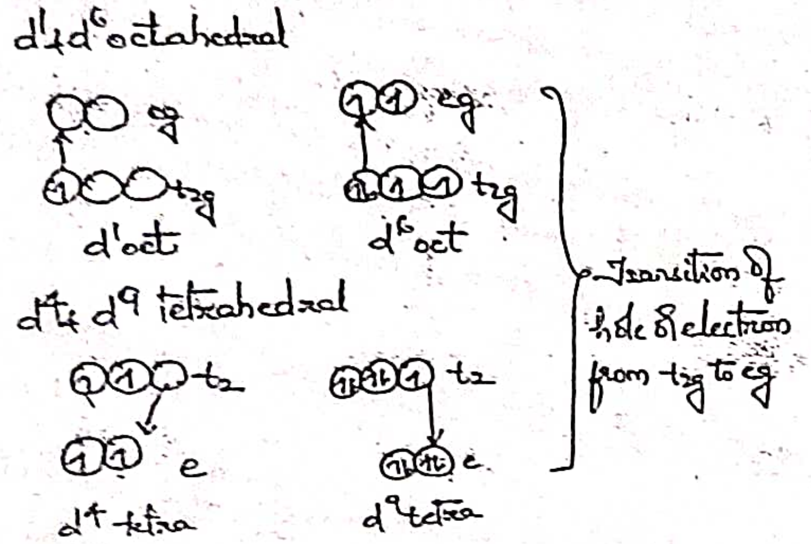
The d^1 orbitals of a free gaseous metal ion are degenerate. The electronic transitions between degenerate energy levels is not possible. But when the metal ion is placed in a ligand field, then the d-orbitals split into two groups t_{2g} and e_g.

Now consider the simplest case of d^1 complex $[TiCl_6]^{-3}$, in such complexes the single electron occupies the lower t_{2g} level. If this electron absorbs energy, it will move into high energy e_g level and hence only one transition is possible. The magnitude of splitting of d orbitals depends upon the nature of the ligands. The spacing between the two sets of d-orbitals affect the energy of transition and hence frequency of maximum absorption in the spectrum.

The term symbol for free metal ion with d^1 configuration is ^2D. Under the influence of ligand field this will split into two ~~sets~~ sets T_{2g} and E_g [T_{2g} and E_g are known as Mulliken symbols]. The T_{2g} mulliken symbol corresponds to t_{2g} set of low energetic orbitals containing the single electron and E_g symbol corresponds to e_g set of higher energy orbitals. The spacing between the T_{2g} and E_g states depends upon the strength of the field.

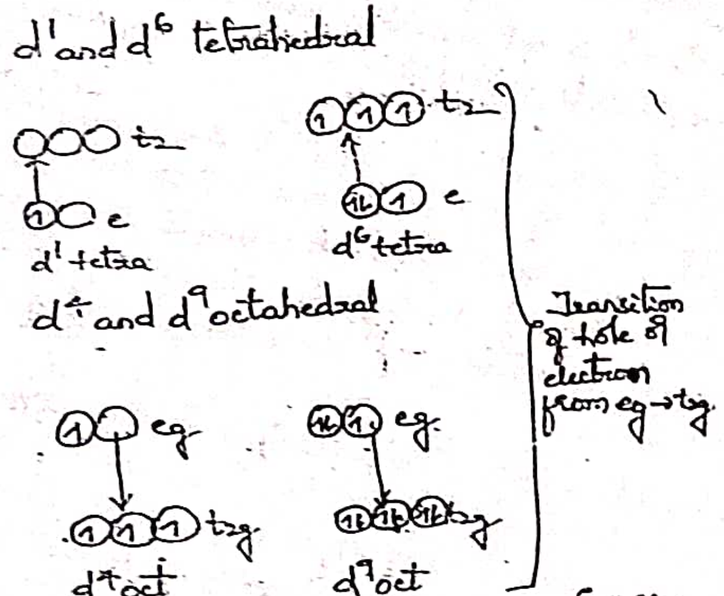
The electronic spectra of d^9 metal ion octahedral complex can be explained in a similar way as that of the d^1 metal ion octahedral complex. The single electron in t_{2g} level of d^1 case and single hole in the upper e_g level of d^9 case will undergo transition. In $d^{(1)}$ case the single electron is promoted from t_{2g} to e_g level and a hole is promoted from e_g to t_{2g} level in case of d^9 complex.

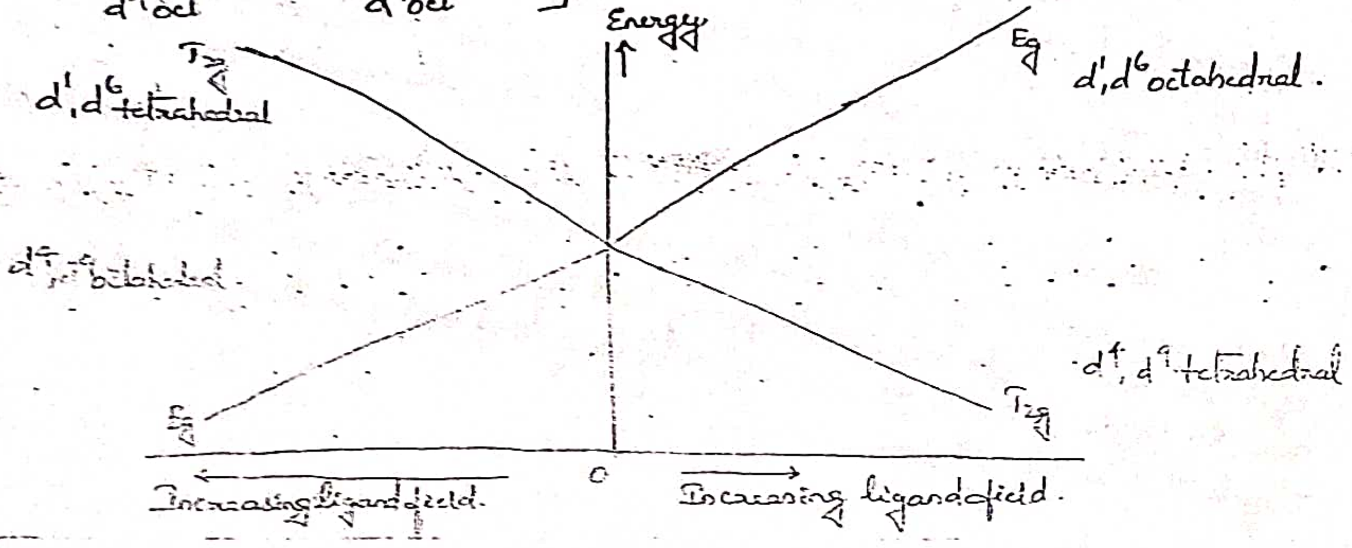
This transition of a hole from e_g level to t_{2g} level in d^9 octahedral case is same as the electron transfer from $\overset{e}{e_g}$ to t_{2g} level in d^1 tetrahedral case.



The electronic transition in d^6 high spin octahedral complex is exactly similar to the electron transfer from t_{2g} to e_g level in d^1 octahedral complex. In in case of d^4 and d^9 tetrahedral complexes a hole is transferred from t_{2g} level to e_g level which is similar to the electron transition from t_{2g} to e_g level in d^1 and d^6 (high spin) octahedral complex.

Similarly the electron transfer from e to t_2 level in d^1 and d^6 tetrahedral complexes is same as the hole transition from e_g to t_{2g} level in d^4 and d^9 octahedral complexes.



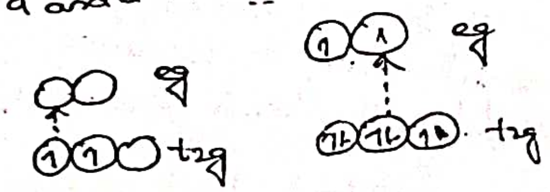


Combined Orgel diagram for d^2, d^3, d^7, d^8 octahedral and tetrahedral fields:

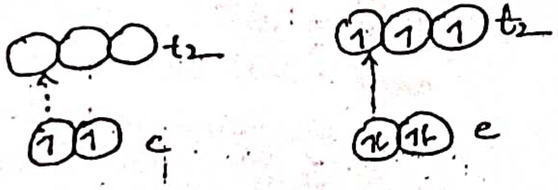
The Russell-Saunder states for d^2 configuration are lower energy ^3F and higher energy ^3P states. The other possible higher energy states for d^2 configuration are ^1G, ^1D and ^1S. The transition of an electron from the ground state to these states are spin forbidden. The ^3F state splits T_{1g}, T_{2g} and A_{2g}, where as the p state does not undergo any splitting. But the ^3P state transforms into T_{1g} state. Three Transitions are possible from ground state $^3T_{1g}(F)$ to $^3T_{2g}$, $^3T_{1g}(P)$ and $^3A_{2g}$ respectively.

The two electrons of d^2 configuration will occupy two of the t_{2g} orbitals. When an electron is promoted from $t_{2g}^2 \rightarrow (e_g^1)(t_{2g}^1)$ Thus there are two possibilities. The electron may be promoted from d_{xz} or d_{yz} orbitals to the d_{z^2} or it may be promoted to $d_{x^2-y^2}$. If the electron is promoted from d_{xz} or d_{yz} to the d_{z^2} orbital the electronic repulsions will be minimum as the electrons are spread around all three directions. If the electron is promoted to $d_{x^2-y^2}$ orbital the repulsions will be more.

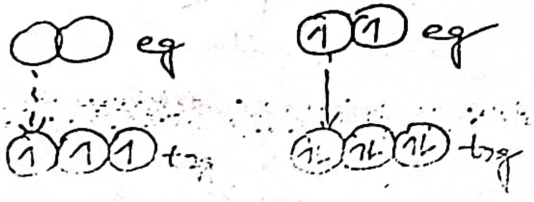
d^2 and d^7 octahedral



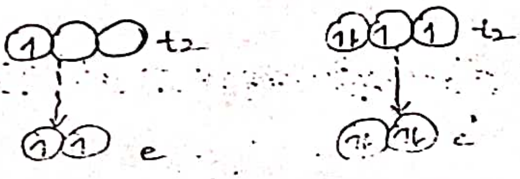
d^2, d^7 tetrahedral



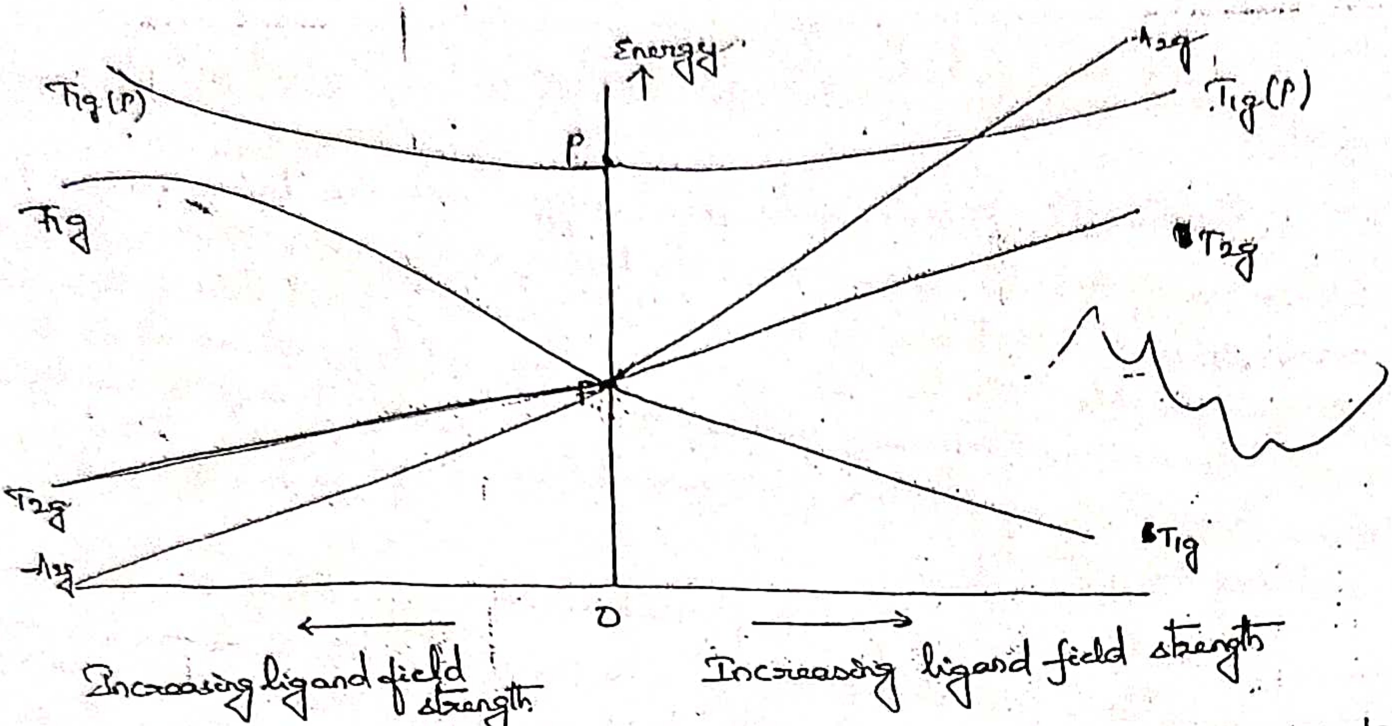
d^3 and d^8 octahedral



d^3, d^8 Tetrahedral



The below figure is a Combined Orgel diagram for two electron and two hole configuration.

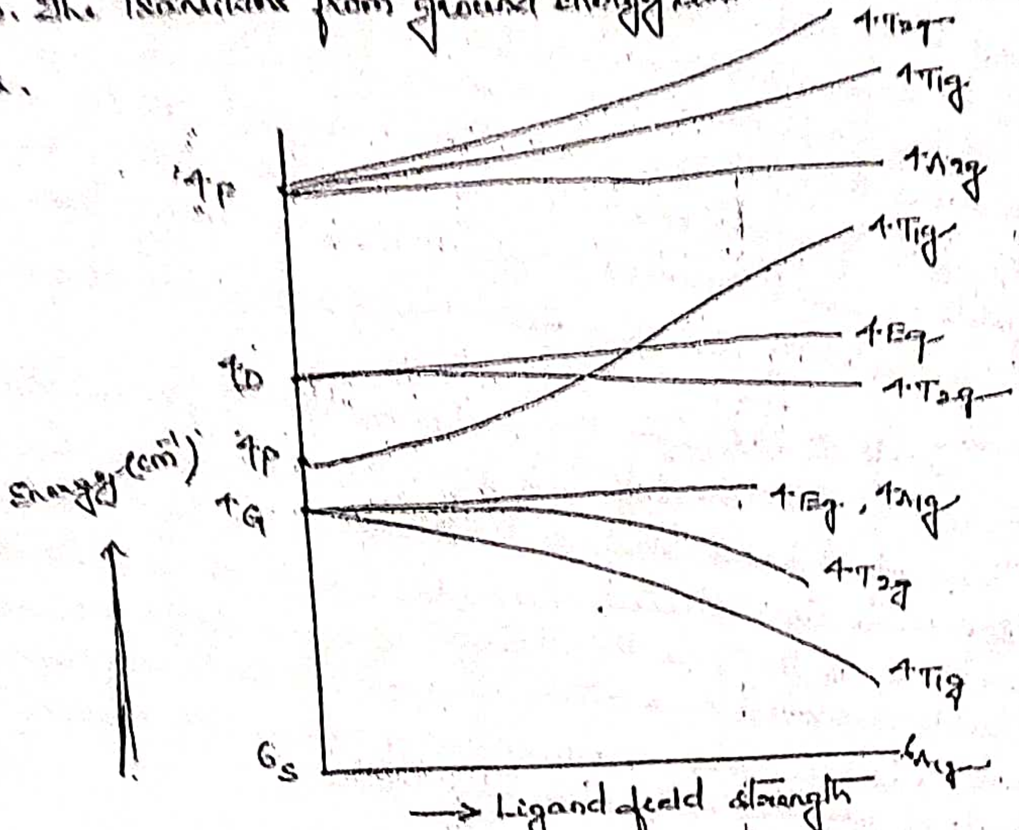


There are two T_{1g} states one from P state and the other from the F state. The two T_{1g} states are slightly curved lines, because they have the same symmetry, and they interact with one another. This interelectronic repulsion lowers the energy of the lower state and increases the energy of the higher state. If the two lines would have been straight, they would cross each other. This would be impossible according to non-crossing rule. Non-crossing rule says that the states of same symmetry and spin multiplicity cannot cross each other. The interelectronic repulsion which causes the bending of the lines is expressed by the Racah parameters B and c.

Orgel diagram for d^5 octahedral and tetrahedral fields

The d^5 configuration can be observed in Mn(II) and Fe(III). All the five d orbitals are singly occupied, in case of weak octahedral field. The electron transition from t_{2g} to e_g will result in spin pairing in one of the orbitals. Thus these transitions are spin forbidden. The spin forbidden absorption bands are extremely weak. This accounts for the pale pink colour of Mn(II) salts. The ground state term is ^6S for d^5 configuration (weak field) and eleven excited states are possible [^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2F, ^2D, ^2P, ^2S]. Of the eleven excited states, the transitions from ground state to ^4G, ^4F, ^4D and ^4P can be observed. These four states split into 10 levels and hence ten absorption bands may be observed.

The ground state ^6S will not split and becomes $^6A_{1g}$ level. It is important to note that $^4E_g(G)$, $^4A_{1g}(G)$, $^4E_g(D)$ and $^4A_{2g}(P)$ are horizontal lines on the diagram. The transitions from ground energy level to these levels give rise to sharp peaks.



The same diagram diagram applies for d^5 tetrahedral complexes if the g subscripts are omitted.

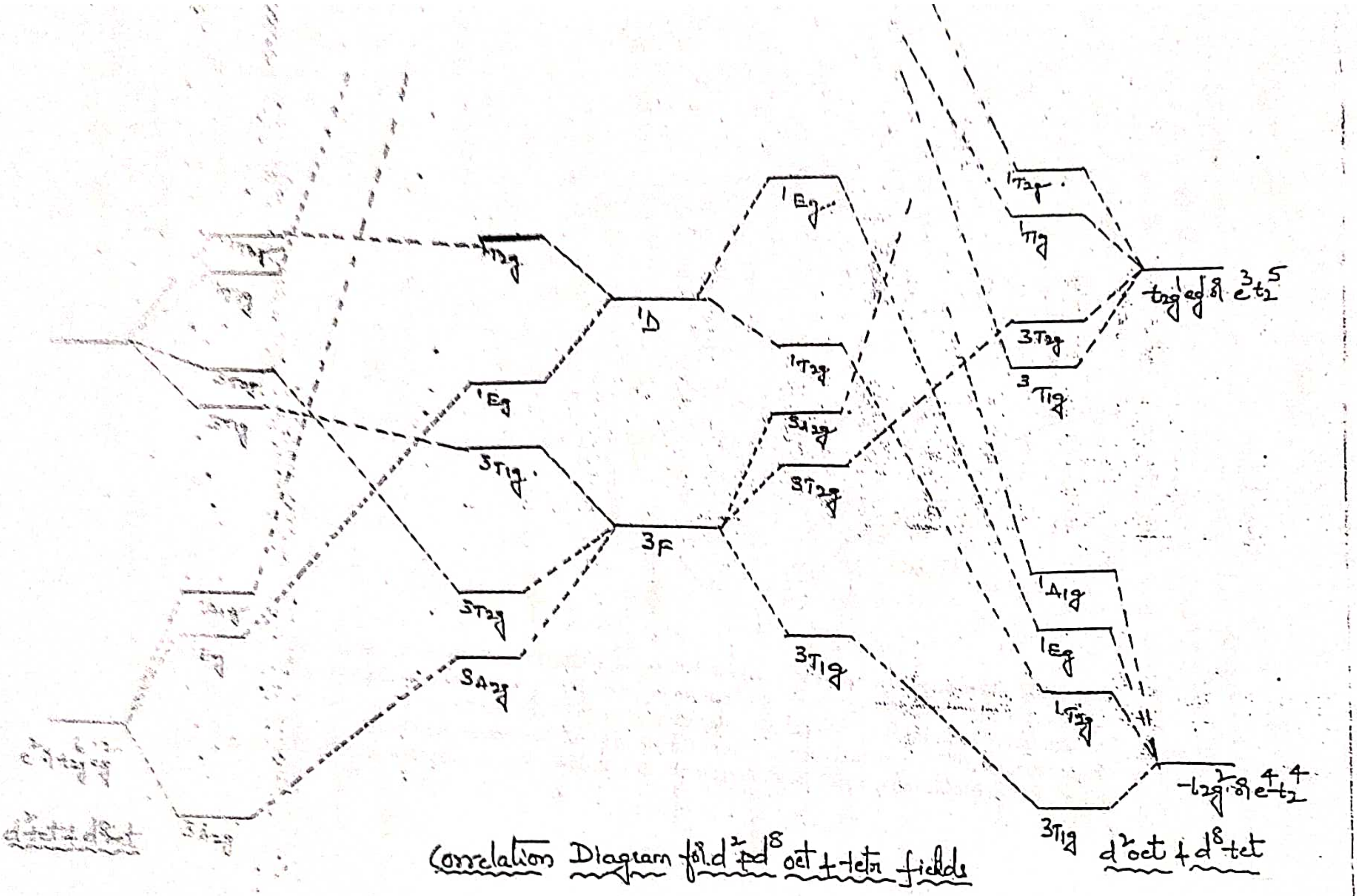
Higher levels: The ground state and higher energy terms of the d^n ion.

Configuration	Ground State term	Higher Energy terms.
d^1, d^9	^2D	—
d^2, d^8	^3F	^3P, ^1G, ^1D, ^1S
d^3, d^7	^4F	^4P, ^2H, ^2G, ^2F, $2\times{}^2D$, ^2P
d^4, d^6	^5D	^3H, ^3G, $2\times{}^3F$, ^3D, $2\times{}^3P$, ^1I, $2\times{}^1G$, ^1F, $2\times{}^1D$, $2\times{}^1S$
d^5	^6S	^4G, ^4F, ^4D, ^4P, ^2I, ^2H, $2\times{}^2G$, $2\times{}^2F$, $3\times{}^2D$, ^2P, ^2S

CORRELATION DIAGRAMS :

For the d^2 configuration, the ground state free ion term is ^3F and the excited state terms are ^3P, ^1G, ^1D, ^1S. If the separation between the terms is large compared to the perturbation produced by the ligands, we have the ~~strong~~ weak field case. If the separation between the terms is less compared to the perturbation produced by the ligands we have strong field case. The right ~~of~~ side of the diagram shows the effect of a strong octahedral field. The left side of the diagram shows the effect of a weak octahedral field. The lines connecting the strong and weak fields represent relative energies of states resulting from intermediate fields. Construction of the strong field side of a correlation diagram is very complex.

In all the correlation diagrams (except for d^5) free ion terms are shown in the centre, with the d^n octahedral and d^{10-n} tetrahedral splittings on the right and d^{10-n} octahedral and d^n tetrahedral splittings on the left. In these diagrams only low energy terms are included. An important point which is noteworthy about these diagrams is that, as the strength of ligand field increases a number of energy levels crossover each other. An important rule was imposed on these cross-overs which is known as non-crossing rule. Non-crossing rule states that levels of identical designation never cross.



Correlation Diagram for d^2 & d^8 oct + tetra fields

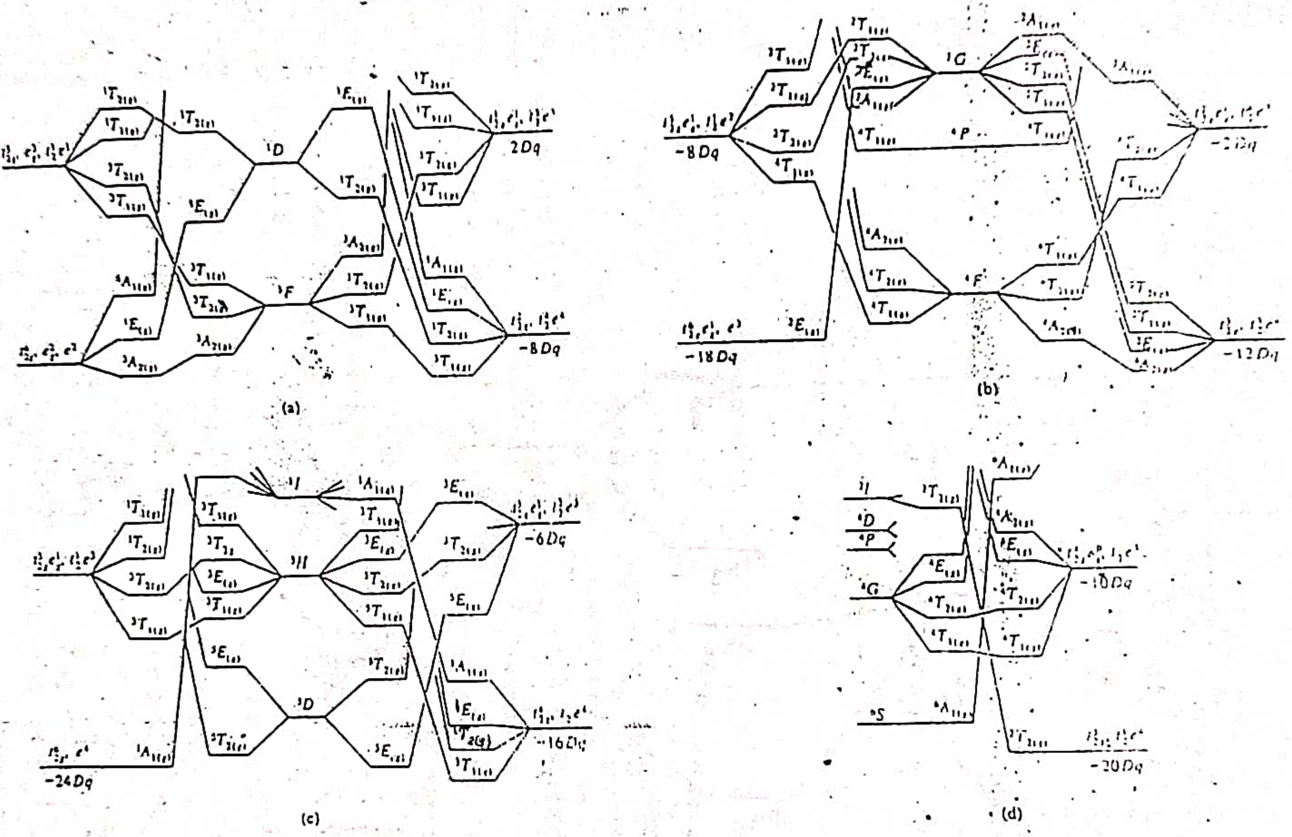


Fig. 11.37 Correlation diagrams for d^n and d^{10-n} ions in octahedral and tetrahedral fields: (a) d^2 and d^8, (b) d^3 and d^7, (c) d^4 and d^6, (d) d^5. For (a–c), free ion terms are in the center, with field strength increasing in both directions. At the two extremes are strong field configurations for octahedral d^{10-n} and tetrahedral d^n complexes (left) and octahedral d^n and tetrahedral d^{10-n} complexes (right). [From Figgis, B. N. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 1, Chapter 6, pp 236–237. Used with permission.]

TANABE-SUGANO DIAGRAMS

Orgel diagrams include only weak field cases, where the interelectronic repulsion is stronger than the ligand field strength. Correlation diagrams discussed for a smooth transition from the weak field to the strong field cases. The orgel and correlation diagrams provide only qualitative treatment of electronic transitions. In an orgel diagram, the ground state of the complex is derived from the ground spectral state of the free ion and hence the multiplicity of the ground state in the complex remains same as the free ion ground state. The splitting pattern of the higher energy free ion states is not of much importance in the orgel diagram. In correlation diagrams the construction of strong field case is some what complex and involves group theoretical calculations.

In order to have good interpretation of electronic transition, it is necessary to have some quantitative results from these energy level diagrams. However it is difficult to calculate the energies of all the energy levels for a given strength of the crystal field (10Dq) and in the presence of interelectronic repulsions (B and C). In this connection, two Japanese workers Tanabe and Sugano devised some useful diagrams to explain the quantitative aspects of these parameters. These diagrams were called after them as Tanabe-Sugano diagrams.

In a strong field, Δ is greater than interelectronic repulsion and hence the ground state of the complex may be derived from a free ion state of higher energy and lower multiplicity than the free ion ground state. The splitting pattern of the ground and also the higher spectral states of the free ion as a function of Dq in weak and strong fields has been considered by Tanabe and Sugano.

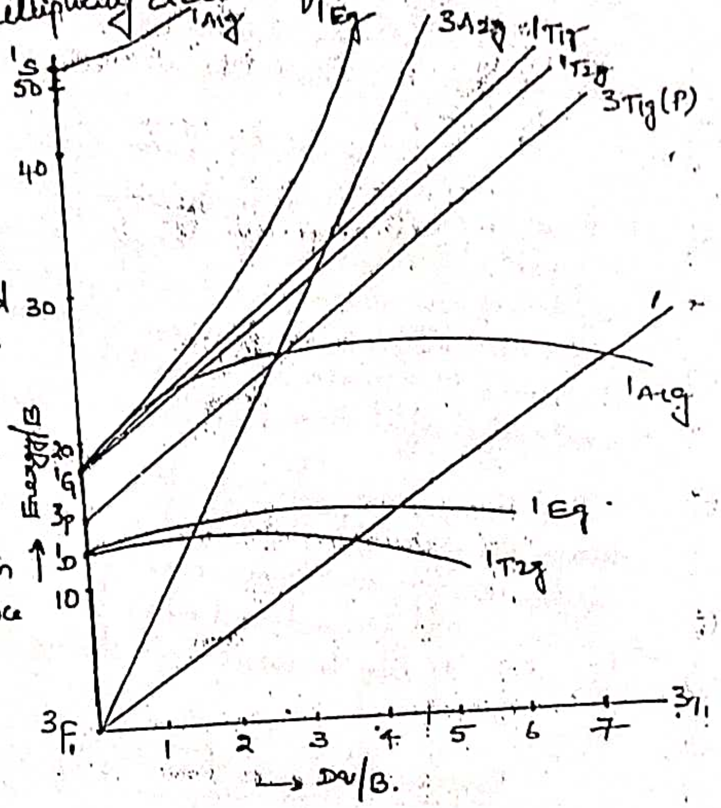
Important characteristics of TS diagrams:

(1) In these diagrams the energies of split up states divided by Racah parameter B i.e. E/B is plotted against Dq/B. Thus the positions of the spectral states are shown as a function of two parameters Dq and B. Hence these diagrams are valid for all central ions.

(2) In TS diagrams the ground term is made the horizontal base line so that the energy of the transition of electron from the ground to the excited states can be calculated by the vertical distance from the base line.

(3) For d^1, d^2, d^3, d^8 and d^9 cases the ground state remains the same in weak and strong fields. For d^4, d^5, d^6 and d^7 cases there is term crossing for a critical value of field strength. A state with lower multiplicity derived from a higher free ion spectral state becomes ground state with increasing Δ. In all these cases (d^4, d^5, d^6 and d^7) a higher state in weak field becomes ground state in the strong field and becomes the base line. Thus there is a break in the original ground state and a sharp change in the slopes of all the lines.

(4.) In Tanabe Sugano diagrams, some spectral states are shown by curved rather than straight lines. This is because there is interaction between state of same symmetry and same multiplicity derived from different free ion spectral states.



TS diagram for d^2 system:

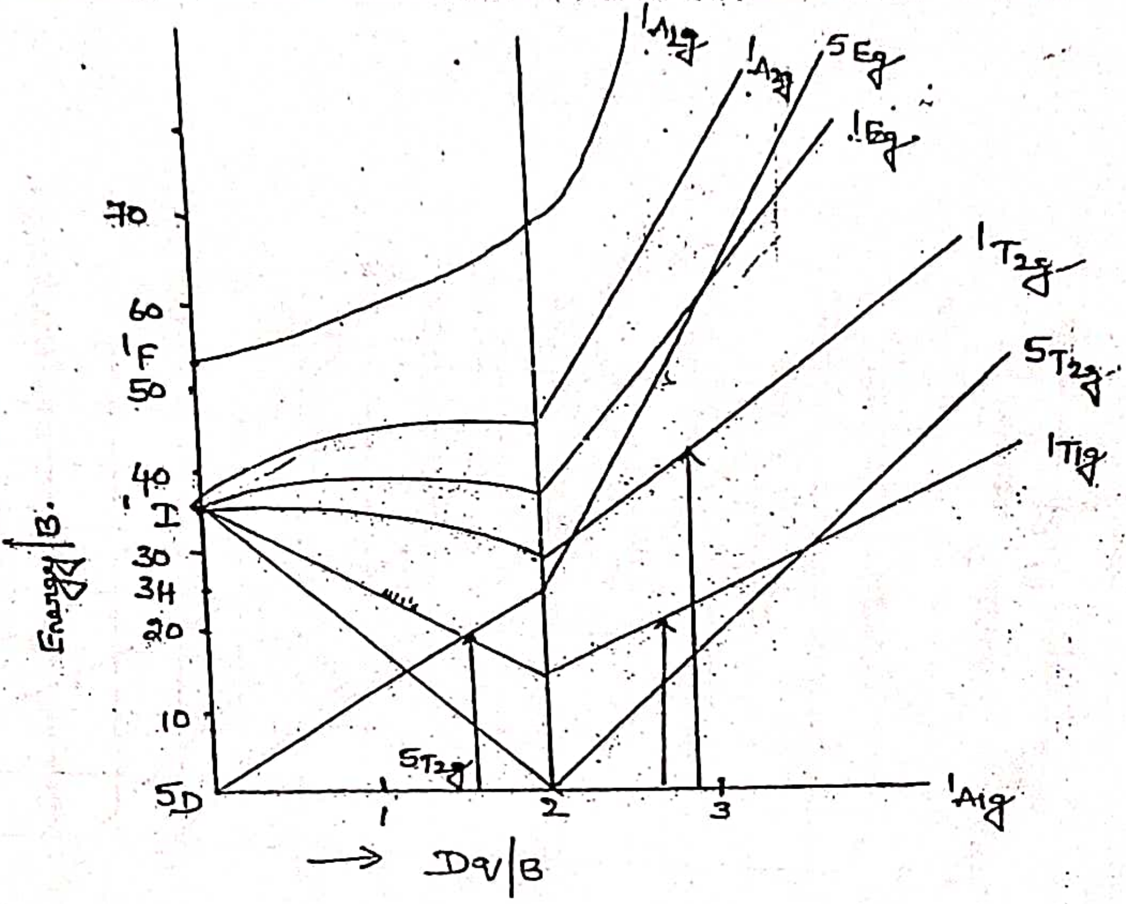
The various Russell-Saunders states for d^2 configuration are ^3F, ^3P, ^1G, ^1D and ^1S. The ^3P and ^1S will not undergo any splitting in an octahedral field. The ^3F state splits into $^3T_{1g}$, $^3T_{2g}$, $^3A_{2g}$. The ^1D state splits into $^1T_{2g}$, ^1E_g and ^1G state splits into $^1T_{1g}$, $^1T_{2g}$, ^1E_g and $^1A_{1g}$. In d^2 case there is no fundamental difference between strong and weak fields.

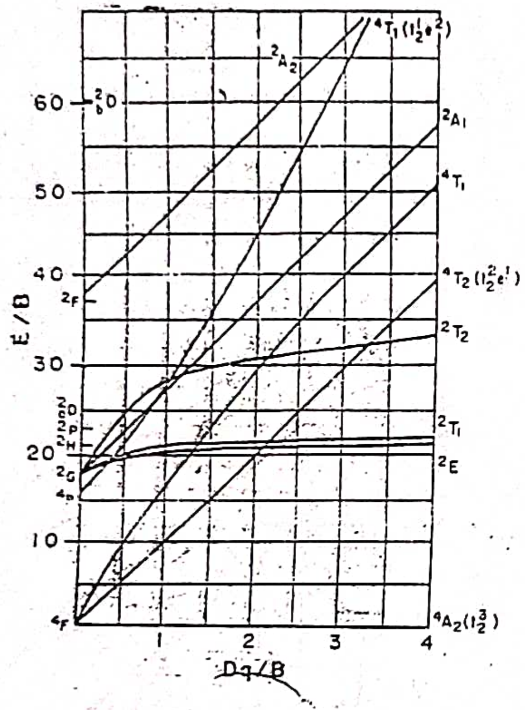
TS Diagram for d^6 system

The diagram is a simplified version and only the singlet and quintet terms are shown. There is a discontinuity at $10Dq/B = 20$ which is shown by a vertical line. At the point of discontinuity spin pairing of electrons occur. The splitting pattern in weak field can be observed to the left of the vertical line and the splitting pattern in strong field can be observed to the right of the vertical line. The ground state term for d^6 configuration in weak field case is ^5D and in strong field case the $^1A_{1g}$ state becomes the ground state.

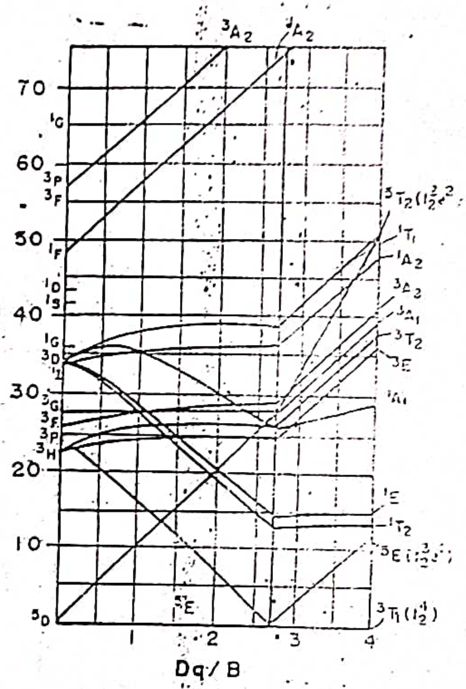
Orgel diagrams	Ts diagrams
Orgel diagrams were developed by Leslie Orgel in 1955	these diagrams were developed by two Japanese scientists i.e. Tanabe Sug...
1. These diagrams are applicable for weak field cases only.	They are applicable for both field as well as strong field
2. Except in d^5, in all other Orgel diagrams. only terms of same spin multiplicity were included.	All the possible terms for the corresponding configuration were included in Tanabe sugano diagram.
3. Except in d^5, in all other Orgel diagrams the energy of ground component decreases with increase in ligand field strength	Always the ground components is coincides with the horizontal axis.
4. The energy of a terms depends on the extent of interelectronic repulsions and there is no inclusion of inter electronic repulsion parameter in these diagrams.	The interelectronic repulsion parameter was included in these diagrams. The vertical axis in ~~the~~ these diagrams is E/B.
5. only, the strength of ligand field is considered along x-axis	The strength of ligand field divides by Racah parameter B has been taken along x-axis.
6. orgel diagrams are energy level diagrams to explain the possible electronic transitions of LF Spectra.	Ts diagrams are also energy level diagrams to explain the possible transitions of LF spectra of complexes
7. These diagrams were devised basing on the strength of the ligand field alone and no importance ~~property of~~ give metal ion ~~introduced~~.	These diagrams were devised basing on LFS as well as nature of a metal ion. The splitting energy depends on the strength of the ligand field and nature metal ion.
8. Racah parameter values was not considered in devising these diagrams.	The Racah parameter value is different for different metal ions and hence these diagrams are much generalised and are useful for all types of metal ion. Complexes.
9. Non Crossing rule is applicable and the diagrams.	non crossing rule was followed solutions

10.	A good interpretation of electronic spectra is not possible from orgel diagrams as these diagrams provide only qualitative information.	A good interpretation of electronic spectra is possible as these diagrams provide quantitative information.
11.	Applicable for only weak field cases.	For d^1, d^2, d^3, d^8 and d^9 cases the ground state remains the same in weak and strong fields.
12.	Applicable for only weak field cases.	For d^4, d^5, d^6 & d^7 cases, there is a vertical line in the diagram which separates strong field from weak field. At critical Dq/B value, where the vertical line crosses the horizontal axis, the weak field changes to strong field and the ground components will be different in strong field cases.


$^1A_{1g}$
$^1A_{2g}$
^5E_g
^1E_g
$^1T_{2g}$
$^5T_{2g}$
$^1T_{1g}$
70
60
^1F
50
40
^1I
30
^3H
20
10
^5D
$^5T_{2g}$
1
2
3
$^1A_{1g}$
Energy/B
Dq/B



TANABE SUGANO energy level diagram for d^3 configuration



Tanabe Sugano Energy level diagram for d^4 configuration.

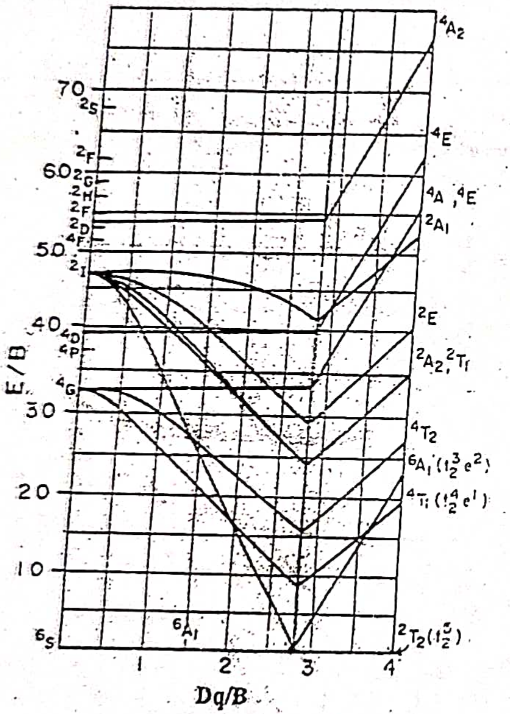


Figure 11.35: Tanabe-Sugano energy level diagram for d^5 configuration.

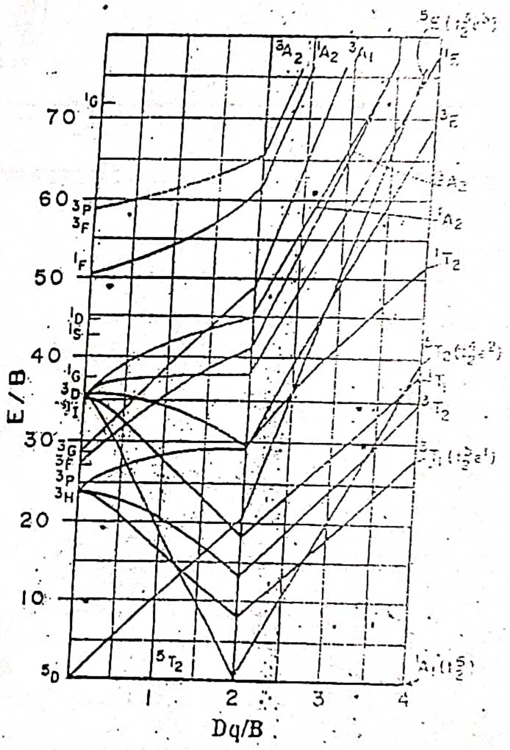


Figure 11.36: Tanabe-Sugano energy level diagram for d^6 configuration

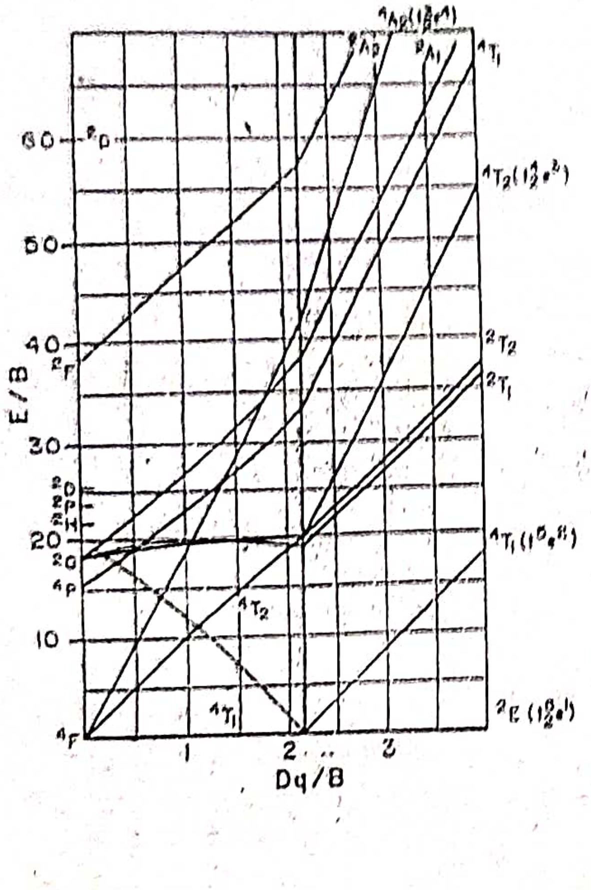


Figure 11.37: Tanabe-Sugano energy level diagram for d^3 configuration.

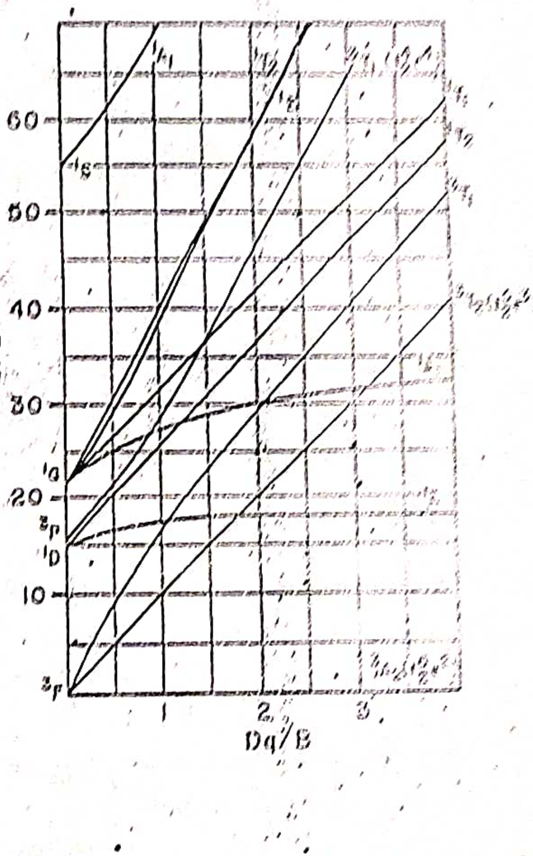


Figure 11.38: Tanabe-Sugano energy level diagram for d^8 configuration.

Calculation of Dq, B and B' Parameters :

B is known as Racah Parameter, which is interelectronic repulsion parameter. This parameter is very useful in having a good interpretation of spectra. The interelectronic repulsion which causes the bending of the lines is expressed by the Racah parameters B and C.

The Racah Parameters can be calculated from linear combinations of exchange integrals and coulumbic integrals. They are usually obtained empirically from the spectra of free ions. The difference in energy between two states of same multiplicity can be explained in terms of B. For example In a d^3 ion the separation between ^4F and ^4P is 15B where as the difference between energies of two states of different multiplicities can be explained in terms of B and C.

For example: In a d^3 ion, the separation between ^4F and ^2G is $4B+3C$. For most transition metal ions B is approximately 700–1000 cm^{-1} and C is approximately four times B.

The value of Dq can be calculated from Tanabe - Sugano diagram. In addition to Dq value, it is possible to evaluate, the interelectronic repulsion parameter B. The value of B for a complex is less than that for a free ion. This is attributed due to the phenomenon of nephelauxetic effect - Nephelauxetic effect is attributed to the delocalisation of the metal electrons over molecular orbitals that encompass both the metal and the ligands. As a result of this delocalisation of 'cloud expanding', the average interelectronic repulsion is reduced making B' smaller than B. The value of Racah parameter B relates to free ion and the value of B' relates to complex.

The nephelauxetic ratio, β is given by

$$\beta = \frac{B'}{B}$$

The value of β is always less than one and it decreases with increasing delocalisation.

For example in the low spin complex $[Co(en)_3]^{+3}$ two bands are observed at 21,550 and 29,600 cm^{-1} these bands are assigned to the following transitions.

$$^1A_{1g} \longrightarrow {}^1T_{1g} \qquad 21{,}550\ \mathrm{cm^{-1}}$$

$$^1A_{1g} \longrightarrow {}^1T_{2g} \qquad 27{,}600\ \mathrm{cm^{-1}}$$

The ratio of these two energies, given by

$$\frac{^1A_{1g} \longrightarrow {}^1T_{2g}}{^1A_{1g} \longrightarrow {}^1T_{1g}} = \frac{27{,}600}{21{,}550} = 1{\cdot}27.$$

This ratio can be fitted to the T-S diagram by sliding a ruler along the abscissa until a point is found at which the measured energy level separations have this same ratio. The point is observed at $\frac{\Delta}{B'} = 40$. The corresponding $\frac{E}{B}$ (actually B') for the lowest energy transition is noted as 38.

$$\therefore \frac{^1A_{1g} \longrightarrow {}^1T_{1g}}{B'} = \frac{21{,}550\ \mathrm{cm^{-1}}}{B'} = 38 \Rightarrow B' = 570\ \mathrm{cm^{-1}}$$

The value of Dq can be calculated from $\frac{\Delta}{B}$

$$\rightarrow \frac{\Delta}{B'} = 40 \rightarrow \Delta = 40B' \rightarrow \Delta = 40 \times 570 = 22{,}800\ \mathrm{cm^{-1}}$$

Charge transfer Spectra:

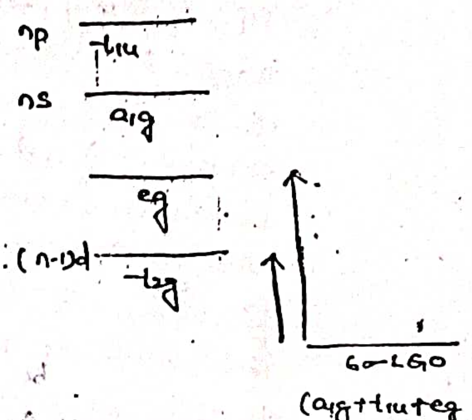
Most of the visible spectra pertaining to d-d type were studied by inorganic chemists in evaluating the coordination compounds. A more valuable information can be obtained from charge transfer transitions. These transitions involve electron transfer from one part of a complex to another. In complexes usually these transitions occur between metal ion and the ligands. These transitions are bidirectional i.e. transitions can take place either from ligand to metal or from metal to ligand. These transitions are internal redox processes i.e. If charge is transferred from metal to ligand then the ligand is reduced and if the charge is transferred from ligand to metal then the metal is reduced. The energies of these transitions fall in the visible or UV region of the electromagnetic radiation. These bands have 100 to 1000 times greater intensity than the ligand field (d-d) bands. Metal reduction bands generally lie at lower energy (longer wave lengths) if the ligands are easier to be oxidised.

In octahedral complexes (ML_6), usually three different cases of charge transfer transitions are observed. These transitions can be pictorially represented by means of molecular orbital energy level diagram.

Case i) Each of the ligand (L) has one lone pair of electrons which is involved in co-ordinate σ-bond to the metal. Hence following transitions are possible.

$\sigma(LGO) \longrightarrow t_{2g}$

$\sigma(LGO) \longrightarrow e_g$



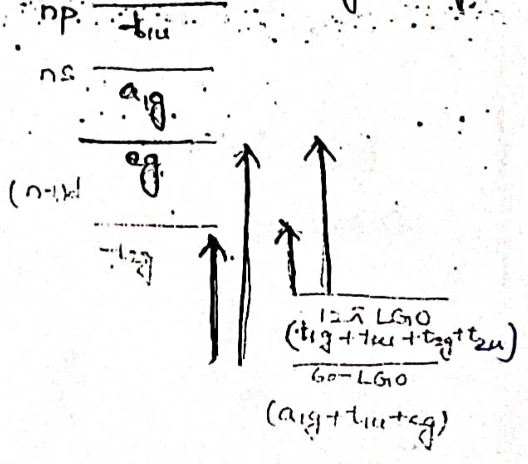
Case ii) The ligand (L) can have both σ and π donor electrons, so that the following type of transitions are possible

$\sigma(LGO) \longrightarrow t_{2g}$

$\sigma(LGO) \longrightarrow e_g$

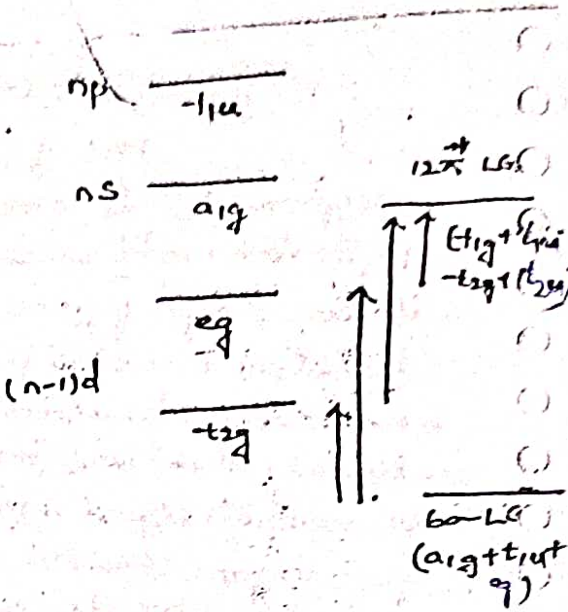
$\pi(LGO) \longrightarrow t_{2g}$

$\pi(LGO) \longrightarrow e_g$.



case(iii) There are ligands which have empty π^* orbitals of lower energy for back donation of electron density from the metal ion. Then besides the transitions of the type in case(i), there will be additional transitions of the following type.

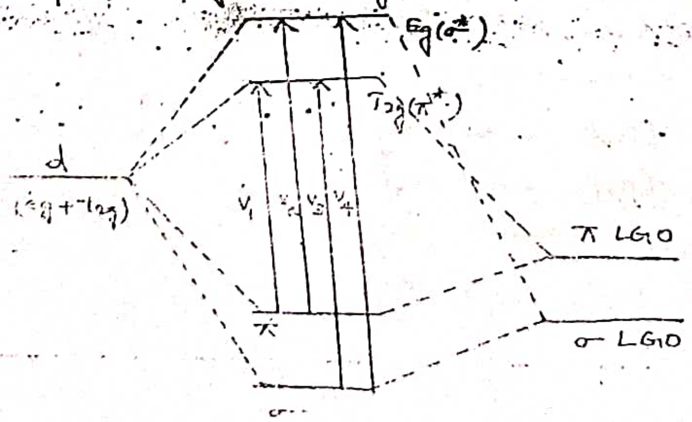
$$t_{2g} \longrightarrow \pi^* (LGO)$$
$$e_g \longrightarrow \pi^* (LGO)$$



The occurrence of the bands discussed in case(i), case(ii) and case (iii) depends on d^n configuration of the central metal ion. If t_{2g} orbital is completely filled, the bands due to $\sigma(LGO) \rightarrow t_{2g}$ and $\pi(LGO) \rightarrow t_{2g}$ transitions do not occur at all.

(a) Ligand to Metal charge Transfer

Consider an octahedral complex (ML_6) where L = F, Cl, Br, I and M is a heavy metal ion. The charge transfer bands of these complexes have been reported in three main regions. (i) A group of narrow bands in the range of 15,000 – 30,000 cm^{-1} for d^3, d^4, d^5, but not d^6 complexes. (ii) All hexahalo complexes of 4d and 5d metal ions exhibit strong and broad absorption bands in the range of 25,000 – 45,000 cm^{-1}. In the case F^- and Cl^- ligands this region consists of a single band and a double and triple band spectra for Br^- and I^- ligands. Multiplicity increases as the electronegativity decreases. (iii) Sometimes it is possible to observe a strong band above 45,000 cm^{-1}. These transitions can be interpreted by means of a simple MO energy level diagram



$V_1 : \pi \longrightarrow T_{2g}(\pi^*)$

$V_2 : \pi \longrightarrow E_g(\sigma^*)$

$V_3 : \sigma \longrightarrow T_{2g}(\pi^*)$

$V_4 : \sigma \longrightarrow E_g(\sigma^*)$

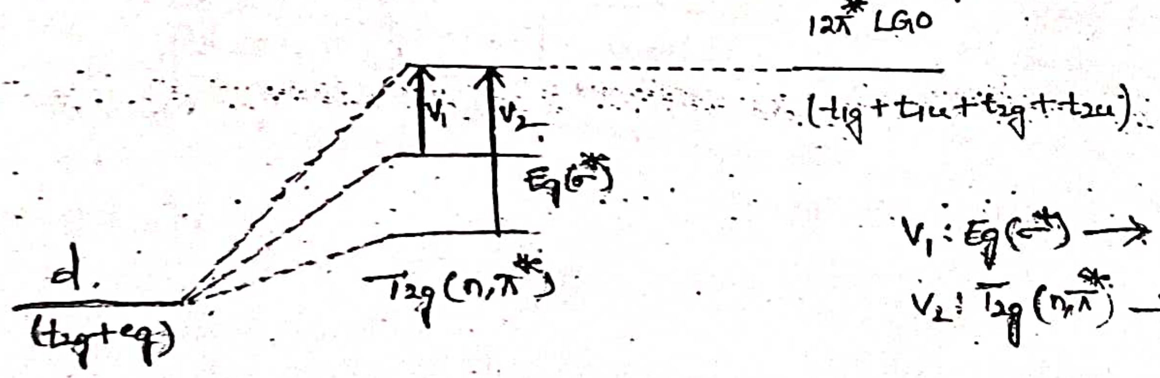
The four possible transitions of L → M are shown in the MO energy level diagram. All the four bands can be observed for d^1–d^5 complexes. In case of d^6– halo complexes (example $RuCl_6^{-4}$), v_1 and v_3 bands are not observable since t_{2g} orbital is filled with six electrons, so that the transitions to (T_{2g} π^*) level are not possible. The spectra of d^6 complexes however contain two bands assignable to V_2 and V_4 type. V_1 type of bands occur in the low energy region as narrow bands. V_2 and V_4 bands which occur essentially in d^6– halocomplexes are of high energy and considerably broader since they involve transitions to $E_g(\sigma^*)$ antibonding level. Sometimes V_4 bands occurs above 45,000 cm^{-1}, this band cannot be observed. 2

Multiplicity of bands is observed in the second region: The multiplicity of the band arises in case of ligands capable of lifting the degeneracy associated with π LGO (t_{1g} + t_{1u} + t_{2g} + t_{2u}). For example, I^- lifts the degeneracy.

(b) Metal–ligand charge transfer:

This type of transitions are possible only when the metal has highest filled molecular orbital and ligand has an empty low lying molecular orbital of mostly π^* type. Generally, these transitions involve only π– molecular orbitals. The ligands of the pyridine, pyrazine, bipyridyl, phenanthroline, CN^-, CO etc., form complexes that exhibit M → L charge transfer bands. In most of these cases, the metal is easily oxidisable and the ligands are easily reducible.

The possible M → L transitions are of the type given below



V_1 : $E_g(\sigma^*) \rightarrow \pi^*$ (LGO)

V_2 : $T_{2g}(n,\pi^*) \rightarrow \pi^*$ (LGO)