Energy Terms:—

The energy levels obtained by S-S and L-L coupling of any electronic configuration are called energy term. For this first of all the resultant spin and orbital angular quantum Number is determined by azimuthal quantum number of electrons. For example of d^2 electronic configuration, in table — the micro-states. To determine the energy term for these microstates one should follow the following order:—

(1) To determine the total spin quantum number M_S and total orbital angular quantum number M_L for all the microstates.

M_S = Sum of spin quantum no. of each electrons.
M_L = Sum of magnetic quantum no. of each electron.

(2) To determine the resultant spin (S) and orbital angular (L) momentum.

Values of (L) $= M_L, M_{L-1}, M_{L-2}, \text{———} 0$

Values of (S) $= M_S \times \frac{1}{2}, M_S \times \frac{1}{2} - 1, M_S \times \frac{1}{2} - 2, \text{———}$

(3) To write all possible energy terms from L and S values.

(4) To determine the energy terms used for microstates. Write the microstates of d^2 electronic configuration in the decreasing order of M_L values.

In the table 1 the maximum value of M_L is 4. Hence the value of L are 4, 3, 2, 1 and 0. The maximum value of M_S is 1 and minimum is 0. Hence spin multiplicity will be 3 and 1 respectively.

Now, we alredy know the symbols for various values of L.

L →	0	1	2	3	4
Symbol →	S	P	D	F	G

In this way the total energy terms for d^2 electronic Configuration will be obtained as follows.—

L=0	L=1	L=2	L=3	L=4
S=1	S=1	S=1	S=1	S=1
→ ^3S	^3P	^3D	^3F	^3G
and L=0	L=1	L=2	L=3	L=4
S=0	S=0	S=0	S=0	S=0
→ ^1S	^1P	^1D	^1F	^1G

Now we will determine allowed energy terms for 45 microstates.

The maximum values of M_L is 4 i.e. its L value is 4. Its symbol is G. In the table it is present at one place only, hence its spin multiplicity will be 1. For L=4, there will be 9 values of M_L. For each, the value of S will be zero.

Nine value of M_L -	+4	+3	+2	+1	0	-1	-2	-3	-4
Values of M_S -	0	0	0	0	0	0	0	0	0
Term symbol -	^1G	^1G	^1G	^1G	^1G	^1G	^1G	^1G	^1G

Now, for the remaining microstates, the maximum value of M_L i.e. L is 3. The maximum value of M_S is 1; hence spin multiplicity (2×1+1) will be 3.

Thus total values of M_L will be 7. There will be 3 values of M_S (+M_S to −M_S) means (+1, 0, −1). The symbol is F. Hence symbol is ^3F. It will be repeated 21 times.

Values of M_L -	+3	+2	+1	0	−1	−2	−3
Values of M_S =	+1	+1	+1	+1	+1	+1	+1
(+M_S to, −M_S) =	0	0	0	0	0	0	0
=	−1	−1	−1	−1	−1	−1	−1
Term Symbol →	^3F	^3F	^3F	^3F	^3F	^3F	^3F

The maximum values of M_L is 2. Hence the value of is 2. Its symbol is D, M_S value corresponding to it is zero. Hence spin multiplicity will be One. Hence total energy terms will be 5.

Values of M_L -	+2	+1	0	−1	−2
Values of M_S =	0	0	0	0	0
Term symbol -	^1D	^1D	^1D	^1D	^1D

Total 9+21+5 = 35 term symbols of microstates have been determined.

Now in remaining values of M_L, the maximum value is 1. Its symbol is P. The maximum value of M_S for this M_L value is 1, and spin multiplicity will be 3. Now three values of M_L (+1, 0, -1) and three values of M_S will produce nine term symbols, the term symbol will be ^3P.

Values of M_L —	+1	0	-1
Values of M_S ($+M_S$ to $-M_S$)	+1	+1	+1
	0	0	0
	-1	-1	-1
Term Symbol —	^3P	^3P	^3P

Now only $M_L = 0$ and $M_S = 0$ term symbol will be ^1S.

Thus for d^2 electronic configuration allowed term symbols or energy terms will be $^1G, ^3F, ^1D, ^3P$ & ^1S.

Determination of Spectroscopic States —

In a free ion a new quantum number J is obtained by L-S coupling. Energy level determined by J quantum numbers are the spectroscopic states. J values are between |L+S| to |L-S| always positive. For d^2 electronic configuration the values of J will be given in the following table 2.

Table 2 Calculation of J values for d^2 configuration.

Energy terms	L value	S value	|L+S|	|L-S|	J
^1G	4	0	4+0=4	4-0=4	4
^3F	3	1	3+1=4	3-1=2	4,3,2
^1D	2	0	2+0=2	2-0=2	2
^3P	1	1	1+1=2	1-1=0	2,1,0
^1S	0	0	0	0	0

These energy levels are spectroscopic states, for d^2 configuration the spectroscopic states obtained from various energy terms are given in the following table. 3.

Table-3. Spectroscopic States in Free state of d^2 Electronic Configuration

Energy step	Spectroscopic States
^1G	$^1G_4$
^3F	$^3F_4$, $^3F_3$, $^3F_2$
^1D	$^1D_2$
^3P	$^3P_2$, $^3P_1$, $^3P_0$
^1S	$^1S_0$

Spectroscopic states of d^2 configuration can be shown in Fig —

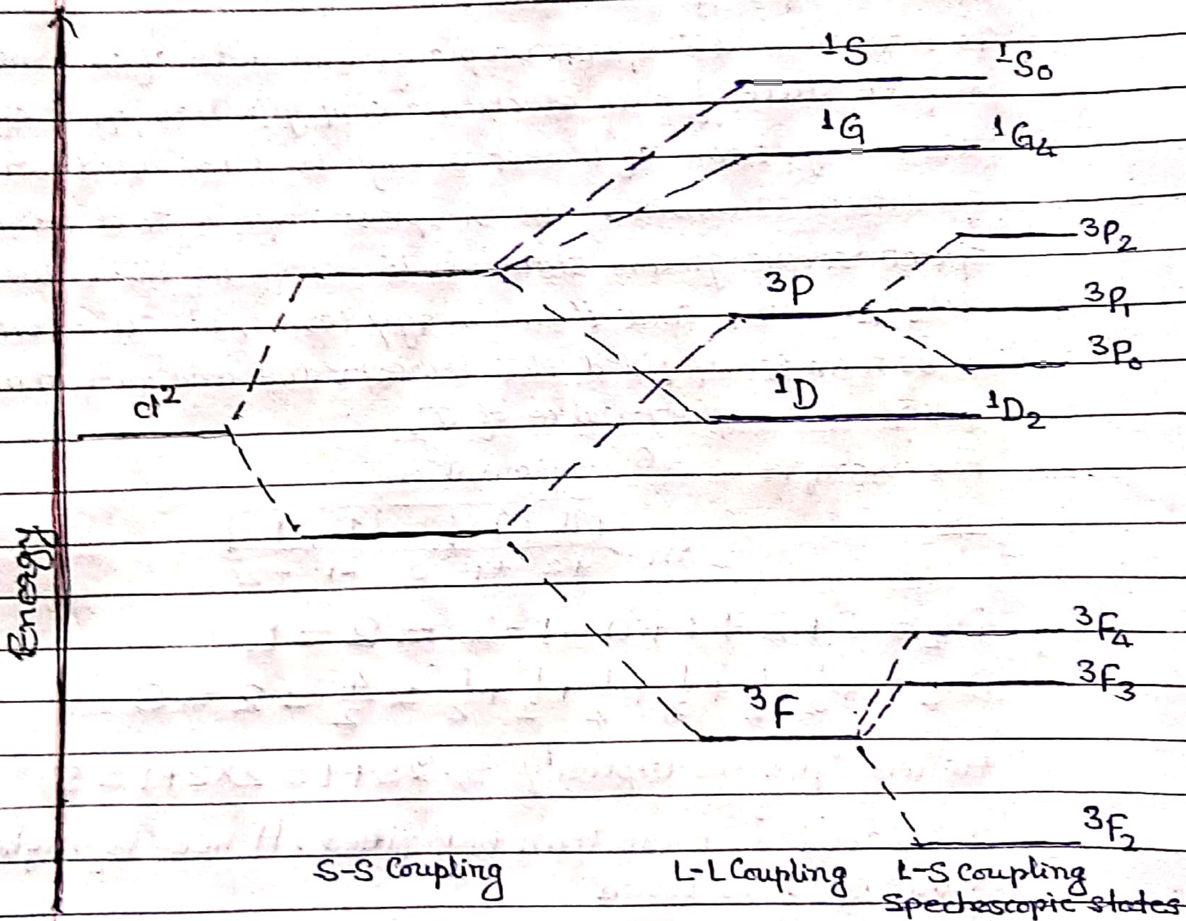

Fig. ——

Determination of order of energy of Spectroscopic States

Spectroscopic states of highest spin multiplicity has the lowest energy. In d^2 configuration Lowest energy of ^3P and ^3F as compared to ^1D, ^1G and ^1S, Hence

$$^3F < {}^3P \quad \text{and} \quad {}^1G < {}^1D < {}^1S$$

$L=3 \quad L=1 \quad\quad L=4 \quad L=2 \quad L=0$

Now three-three spectroscopic states will be obtained from ^3F and ^3P states. In d^2 electronic configuration 3d suborbit is less than half filled. Hence the minimum value of J will have lowest energy. Then order of energy in

$^3F \rightarrow {}^3F_2 < {}^3F_3 < {}^3F_4$

and $^3P \rightarrow {}^3P_0 < {}^3P_1 < {}^3P_2$

Determination of Spectroscopic Ground States —

The lowest spectroscopic energy states is called spectroscopic ground state. In d^2 configuration $^3F_2$ is the spectroscopic ground state.

To determine the spectroscopic ground state of any metal ion in free state for an electronic configuration, first of all the energy term of lowest energy is determined with J quantum number. The simplest method to determine the spectroscopic ground states is to determine the values of M_S and M_L and then energy term. If suborbit is less than half filled the lowest value and more than half filled the highest value of J.

For example — d^6 configuration

↑↓	↑	↑	↑	↑
+2	+1	0	−1	−2

m

$M_L = 2+2+1+0-1-2 = 2 = L$

$M_S = +\frac{1}{2} - \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{4}{2} = 2 = S$

Hence Spin multiplicity $\Rightarrow 2S+1 = 2\times2+1 = 5$

'd' suborbit is more than half filled. Hence the highest value of J is used

$J = 2+2 = 4$

and L = 2 than symbol is D

Spin multiplicity is 3

Hence the spectroscopic ground state for d^6 configuration will be $^5D_4$.