Advanced Transition Metal Chemistry_Spectroscopic Methods
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Module - 11
Lecture - 54
Methods of Characterisation UV-Visible Spectroscopy

Hello everyone. Once again, I welcome you all to MSB lecture series on Transition Metal Chemistry. And let us begin fifty-fourth lecture continuing discussion on UV-visible spectroscopy from where I had stopped. So, in my previous lecture, I was discussing about metal to ligand charge transfer transitions. In order to see metal to ligand charge transfer transition, metal should be in lower oxidation state and also it should be electron rich.

And then, the ligand should be having suitable empty orbitals to accommodate electrons that are coming from metal, through back donation, I would say. So, wherever the ligands are capable of acceptor properties, capable of taking electrons to their suitable empty orbitals such as pi star or sigma star, in those cases, one can anticipate metal to ligand charge transfer transition. Then what is ligand to metal charge transfer transition?

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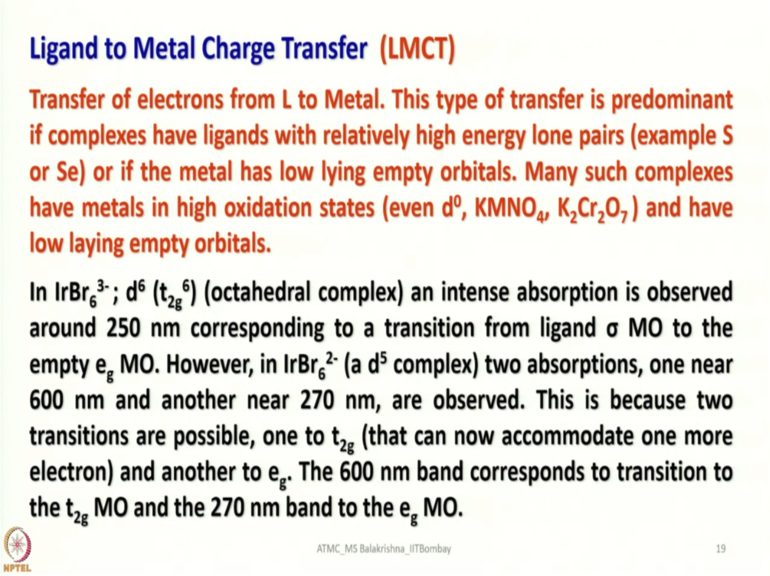

Ligand to Metal Charge Transfer (LMCT)

Transfer of electrons from L to Metal. This type of transfer is predominant if complexes have ligands with relatively high energy lone pairs (example S or Se) or if the metal has low lying empty orbitals. Many such complexes have metals in high oxidation states (even d^0, $KMNO_4$, $K_2Cr_2O_7$) and have low laying empty orbitals.

In $IrBr_6^{3-}$; d^6 (t_{2g}^6) (octahedral complex) an intense absorption is observed around 250 nm corresponding to a transition from ligand σ MO to the empty e_g MO. However, in $IrBr_6^{2-}$ (a d^5 complex) two absorptions, one near 600 nm and another near 270 nm, are observed. This is because two transitions are possible, one to t_{2g} (that can now accommodate one more electron) and another to e_g. The 600 nm band corresponds to transition to the t_{2g} MO and the 270 nm band to the e_g MO.

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That means, as name says, transfer of electrons occurs from ligand to metal. This type of transition or transfer is predominant if complexes have ligands with relatively high energy lone pairs; example, sulphur or selenium; or if the metal has low lying empty orbitals. Many such complexes have metals in highest oxidation state, you should remember. In case of MLCT, metal should be in lower oxidation state, so that they are electron rich.

In case of LMCT, ligand to metal what happens, metal exists in a higher oxidation states and also they have less or very fewer electrons in their d orbitals. For example, $KMNO_4$, potassium permanganate or potassium dichromate if you see, they have 0 electrons in their d orbital and hence, you can anticipate ligand to metal charge transfer transition. And that LMCT is responsible for intense colour of potassium permanganate or potassium dichromate.

In case of ligand to metal, one can see in case of $KMNO_4$ and potassium dichromate. If you consider hexabromo iridate 3-, it has d^6 electronic configuration. And here it is $t_{2g}{}^6$ here, octahedral complex. An intense absorption is observed around 250 nanometre corresponding to a transition from ligand sigma molecular orbital to the empty e_g molecular orbital. However, in case of iridium hexabromide or you can say iridate we should call because hexabromo iridate 2-.

This is a d^5 complex because iridium is in +4 state, 2 absorptions are seen; one near 600 nanometre and another near 270 nanometre. This is because 2 transitions are possible in this case, one to t_{2g} that can now accommodate one more electron, and another one to e_g. Though, the 600 nanometre band corresponds to transition to t_{2g} molecular orbital and the 270 nanometre band corresponds to the same transition to e_g molecular orbital so that an electronic configuration can tell you about possible transitions.

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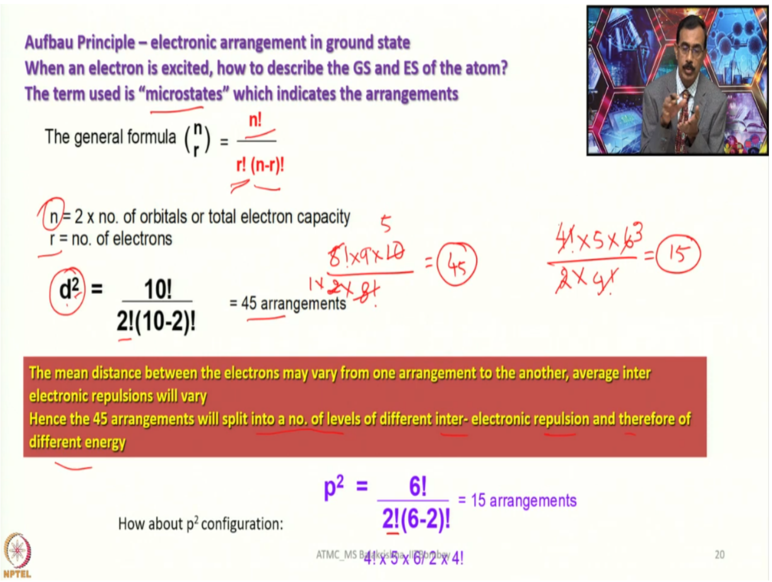

Aufbau Principle – electronic arrangement in ground state
When an electron is excited, how to describe the GS and ES of the atom?
The term used is "microstates" which indicates the arrangements

The general formula $\binom{n}{r} = \frac{n!}{r!\,(n-r)!}$

n = 2 x no. of orbitals or total electron capacity
r = no. of electrons

$d^2 = \frac{10!}{2!(10-2)!}$ = 45 arrangements

$\frac{\cancel{8!}\times 9\times \cancel{10}^{5}}{1\times \cancel{2}\times \cancel{8!}} = \boxed{45}$

$\frac{\cancel{4!}\times 5\times \cancel{6}^{3}}{\cancel{2}\times \cancel{4!}} = \boxed{15}$

The mean distance between the electrons may vary from one arrangement to the another, average inter electronic repulsions will vary
Hence the 45 arrangements will split into a no. of levels of different inter- electronic repulsion and therefore of different energy

How about p^2 configuration: $p^2 = \frac{6!}{2!(6-2)!}$ = 15 arrangements

4! x 5 x 6/ 2 x 4!

Let us try to understand what is microstate. Microstate is very important when we talk about electron spectroscopy of metal complexes. And here, we should recall our understanding of Aufbau principle that would give you information about electronic arrangement in ground state. Of course, when we arrange electrons in ground state, we have to follow Aufbau principle, Hund's rule and all those things; but when an electron is exited, it need not have to follow these principles.

So, in that case, for an excited electron, how to describe ground state and excited states of the atom. So, in that case, microstates come very handy. The term used is microstates, which indicates the arrangement. So, that means all possible arrangements when we excite electrons. So, that means, when we write all possible excited states starting from ground state, they need not have to follow Hund's rule or Aufbau principle.

So, the general formula for finding out microstates is n factorial over r factorial into n - r factorial. So, what is n? It is the number of orbitals or total electron capacity. That means it is the twice the number of orbitals or total electron capacity. If we are talking about the p orbital, so, n equals 6. If you are talking about f orbital, it is 14 electrons. If you talk about d orbital, it is 10 electrons. If you talk about s orbital, it is 2 electrons.

So, that is what it refers to, the total capacity of a particular orbital. And then, r is number of electrons. For example, here I have taken d^2 system; d^2 means it is a d orbital; so, total capacity of d is 10; it is 10 factorial. And now, 2 factorial; r is the electrons here; so, 2 factorial; and then, n - r is 8; 10 - 2 factorial means 8 factorial. So, this can be written as, so, 8 factorial x 9 x 10, we can write.

And now what happens, this is 2 factorial; you can write 1 into 2 and then one can write directly 8 factorial. So, this, this goes and this; so, what we have is 45 arrangements. So, this is microstate. That means 2 electrons can be arranged apart from ground state electronic configuration in another 44 different ways. So, that is what the microstate gives. That means it gives about all possible arrangements of excited states.

So, one you leave it for ground state; remaining 44 excited state arrangements, it depicts for d^2 electronic configuration. So, now, let us look into p^2 electronic configuration here. p^2 here, the total capacity is 6 factorial, 6 electrons; 3 p orbital are there. And then, r factorial is 2 electrons, 2 factorial. And now it is 6 - 2; 6 - 2 can be written as 4 factorial. And you can write here; here you can write 4 factorial, 5 into 6. And here 6 factorial; one can write just simply 2. And then this is 4 factorial; we can write here.

If this goes and there is 3, so, number is 15. So, that means in 15 different ways, 2 electrons present in 3p orbitals can be arranged. So, that is what this microstate says. The mean distance between the electrons may vary from one arrangement to the another. Average inter-electronic repulsion will also vary. Hence, the 44 arrangements will split into a number of levels of different inter-electronic repulsions and therefore of different energies.

So, when we arrange these things, we are looking into all possible arrangements. As a result, what happens, there can be variation in inter-electronic repulsion. Accordingly, the energy of those transitions would also vary.

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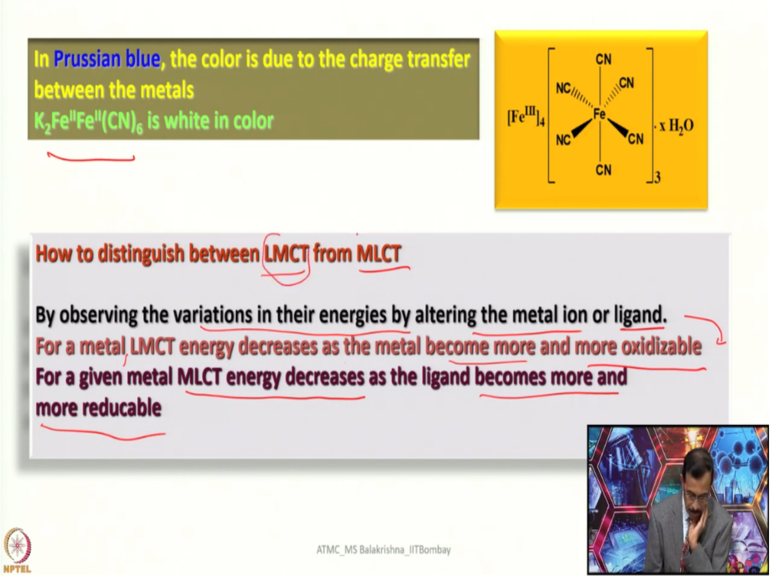

In Prussian blue, the color is due to the charge transfer between the metals

$K_2Fe^{II}Fe^{II}(CN)_6$ is white in color

How to distinguish between LMCT from MLCT

By observing the variations in their energies by altering the metal ion or ligand.

For a metal LMCT energy decreases as the metal become more and more oxidizable

For a given metal MLCT energy decreases as the ligand becomes more and more reducable

In Prussian blue, the colour is due to the charge transfer between metal, I mentioned. So, here you can see, instead of Prussian blue where we have iron 2 and iron 3, if we look into this complex here where both the iron atoms are in +2 state, it is white in colour. So, you can see the difference between these 2 species.

And how to distinguish LMCT from MLCT? For example, let us say we have moderate oxidation state of the metal and also ligands are capable of accepting and also donating; in those cases, if the colour is there, how to interpret or how to distinguish between metal to ligand charge transfer or ligand to metal charge transfer? It is very simple, by observing the variations in their energies by altering the metal ion or ligand.

So, what we can do is, we can keep the metal ion steady, keep on changing the ligands and look into the transitions. And same thing we can do. Now we can keep the ligand intact, keep on changing the metal and we can see. And then this observation should tell you about this one. For a metal, LMCT energy decreases as the metal becomes more and more oxidizable; one should remember this one.

So, this is how you can distinguish between LMCT and MLCT. For a ligand to metal charge transfer, energy decreases as the metal becomes more and more oxidizable. If the more and more oxidizable means it is very rich in electron so that it can readily give electron means probably electron can be excited very easily. For a given metal, MLCT energy decreases as the ligand becomes more and more reducible.

So, if you understand the nature of the ligand and also the nature of the metal, distinguish or understanding or distinguishing between LMCT and MLCT should be a problem. So, we can distinguish these two very clearly with clarity without any problem.

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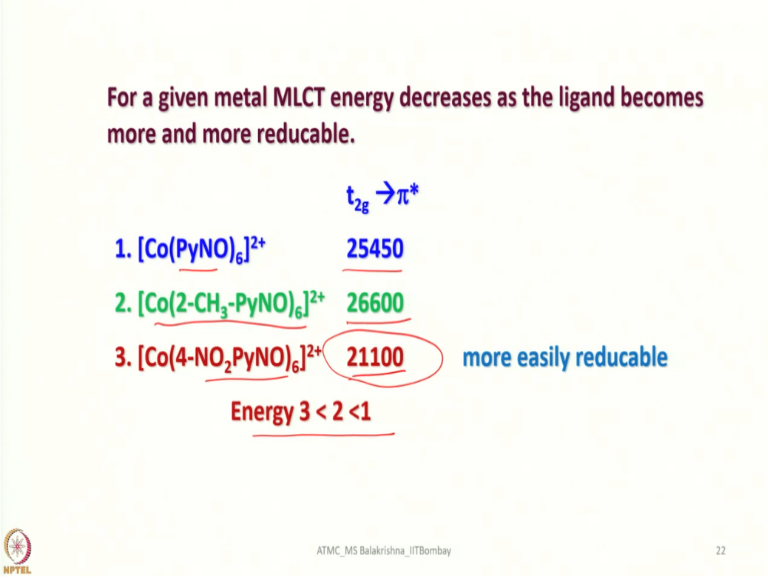

For a given metal MLCT energy decreases as the ligand becomes more and more reducable.

$t_{2g} \rightarrow \pi^*$

1. [Co(PyNO)$_6$]$^{2+}$ 25450
2. [Co(2-CH$_3$-PyNO)$_6$]$^{2+}$ 26600
3. [Co(4-NO$_2$PyNO)$_6$]$^{2+}$ 21100 more easily reducable

Energy 3 < 2 <1

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For a given metal to ligand charge transfer, energy decreases as the ligand becomes more and more reducible, I mentioned. Let us look into that now. We have pyridine N-oxide, and for this one we have 25450 cm^{-1}, t_{2g} to pi star transition. And now we have here in this case, what we have is energy is increasing; whereas here, energy is decreasing. So, that means energy range is this one. This is more easily reducible.

If it is more reducible, you can see the impact of ligand structure on MLCT. We shall try to make ourselves familiar with atomic term we use, term symbols we call it and also the number of states we give what atomic term. This is about term symbols, I am telling you.

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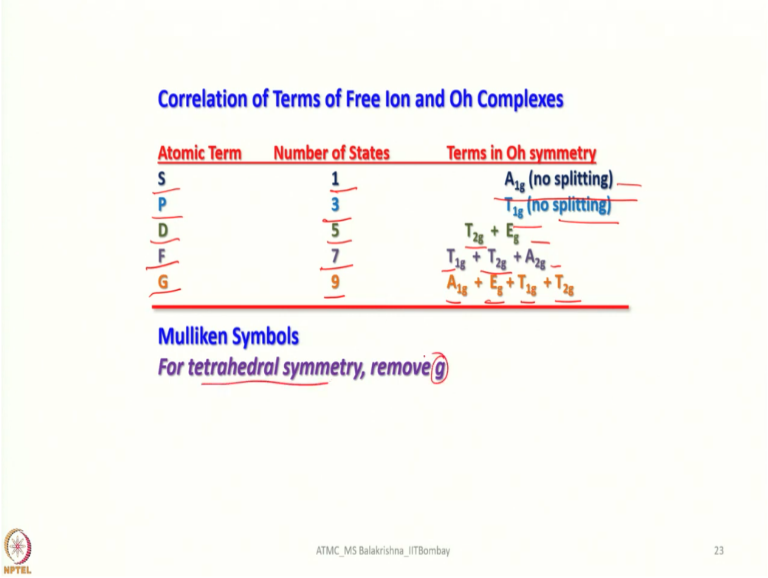

Correlation of Terms of Free Ion and Oh Complexes

Atomic Term	Number of States	Terms in Oh symmetry
S	1	A_{1g} (no splitting)
P	3	T_{1g} (no splitting)
D	5	$T_{2g} + E_g$
F	7	$T_{1g} + T_{2g} + A_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$

Mulliken Symbols

For tetrahedral symmetry, remove g

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And also Mulliken Symbols, how they are used for different orbitals; that I have already showed you earlier in a table. Let us look into some of those things keeping UV-visible spectroscopy in mind. So, now, for example, S, number of states, 1; A_{1g} is the term given; no splitting; it is spherically symmetrical. And then P; 3 is there; T_{1g}; no splitting. And when D, 5, T_{2g} and E_g; two splittings, splits into triply degenerate and doubly degenerate.

And F will split into of course, 7 states; 7 splits into 3 triply degenerate and 1 single state. And in case of G, what would happen is 9 are there; as a result, 1 single; no splitting; 1 double degenerate and 1 triply generate, another 1 triply degenerate; that means 3 3 2 1, 9. Here, 3 3 1; here, 3 2; so, like that. So, this is how the terms in octahedral symmetry can be seen. And of course, for tetrahedral symmetry, remove g, because it does not have centre of symmetry.

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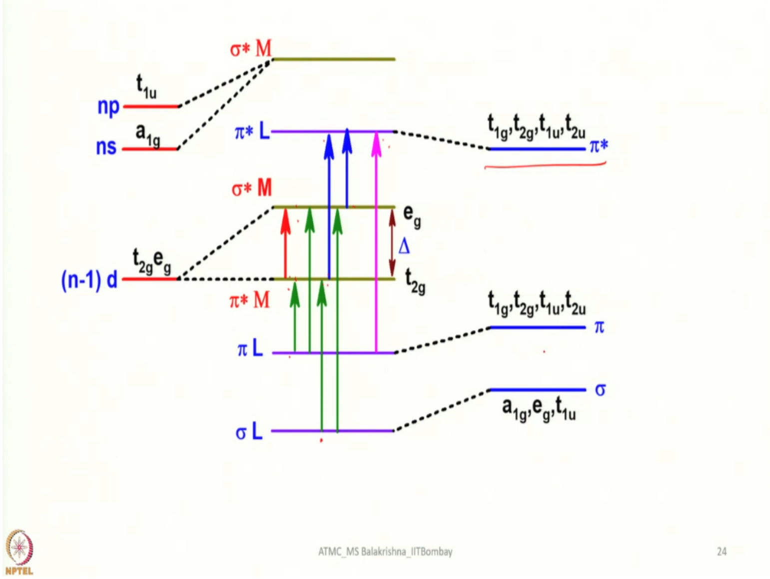

Now, this shows all possible transitions, of course, label is there for each energy level; you should be able to guess what transition this is. For example, if it is going from here to here, yes, it is a ligand to metal. And this is also ligand to metal. And this is d-d transition. And then, if it is going from ligand to ligand, it is there ligand to ligand. And then, this is metal to ligand. And this is metal to ligand.

So, this picture gives you an idea about all transitions, metal to ligand, ligand to metal and also d-d transition. And also, you should remember relative energies of various orbitals. You can see here, this is a typical sigma donor and pi donor. So, there you can anticipate ligand to metal charge transfer transitions. And whereas, in this case what happens, it is metal to ligand back bonding.

So, now, how to examine the arrangement of microstates? In case of p^2, I wrote 15 microstates; in case of d^2, I wrote 45. You may be wondering how one can arrange these two electrons in 5 different d orbitals. What are the possible ways? Let us examine in case of p^2.

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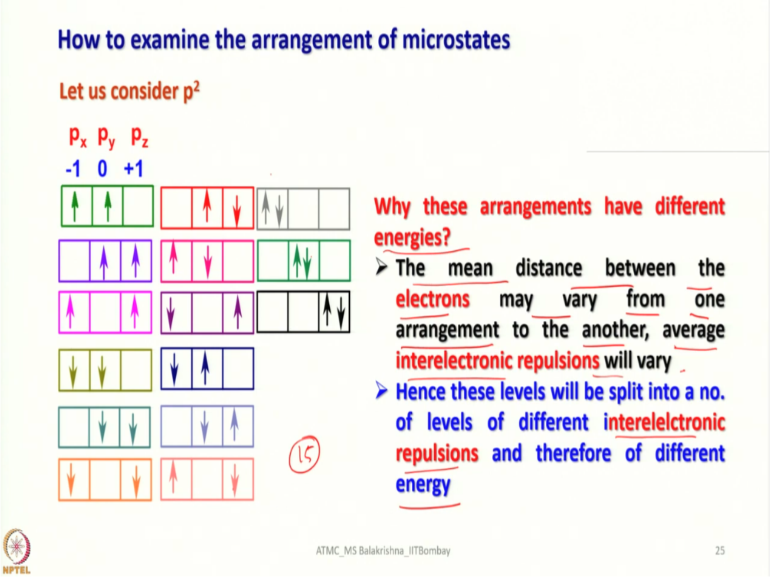

How to examine the arrangement of microstates

Let us consider p^2

p_x p_y p_z

-1 0 +1

15

Why these arrangements have different energies?

- ➤ The mean distance between the electrons may vary from one arrangement to the another, average interelectronic repulsions will vary
- ➤ Hence these levels will be split into a no. of levels of different interelelctronic repulsions and therefore of different energy

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Of course, we labelled p_x, p_y, p_z; and also we put -1, 0, +1 quantum numbers. Now, 2 electrons we put in ground state; it is like this. And as I said, when we write excited states, they need not have to follow Pauli's exclusion principle or Aufbau principle or Hund's rule. So, now, one is like this, one is down; another one is, both of them can be paired. And when both of them can be paired, they can be there in p_x, p_y, or p_z.

And similarly, you can keep on arranging. And then, one upward spin and one lower spin, also you can have something like that. Again, these possibilities are there. So, total if you count, it will be about 15 different states are there including this ground state. That means now, your job will be to see whether any other possible arrangement is left out. So, then this microstate calculation would go wrong.

But however, you can just see, try to write and try to make yourself familiar in writing all possible microstates at least for smaller ones. When we get 210, all those things, it is very tedious; nevertheless, one should be able to write. And as in case of d^2, we have only 45; make an attempt to write all 45 arrangements of microstates. So, why these arrangements have different energies? That is the question.

As I mentioned already, the mean distance between the electrons may vary from one arrangement to another. As a result, average inter-electronic repulsion will vary. So, as a result, these levels will be split into a number of levels of different inter-electronic repulsions and therefore of different energies. So, this can tell you satisfactory answer why these arrangements have different energies.

As a result, you can see more transitions. Of course, we get lot of transitions; but when we apply selection rules, most of them will be eliminated and further spectrum will be simplified. So, that is really good, so that understanding would be less complicated and much easier.

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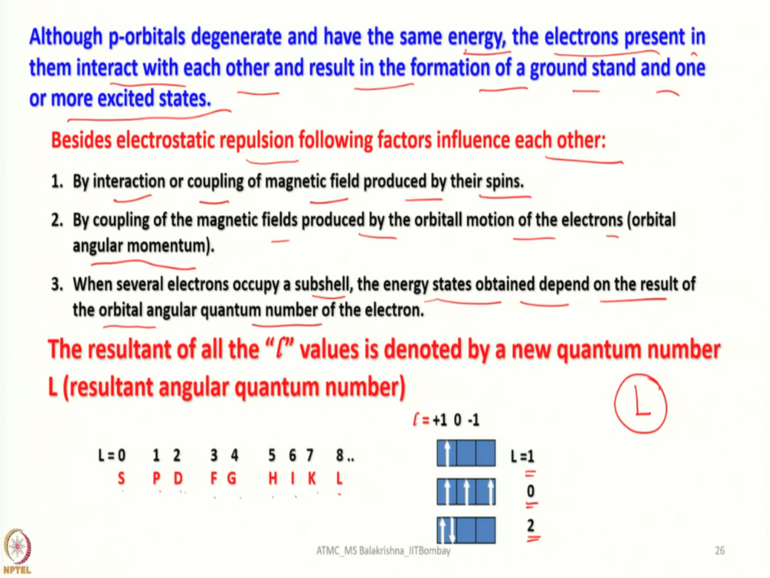

Although p-orbitals degenerate and have the same energy, the electrons present in them interact with each other and result in the formation of a ground stand and one or more excited states.

Besides electrostatic repulsion following factors influence each other:

1. By interaction or coupling of magnetic field produced by their spins.
2. By coupling of the magnetic fields produced by the orbitall motion of the electrons (orbital angular momentum).
3. When several electrons occupy a subshell, the energy states obtained depend on the result of the orbital angular quantum number of the electron.

The resultant of all the "l" values is denoted by a new quantum number L (resultant angular quantum number)

L = 0	1	2	3	4	5	6	7	8..
S	P	D	F	G	H	I	K	L

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So, now, although p orbitals degenerate and have the same energy, the electrons present in them interact with each other and result in the formation of a ground state and one or more excited states. This is again little bit stressing upon the origin of microstates. Besides electrostatic repulsion, following factors also influence each other. So, by interaction or coupling of magnetic field produced by their spins.

Electrons, when they are spinning with respect to a particular axis, its own axis, what happens, they can also produce a magnetic field. By coupling of the magnetic fields produced by the orbital motion of the electron; so, since electrons are moving in orbital motion, any circulating charge would also produce magnetic field when it is placed in a magnetic field. So, that means that it is called orbital angular momentum also should be accounted.

And when several electrons occupy a subshell, the energy states obtained depend on the result of orbital angular quantum number of the electron. So, the resultant of all the l values is denoted by a new quantum number called resultant angular quantum number, represented by L. L is the term. L can take any value like this, 0, 1, 2, ..., 7 corresponding to this term such as S, P, D, F, G, H, I, J, K, L we have given.

And if the L, when L = 2, we have to go for term D; these are the terms and these are the symbols we are using. So, for example, if we have one electron say in p orbital, we have 1 electron is there, L = 1 here. And if 3 electrons are there L = 0; and if 2 electrons are paired here, L = 2. So, this is how we can arrive this resultant angular quantum number.

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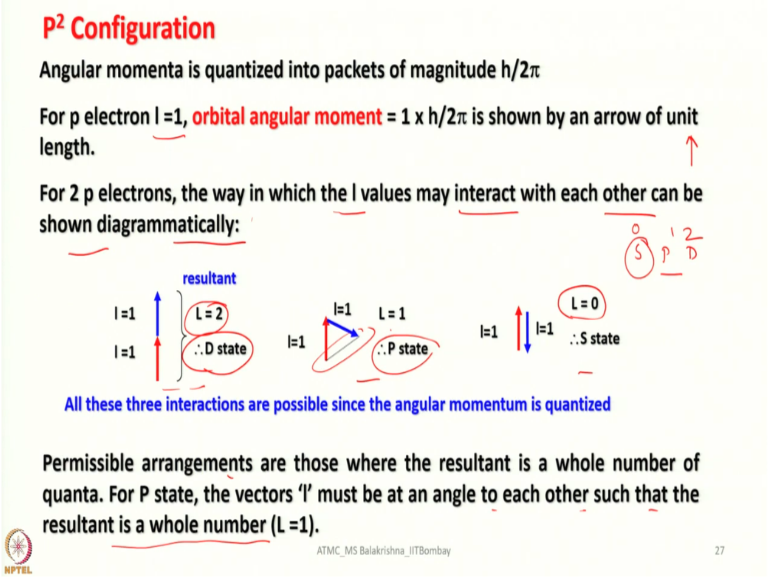

P^2 Configuration

Angular momenta is quantized into packets of magnitude h/2π

For p electron l =1, orbital angular moment = 1 x h/2π is shown by an arrow of unit length.

For 2 p electrons, the way in which the l values may interact with each other can be shown diagrammatically:

All these three interactions are possible since the angular momentum is quantized

Permissible arrangements are those where the resultant is a whole number of quanta. For P state, the vectors 'l' must be at an angle to each other such that the resultant is a whole number (L =1).

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So, now, once again go back to p^2 electronic configuration. So, here, angular momenta is quantised into packets of magnitude h/2π. That you must have studied in your +2. For p electron l = 1, orbital angular momentum, 1 x h/2π is shown by an arrow of unit length, 1 unit length like this. For 2p electrons, the way in which the l values may interact with each other can be shown diagrammatically in this format.

For example, if 2 are there, so, 2 will be having unit length like this. And what are the possible ways these interactions can be seen here. So, for example, if both of them are interacting in this direction, the net resultant would be 2; value is 2. So, this is, since value equals 2, if you go for S, P, D, 0, 1, 2, so, this is D state we call it as. Here, if they interact in an angle such that this is quantised; this is unit; in that case what happens, L = 1.

If L = 1, we can go for P state. And if they interact in this opposite direction, so, net resultant would be L = 0. So, then, this is S state here. So, this is how orbital angular momentum we can see here; orbital angular moment can be seen here, not moment. So, one can see, this is how you can calculate orbital angular moment for p^2 electronic configuration. All these 3 interactions are possible since the angular momentum is quantised.

Permissible arrangements are those where the resultant is a whole number; that you should remember. So, we should put in an angle such that the resultant will be a fraction 1.5, 1.7; that is not allowed. One should remember, the permissible arrangements are those where the resultant is a whole number. It should be 1, 2, 3 or 0 or even more. For P state, the vectors l must be at an angle to each other such that the resultant is a whole number. So, here, resultant is a whole number, here whole number, it is a whole number, 0, 1. So, this is the criteria for arrangement.

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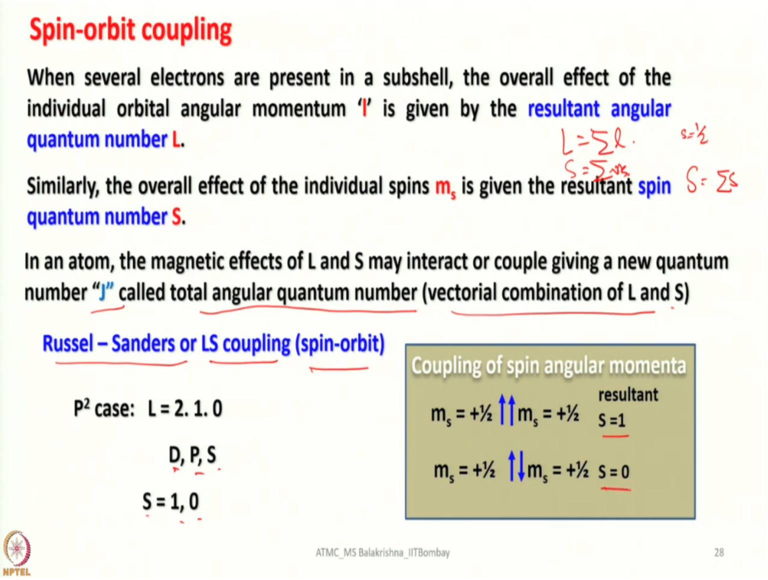

Spin-orbit coupling

When several electrons are present in a subshell, the overall effect of the individual orbital angular momentum 'l' is given by the resultant angular quantum number L.

$L = \Sigma l$. $s = \frac{1}{2}$

$S = \Sigma m_s$

Similarly, the overall effect of the individual spins m_s is given the resultant spin quantum number S. $S = \Sigma s$

In an atom, the magnetic effects of L and S may interact or couple giving a new quantum number "J" called total angular quantum number (vectorial combination of L and S)

Russel – Sanders or LS coupling (spin-orbit)

P^2 case: L = 2. 1. 0

D, P, S

S = 1, 0

Coupling of spin angular momenta

	resultant
$m_s = +\frac{1}{2}$ ↑↑ $m_s = +\frac{1}{2}$	S = 1
$m_s = +\frac{1}{2}$ ↑↓ $m_s = +\frac{1}{2}$	S = 0

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Now, let us look into spin-orbit coupling. When several electrons are present in a subshell, the overall effect of the individual orbital angular momentum l is given by the resultant angular quantum number L that I showed you. So, similarly, the overall effect of the individual spins m_s is given by the resultant spin quantum number capital S. The small represents this one, m_s, whereas the larger one is essentially Sigma-s or Sigma-m_s, I would say.

In an atom, the magnetic effect of L and S may interact or couple giving a new quantum number called J. This is called total angular quantum number. This is very important. This is essentially vectorial combination of L and S. This is also called as Russel-Sanders coupling or LS coupling or spin-orbit coupling. In an atom, the magnetic effects of L; L is Sigma l, and then S is Sigma m_s.

So, this one; in an atom, the magnetic effects of L and S may interact or couple giving a new quantum number that is designated as J called total angular quantum number. This is also called as Russel-Sanders or LS coupling. Now, P^2, we have 2, 1, 0 are there; D, P, S is there; and S equals 1 and 0 is there. And then, coupling of spin angular momenta also one can see, m_s + 2 electrons can be like this, then s = 1; and 1, they can be paired; in that case, s = 0.

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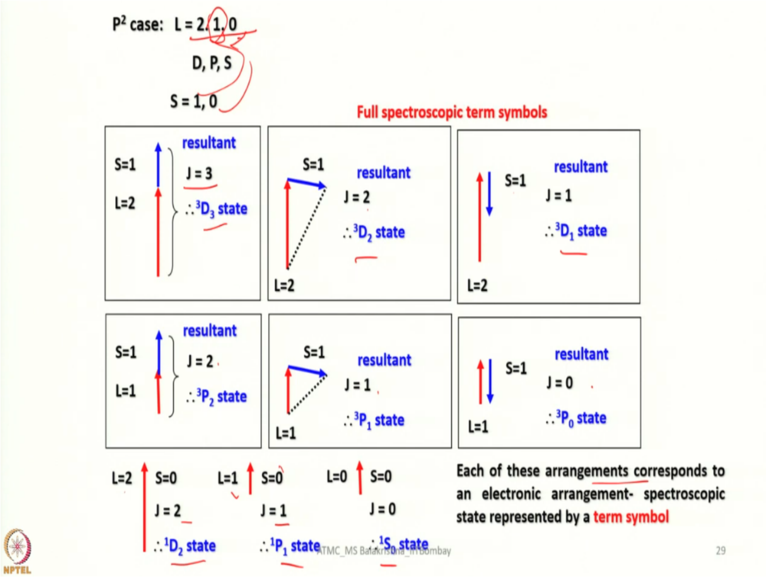

P^2 case: L = 2, 1, 0

D, P, S

S = 1, 0

Full spectroscopic term symbols

Each of these arrangements corresponds to an electronic arrangement- spectroscopic state represented by a term symbol

Now, let us try to see spin-orbit interactions or LS interaction. Now, we have to take this one and start interacting. This one should interact with all 3 and this also should interact with all 3; and see totally how many we get. For example, here, L = 2 we shall start and S = 1. They can interact in such a way that the resultant will be sum 3; this is J = 3. And when they interact something like this, L = 2 is interacting with S 1, J = 2 and L = 2 can interact with S = 1 in this fashion.

So, 3 possible ways are there. In angle 1, net is the same. And then, other interaction will be having a whole number 2; other one, whole number 1 will be there. So, now, we have generated 1, 2, 3 states. And now, if you take one value now; take one; and then, 1, L = 1, S = 1 can interact in this way or it can interact J = 2 and J = 1 and J = 0. Similarly, L = 2 can interact with S = 0.

S is not there, so, it is J, 2 is there and L = 1 can also interact with this one; it is not there, 1. So, like that, we have again another 3 states are there. So, this is how you can calculate. Each of these arrangements corresponds to an electronic arrangement spectroscopic state represented by a term symbol. This is how we can view term symbols or this is the origin of term symbol.

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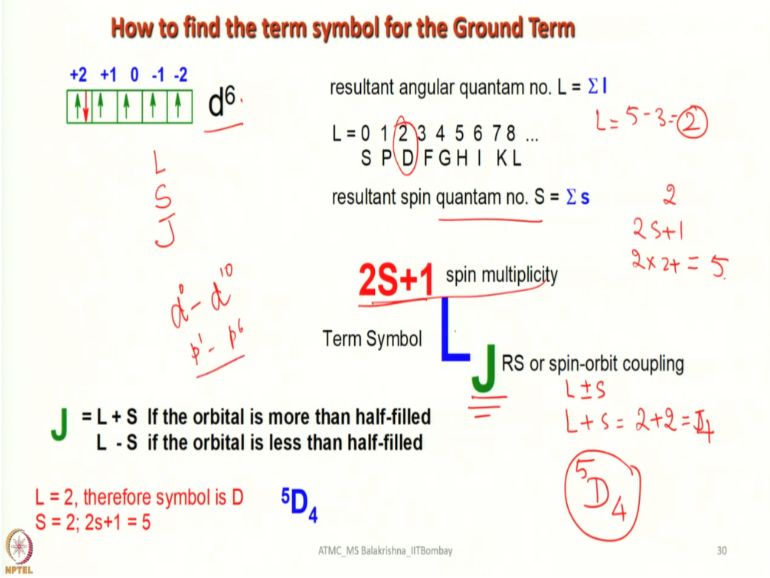

How to find the term symbol for the Ground Term

+2 +1 0 -1 -2

d^6

L
S
J

resultant angular quantam no. L = Σl

L = 0 1 2 3 4 5 6 7 8 ...
S P D F G H I K L

$L = 5 - 3 = 2$

resultant spin quantam no. S = Σs

2
$2S+1$
$2 \times 2 + 1 = 5$

$d^0 - d^{10}$
$p^1 - p^6$

2S+1 spin multiplicity

Term Symbol L J RS or spin-orbit coupling

$L \pm S$
$L + S = 2 + 2 = 4$

J = L + S If the orbital is more than half-filled
L - S if the orbital is less than half-filled

L = 2, therefore symbol is D
S = 2; 2s+1 = 5

$^5D_4$

$^5D_4$

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So, now, how to find the term symbol for the ground term. Now, to begin with, let us consider a d^6 electronic configuration. For this one, we have to write the ground term. For this one, what we have to do is, we have to calculate L; we have to calculate S; we have to calculate J. So, once we calculate, we can apply for this one here. And then, that will give you the ground term symbol for this d^6 electronic configuration.

We can place electrons like this. And to calculate L equals Sigma l, we can take 4 + 5; 5 - 3; 5 - 3 will be equals 2. So, this is L = 2. So, we are taking D here. And then, resultant spin quantum number we have to take. We have 1, 2, 3, 4 are there; 4; that means 2. When we take 2s + 1; 2 into 2 plus 1 equals 5; this is 2s + 1. At net J; J equals RS or spin-orbit coupling. So, what it says?

J = L + S if the orbital is more than half-filled; or, J = L - S if the orbital is less than half-filled. That means this can be L plus or minus S. So, in this case, it is more than half-filled; d 6 electronic configuration, we should consider L + S. So, L + S means it is 2 + 2; this is J value. So, now, we have to write this one is D; and then, 2s + 1, spin multiplicity is 5; and this is 4. So, this is 4.

This is the term symbol for d^6 electronic configuration. Let us find out term symbols for a couple of more electronic configurations to make you familiar. Or, now use this formula and try to write ground term symbols for all electronic configurations starting from d^0 to d^{10} and also p^1 to p^6, to make yourself familiar so that you will not do any mistake. Let me stop here and continue further discussion in my next lecture. Until then, have an excellent time reading Inorganic Chemistry especially. And thank you for your kind attention.