Coordination Chemistry
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Lecture - 24
Orgel Diagram

Good evening everybody. So, today we will start from the different electronic states which are arising from multi electronic configurations, because we are trying to have these electronic states and we are looking for the corresponding electronic transitions.

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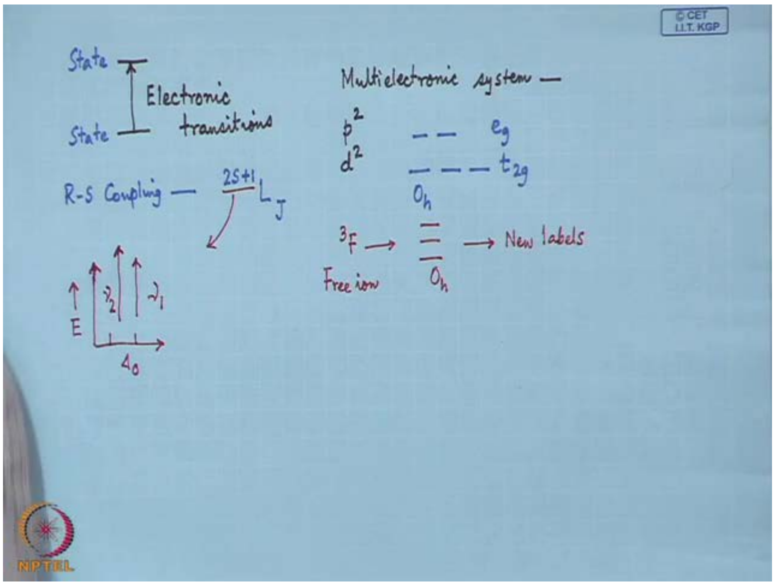

So, to know precisely what are the, those electronic transitions, those are taking place from one particular level to the other; and for multi electronic system, we have seen that let us we have an electronic state, where 2 p electrons are present or 2 d electrons are present. And in crystal field terminology, what we are talking about that in an octahedral crystal field, these two electrons can be present either in the t 2 g level or in the e g level.

So, what we see that during these electronic transitions we can have electrons, both the two electrons in this t 2 g level or these electrons can go up to the e g level. So, if there is any electronic transition which has been taking place, then we can find out the corresponding changes in energy, which is taking place between these two states. So, we have the state number one and the state number two and we will be leveling according to the corresponding Russell Saunders coupling what we have seen. Due to that coupling we can find a particular state which can be defined nicely in terms of its corresponding spin values and the orbital momentum, orbital angular momentum values and the corresponding spin orbit coupling values.

So, these are the three quantities which can nicely explain or which can nicely define a particular state. Since, we are going to apply the corresponding selection rules so looking at this first stage that means the corresponding spin multiplicity and we know that for a particular type of transition involving these metal complexes, we can have certain states where this spin multiplicity or the total spin angular momentum value will not change. So, if we can have some one particular state. Suppose, this state is defined as 3 F and this is the free ion value, the free ion electronic state then we put that in octahedral field and when we are putting this octahedral field this can undergo certain splitting. And we will have new levels for those states and between those states we will be seeing the corresponding electronic transitions.

So, how we can draw this depending upon two things that if we just simply change the corresponding crystal field splitting strength that means the corresponding delta octahedral value with respect to that of our energy. Then how the energy of a corresponding state can change, that clearly tell us that in a particular situation when the crystal field strength is more what we have seen in case of high spin and low spin compounds, that one particular level can have high energy and the other level can have the low energy. And at a particular crystal field strength we can have the transition that means we will be getting the corresponding transitions which will be defined as the nu 1 or nu 2 transitions. So, today we will see that what we can draw the corresponding diagram for those transitions. So, that is known as the corresponding Orgel diagram.

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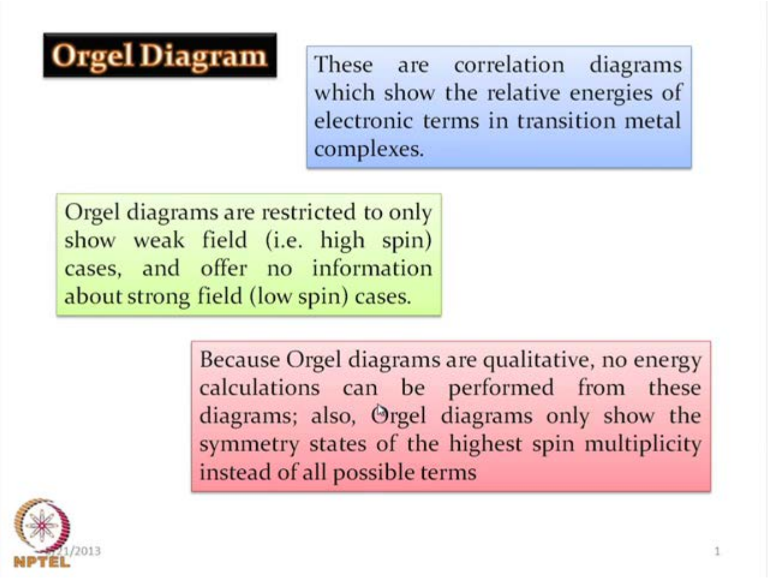

Orgel Diagram

These are correlation diagrams which show the relative energies of electronic terms in transition metal complexes.

Orgel diagrams are restricted to only show weak field (i.e. high spin) cases, and offer no information about strong field (low spin) cases.

Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams; also, Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms

So, is a primitive one is a very basic one compare to that of our other high level diagram which is known as the corresponding Tanabe-Sugano diagram and in this particular case we will be just looking for correlation diagrams. So, these are basically correlation diagrams which can show the relative energies of the electronic terms in transition metal complexes. So, basically we will correlate with respect to the free ion terms. So, we will be having some electronic terms and for a particular electronic configurations say it is d 2 d 3 or d 4. And when we have the corresponding metal complexes of d 2 d 3 and d 4 electronic configurations, these electronic terms will be changing in a particular symmetry of the metal complex. Then we will find that those terms will be responsible for the corresponding electronic transitions that means, involving one particular ground electronic term and the other one, which is the excited one.

So, we basically go for the corresponding correlation diagram for the relative energies of the electronic terms, how the relative energies of these electronic terms will change. And Orgel diagrams are restricted to only so weak field that is mostly we will be talking about the corresponding high spin complexes and offer no information about the strong field cases.

So, it will be basically a very primitive diagram or very primitive correlation diagram involving the corresponding electronic states where we have only the corresponding weak field cases. That means we do not have the strong field cases where we do not know what should be the energy of the corresponding term, when we go for a very strong crystal field. Because these Orgel diagrams are qualitative that is why we are talking this as a very primitive one, no energy calculations can be perform from these diagrams. So, if we want to calculate quantitatively because for energy calculations when we find…

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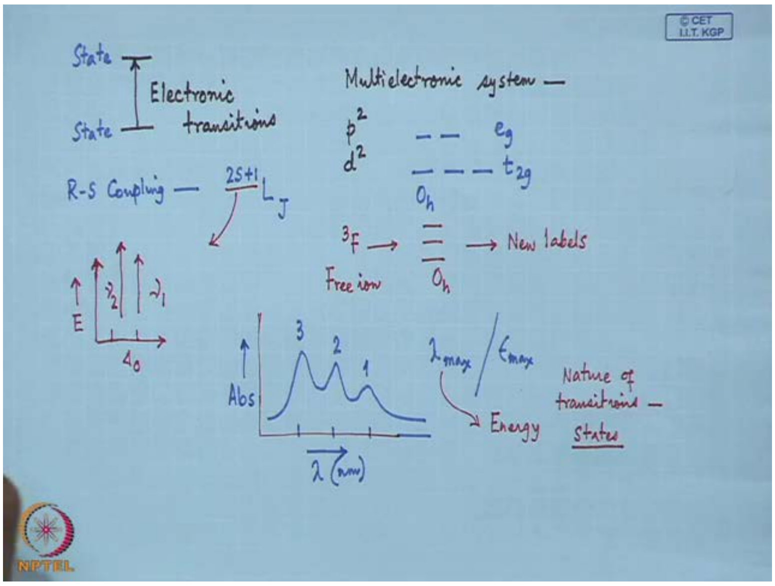

Why we need these energy calculations because when we get the corresponding electronic spectrum and we see that we have the absorption axis and the corresponding lambda axis. So, if we have the corresponding spectrum in this fashion, what we will find we get the corresponding lambda values and these values will be known as the corresponding lambda max values. This can be the corresponding lambda max 1, this can be lambda max 2 and this can be lambda max 3. At the same time, we will have their epsilon max values.

So, these calculation of these lambda max values basically gives us some idea about the corresponding energy packet which is required for a particular electronic transition. Since, Orgel diagrams are not very much quantitative we cannot precisely calculate the corresponding energy values, but only thing that we can predict from the there that what are the corresponding states or the electronic term symbols which are involved for the corresponding metal complexes, those are involved for a particular type of transitions. So, we will be considering the nature of transitions that means the states which are involved for those transitions.

So, we will have the corresponding level for these states for the free ion or in the complexed form and then those states will be responsible for the corresponding transitions. So, we cannot have the corresponding precise calculations of the energies corresponding to these transitions, but they can show only the symmetry states of the highest spin multiplicity instead of all possible terms. Since, we are talking about the high spin cases so we will have the high spin multiplicity. So, the different symmetry states of the higher spin multiplicity system for a particular electronic configurations and how we can go for a corresponding splitting and the transitions. Suppose, we have a simple p 2 electronic configuration; so there are different terms basically.

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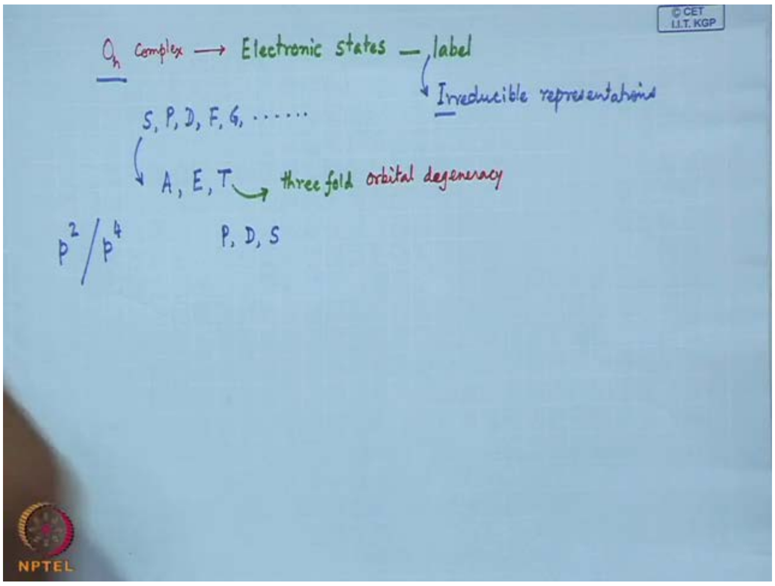

O_h Complex → Electronic states — label

Irreducible representations

S, P, D, F, G, ...

A, E, T → three fold orbital degeneracy

p^2/p^4 P, D, S

So, if we can have say the corresponding octahedral complex and the corresponding electronic states we can have. So, we will have the different electronic states in our hand. And since is the multi electronic configuration we have more number of these electronic states. We have the corresponding level for those electronic states and in group theoretical terminology these levels are nothing but they are corresponding irreducible representation. These are, they are corresponding irreducible representations, those representations which cannot be further reduced; that is why it is irreducible representations in the group theory table, corrected tables we can get that.

So, we have the corresponding S level, P level, D level, F, G etcetera levels. So, these levels basically can split in a particular say octahedral field in A, E and T terms. So, these are the basically the limit where we have this is singlet level, this is doublet level and this is the corresponding triplet level and we cannot have anything which is beyond T that means we cannot have the quartered level. So, we cannot have anything or any state which is higher than the threefold orbital degeneracy. So, this has the threefold orbital degeneracy and that is basically the limit for that orbital degeneracy.

So, what we is find that for a situation where we have the p 2 electronic configuration and which has the corresponding hole equivalent that means the number of holes present in a corresponding close system is equivalent to p 4 also. In these two cases, we can have the corresponding states like P, D and S. So, how we can get all these electronic states from the combination of the corresponding spin angular momentum and the orbital angular momentum that we can see.

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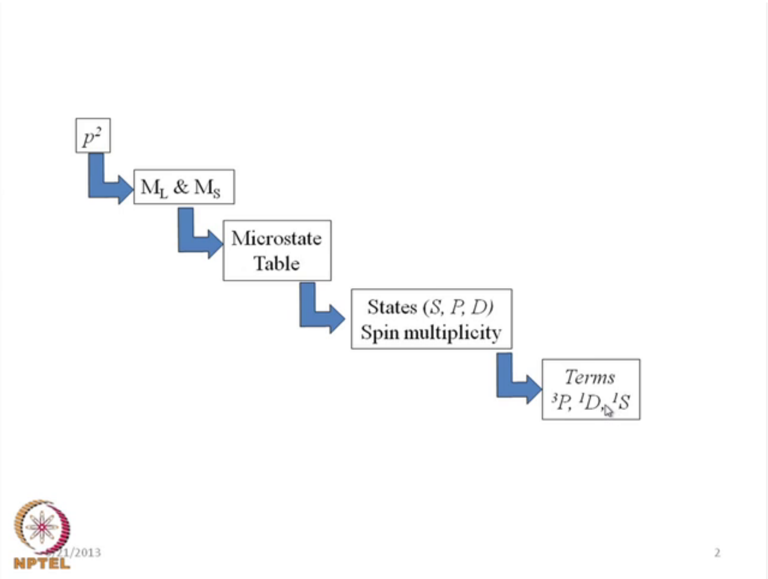

p^2

M_L & M_S

Microstate Table

States (*S*, *P*, *D*)
Spin multiplicity

Terms
^3P, ^1D, ^1S

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Because if we go for more complicated systems like D 8 or D 9 the situation would be much more heavy more number of these states. So, if we have the corresponding p 2 we can have the total M L and the M S values corresponding to the total L value and the corresponding total S values. So, those we can find out and from there we can go for a particular microstate table. And from the microstate table we can have the different combinations of M L and M S values because a particular term will be defined by their individual M L and M S values. Then we can get the corresponding states and states S, P, D having some spin multiplicity. So, these are the corresponding possibility what we can have those are S, P and D level.

So, depending upon the corresponding capital S L values of 0, 1 and 2. So, if it is 0 it will be S, if it is 1 it will be P and if it is 2 it is D. Then we can have the corresponding term so combination will give only the ground state as the corresponding triplet P level, then singlet D level and singlet S level. So, these are the three levels we can have.

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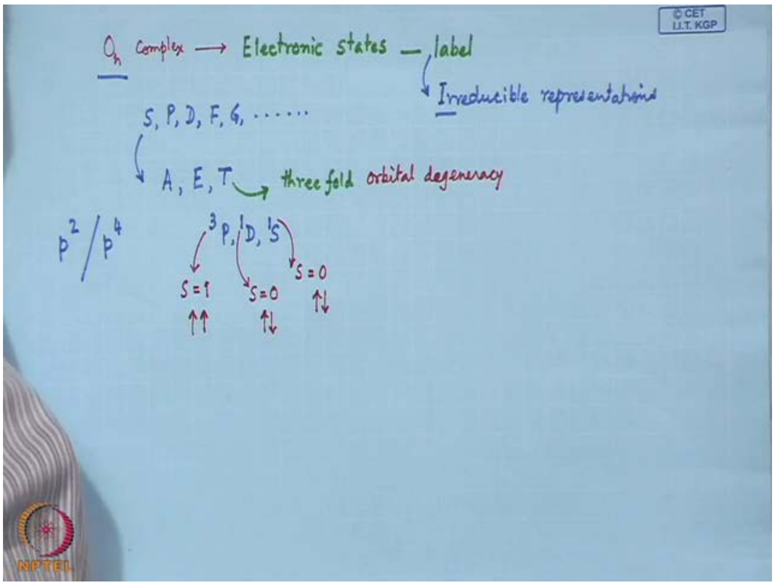

So, once we get this p d and s level we designate at about their corresponding spin multiplicity. This is 1 D and this is 1 S. That means we can have the corresponding capital S value equal to 1, here the capital S value equal to 0 and here also capital S value equal to 0. That means here we can have two unpaired spins, but here we have the paired spins. So, however we see the corresponding electronic transitions we do not expect to corresponding electronic transition from this spin state to the other spin state where spin multiplicity is changing.

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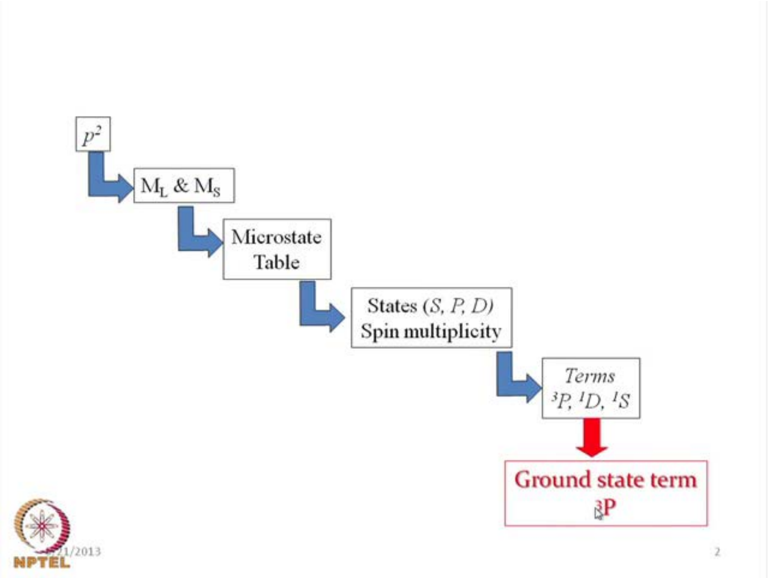

p^2

M_L & M_S

Microstate Table

States (*S, P, D*) Spin multiplicity

Terms ^3P, ^1D, ^1S

Ground state term ^3P

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So, we have this term and from there we just get that the ground state terms should be the corresponding triplet state. So, 3 P will be the its corresponding term, which we can get for a p 2 electronic configuration. Then we will see how this particular 3 P term when we put this in octahedral field what will be its corresponding level for a particular P value. So, P has the corresponding value for this L capital L is 1. So, we can have the corresponding multiplicity value equal to plus 1 0 and minus 1. So, definitely once the state is P we can immediately say it has the corresponding orbital degeneracy is of threefold.

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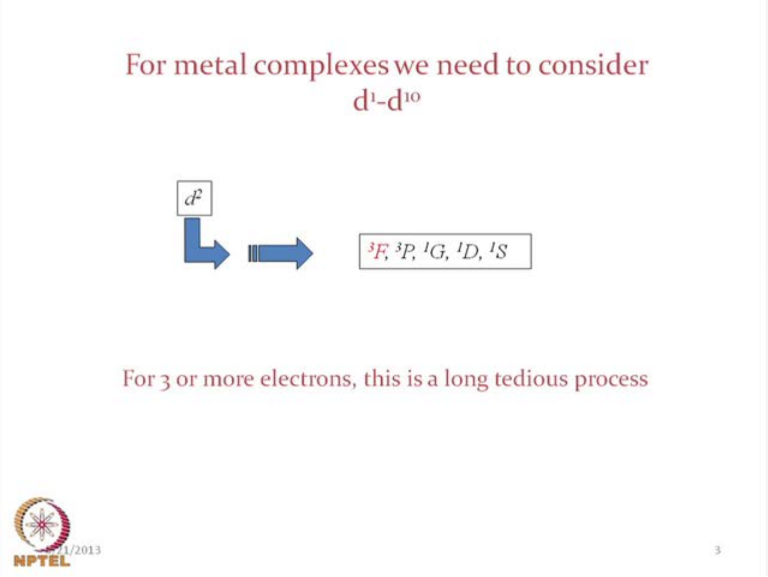

For metal complexes we need to consider d^1-d^{10}

d^2

^3F, ^3P, ^1G, ^1D, ^1S

For 3 or more electrons, this is a long tedious process

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So, for other metal complexes because we should not be happy with only the p 2 electronic configuration at its corresponding term values. We should be happy with other electronic configuration that means at the same time we will be dealing with d 1 to d 10 electronic configuration to get these corresponding term symbols.

So, if we have like p 2, if we have d 2 the d electrons have the corresponding M L values equal to 2. So, we can have the combination of these. So, there we get up to G level also. So, S, P, D and G and F also, we have these all these values we can find it out for a d 2 electronic configuration. So, these triplet states we have two triplet states, one is 3 F and another is 3 P and then 1 G, 1 D and 1 S levels and which is also true for d 8 electronic configuration. So, for 3 or more electrons there is a long tedious process for determining these particular term symbols for the different electronic configurations.

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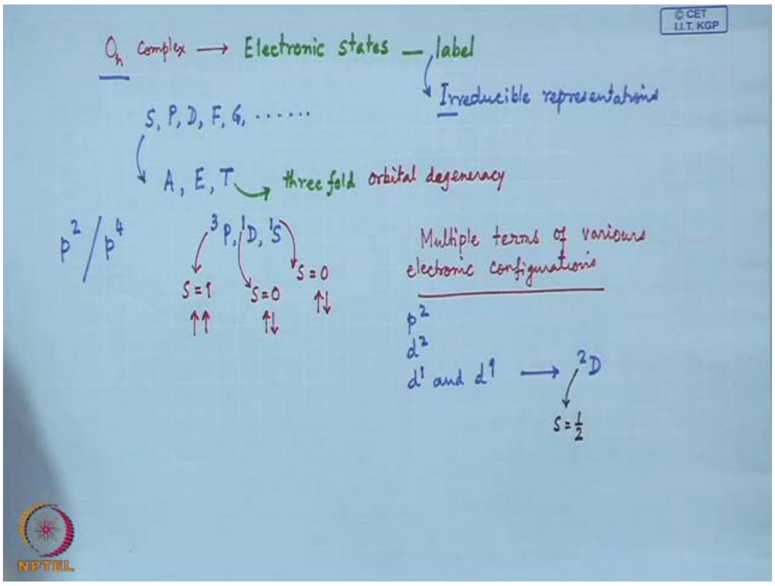

O_h Complex → Electronic states — label → Irreducible representations

S, P, D, F, G, ……

→ A, E, T → three fold orbital degeneracy

p^2/p^4

$^3P, ^1D, ^1S$

$S = 1$ ↑↑ ; $S = 0$ ↑↓ ; $S = 0$ ↑↓

Multiple terms of various electronic configurations

p^2

d^2

d^1 and d^9 → ^2D → $S = \frac{1}{2}$

So, if but if we know the corresponding terms in various electronic configurations. So, what we see there that we have the different terms that means those multiple terms of various electronic configuration. So, we see that we can find it out for p 2, we can find it out for d 2 or we can find it out simply for d 1 and d 9 system. For d 1 and d 9 system we have the corresponding term as 2 D because we have only one unpaired electron. So, one unpaired electron is giving rise to a single half spin. So, the capital S is equal to half. So, how this particular term can split under the corresponding crystal field and what is the corresponding terminology what will change from their and how we get these for the different electronic configurations.

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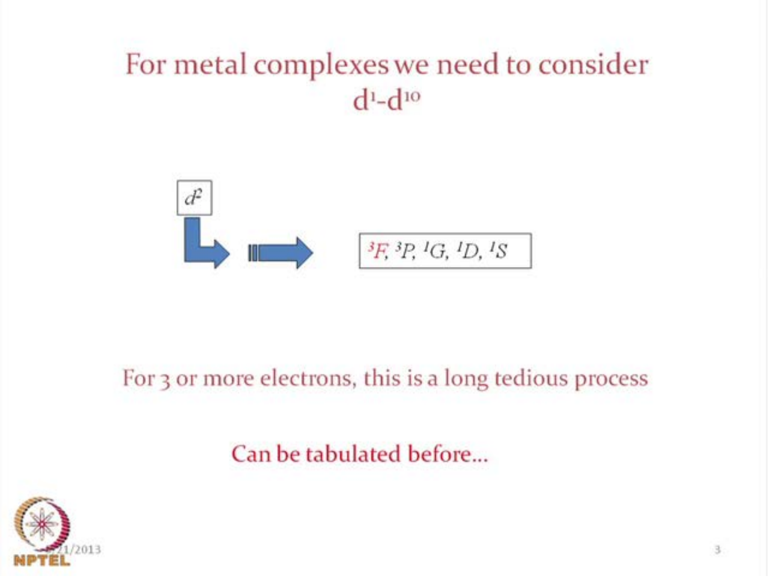

For metal complexes we need to consider d^1-d^{10}

d^2

^3F, ^3P, ^1G, ^1D, ^1S

For 3 or more electrons, this is a long tedious process

Can be tabulated before...

So, from d 1, d 2, d 3 and more we have these, but we can have the corresponding determinations in the tabulated form. What we will be using basically, because we will be interested to know the corresponding terms what we can have a, for a particular electronic configuration and in the tabulated form we have all these values.

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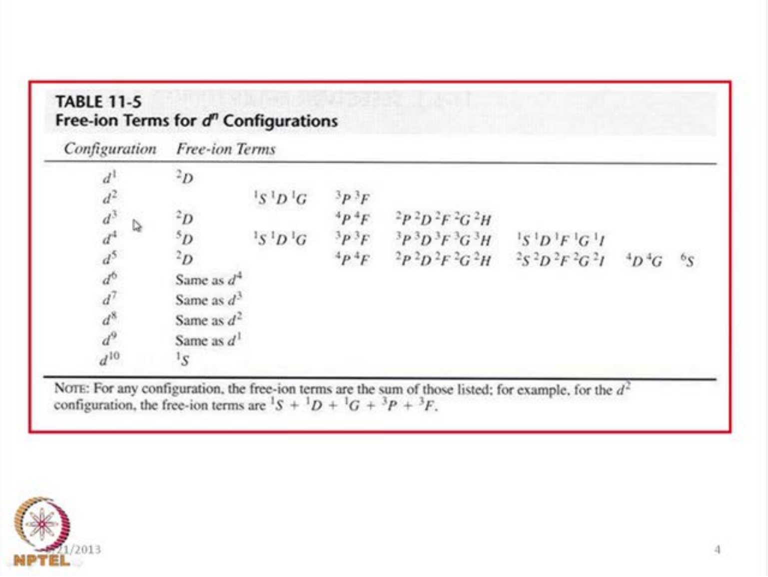

TABLE 11-5
Free-ion Terms for d^n Configurations

Configuration	*Free-ion Terms*						
d^1	^2D						
d^2		$^1S\ ^1D\ ^1G$	$^3P\ ^3F$				
d^3	^2D		$^4P\ ^4F$	$^2P\ ^2D\ ^2F\ ^2G\ ^2H$			
d^4	^5D	$^1S\ ^1D\ ^1G$	$^3P\ ^3F$	$^3P\ ^3D\ ^3F\ ^3G\ ^3H$	$^1S\ ^1D\ ^1F\ ^1G\ ^1I$		
d^5	^2D		$^4P\ ^4F$	$^2P\ ^2D\ ^2F\ ^2G\ ^2H$	$^2S\ ^2D\ ^2F\ ^2G\ ^2I$	$^4D\ ^4G$	^6S
d^6	Same as d^4						
d^7	Same as d^3						
d^8	Same as d^2						
d^9	Same as d^1						
d^{10}	^1S						

NOTE: For any configuration, the free-ion terms are the sum of those listed; for example, for the d^2 configuration, the free-ion terms are $^1S + {}^1D + {}^1G + {}^3P + {}^3F$.

So, this is a full form of these various electronic configurations starting from say we can include also s 2, p 6 and d 10.

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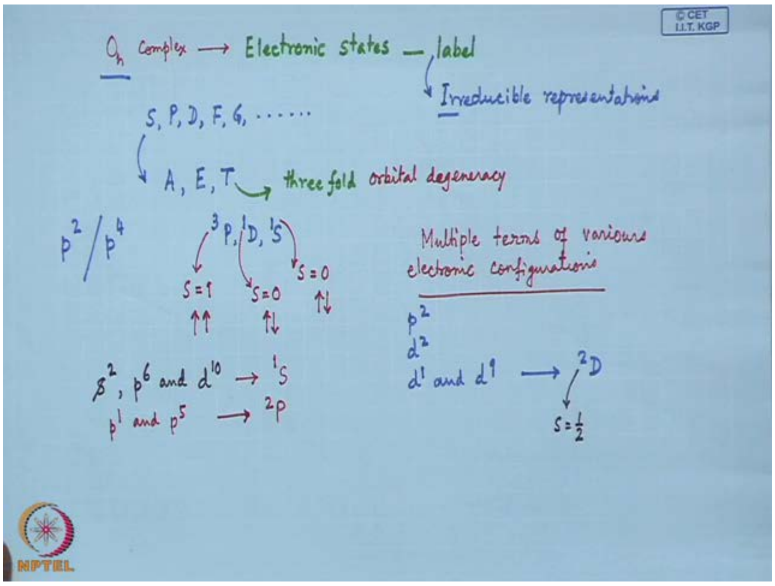

O_h Complex → Electronic states – label → Irreducible representations

S, P, D, F, G, ……

→ A, E, T → three fold orbital degeneracy

p^2/p^4 $\quad {}^3P, {}^1D, {}^1S$

$S = 1 \quad S = 0 \quad S = 0$

↑↑ $\quad$ ↑↓ $\quad$ ↑↓

s^2, p^6 and d^{10} → ${}^1S$

p^1 and p^5 → ${}^2P$

Multiple terms of various electronic configurations

p^2

d^2

d^1 and d^9 → ${}^2D$

$S = \frac{1}{2}$

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Because when we have the corresponding electronic configurations for the field levels such as s 2, p 6 and d 10, when all the orbital sub fields so we have a state where no other combination is permissible. So, we definitely have a singlet state. So, this clearly tells us that this will give rise to a corresponding singlet state and since all are filled so capital S is equal to 0 so is is a 1 S term. Similarly, for p 1 and p 5 we will have a corresponding 2 P term and next we have seen what should be for p 2, what should be for p 3 and for the different d levels. So, what we see for this d 1 the configuration, the electronic configurations and its corresponding free ion terms in different d configurations. What we have seen just now for the d 2 electronic configuration the free ion terms, what we have defined there for d 2 is that 3 F, 3 P, then 1 G, 1 D and 1 S. So, this is the corresponding ground state term.

Similarly, for d 2 we have the 3 F and 3 P, these are the values for d 3 we have 4 F and 4 P and what we see that for d 8 since is the hole equivalent for d 2. So, for the d 2 the corresponding terms where d 2 are also applicable for d 8 which is the corresponding nickel in plus 2 oxidation store. So, whenever we find the corresponding nickel complexes in this electronic configuration we will utilizing the corresponding terms for d 2. So, for nickel complex we will have the corresponding ground term as 3 F.

So, this 3 F term for nickel complex can also be splitted under the corresponding crystal field and the corresponding splitted terms we will just utilize for their corresponding transitions in different levels.

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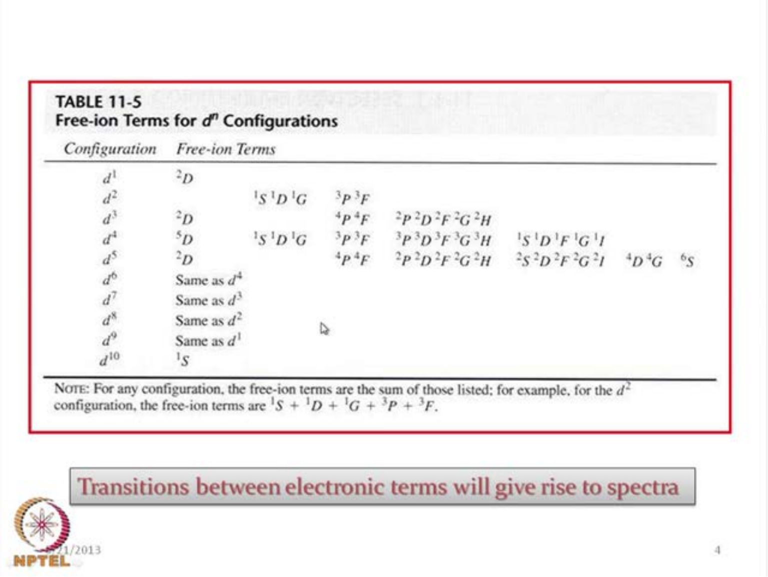

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Free-ion Terms for d^n Configurations

Configuration	*Free-ion Terms*						
d^1	^2D						
d^2		$^1S\,^1D\,^1G$	$^3P\,^3F$				
d^3	^2D		$^4P\,^4F$	$^2P\,^2D\,^2F\,^2G\,^2H$			
d^4	^5D	$^1S\,^1D\,^1G$	$^3P\,^3F$	$^3P\,^3D\,^3F\,^3G\,^3H$	$^1S\,^1D\,^1F\,^1G\,^1I$		
d^5	^2D		$^4P\,^4F$	$^2P\,^2D\,^2F\,^2G\,^2H$	$^2S\,^2D\,^2F\,^2G\,^2I$	$^4D\,^4G$	^6S
d^6	Same as d^4						
d^7	Same as d^3						
d^8	Same as d^2						
d^9	Same as d^1						
d^{10}	^1S						

NOTE: For any configuration, the free-ion terms are the sum of those listed; for example, for the d^2 configuration, the free-ion terms are $^1S + {}^1D + {}^1G + {}^3P + {}^3F$.

Transitions between electronic terms will give rise to spectra

So, these electronic terms will utilized and these electronic terms will give rise to the spectral transitions and the corresponding spectra. So, these atomic electronic states, so, these are the free atomic electronic states. How they can undergo splitting such that we can have the new terms in a particular symmetry. It, if it is an octahedral symmetry so we will get the corresponding term such as the F term or P term or G term within the corresponding O H crystal field such that we can have some important information related to that transitions.

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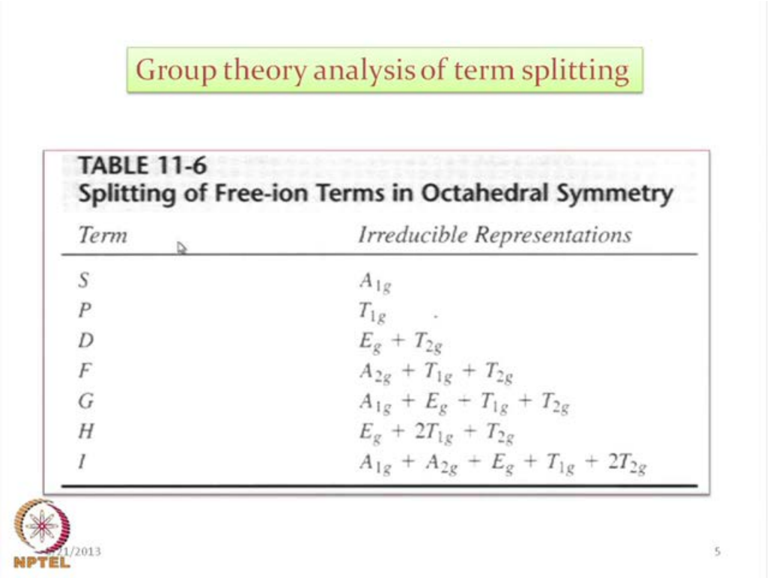

Group theory analysis of term splitting

TABLE 11-6
Splitting of Free-ion Terms in Octahedral Symmetry

Term	Irreducible Representations
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + 2T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + 2T_{2g}$

So, we can have the corresponding group theoretical analysis to term splitting because we get those terms, but we cannot have the corresponding terminology for those terms which can have splitted to say when we have this S, P, D, F and G we will have under the crystal field we have the A term, we have the E term and we have the T term. These are the corresponding splitted terms in the crystal field. So, these are the corresponding terms. So, once we have the term and these particular terms what we can call as the irreducible representations which are nothing but the corresponding terms in octahedral symmetry.

So, if we put octahedral symmetry for this particular these are the terms. So, up to I basically. Say, S P D F G H I. So, these are the maximum limit what we can have while handling d 1 to d 10 electronic configuration. So, if we have the S term and it has only one particular state and that state can be designated within the octahedral field as A 1 g which is also singlet and it has some symmetry requirement for the labeling as 1 or in some cases it will can be labeled as A 2 g. So, with respect to the C 2 axis if it is symmetric we have corresponding level as 1 and if it is symmetric with respect to inversion it will be leveled with g.

Since, the field is corresponding field is octahedral crystal field having one center of symmetry. So, all these states have been leveled as with g, but if we put those terms in tetrahedral field, tetrahedral crystal field these g terms will not be there like that of the splitting of D term into E g and T 2 g, the way we are talking about the splitting of the D orbitals the 5 D orbitals. Similarly, the degeneracy of these D term, the atomic electronic state corresponding to this D term will also be splitted like this that means one doublet and one triplet. So, five states will be divided into a doublet and a triplet.

Similarly, this P term, which is a corresponding triplet one will be termed termed in terms of the corresponding crystal field as T 1 g. So, we will find basically in some cases that if the ground state is F term after splitting the corresponding terms in say the corresponding octahedral field will be A 2 g, T 1 g and T 2 g; and if it has another excited p term, which we are getting in D 2 electronic configuration also, which is also triplet. Triplet F, 3 F is the ground state then the immediate excited state for that particular term is 3 P. So, we will have two T 1 g terms. So, this will be precisely be leveled that this T 1 g term is originating from F term and this T 1 g term is originating from the P term. So, within bracket we will write this as T 1 g p and this will be written as T 1 g simply because this is originating from the F and the F term on the left hand side will also be shown.

Now, we have, if we have G the total number of states will be 2 into 4 plus 1 is equal to 9. So, the 9 states, how we can get those 9 states is equal to a singlet state, a doublet state and two triplet states so, 3 plus 3 plus 2 plus 1 giving all together 9 states. Then we have H, then the number of states is equal to 11. So, we have 3 plus 3 plus 3 9 plus 2 11 and if it is I then the total number of state should be 13 and 13 we are getting like this 2 triplet another triplet. So, 9 plus 2 11 plus 1 plus 1. So, these are the singlet.

So, in all these cases some similarity we can have whatever is the term, corresponding term whether it is S or I we can have only the A term, E term and the T term that this singlet, doublet and the triplet cases. Beyond that we do not have anything which is degenerate beyond a triplet state.

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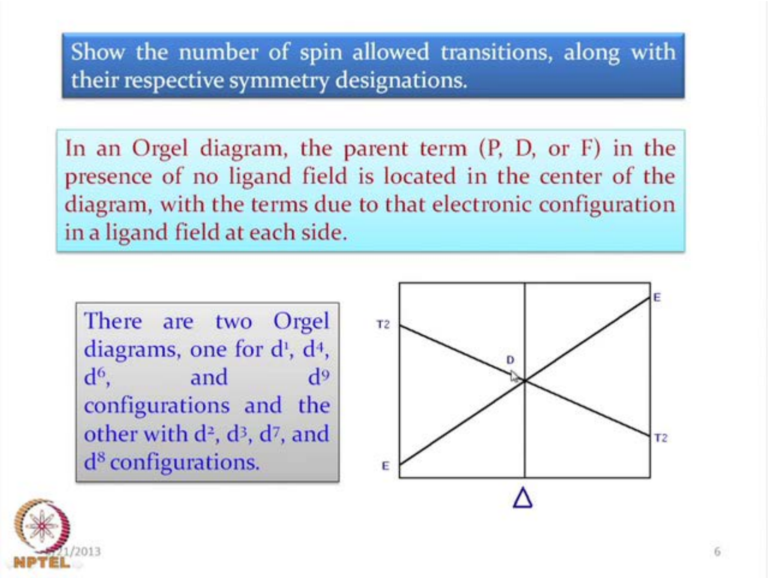

Show the number of spin allowed transitions, along with their respective symmetry designations.

In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side.

There are two Orgel diagrams, one for d^1, d^4, d^6, and d^9 configurations and the other with d^2, d^3, d^7, and d^8 configurations.

So, basically these states show the number of spin allowed transitions because if we consider that only triplet to triplet transition is allowed or singlet to singlet transition is allowed. Then basically the corresponding spin values of those terms can be identified and we can put the corresponding arrow between those two terms for the corresponding electronic transitions and with those allowed transitions we can have the corresponding respective symmetry designations also, whether it is A 1 g or A 2 g because they have two different symmetry levels.

So, the qualitative diagram, the qualitative correlation diagram what we are getting in terms of the corresponding Orgel diagram the free ion terms the P, D and F we are calling these as the corresponding parent terms, because they are originating from the free ions in presence of no ligand field because the free ion we are talking about only the metal ion. That means we are only talking in terms of the nickel 2 plus or cobalt 2 plus or iron 2 plus without the presence of the corresponding ligand field. So, that is why we have the corresponding term as the free ion term.

So, this can be located at the center of the diagram. So, center of the diagram will be putting this particular these terms and with the terms due to that electronic configuration in a ligand field on each side. So, if we are getting a D term for two different types of electronic configuration we will put D. And on the left hand we will have one type of splitting and on the right we can have the another type splitting if it is originating from the D term. So, there are two Orgel diagrams basically we can have, one for d 1, d 4, d 6 and d 9 configurations, d 1 and its hole equivalent d 9 and d 4 and its hole equivalent d 6 because for d 1 and d 9 and d 4 and d 6 we have the corresponding ground terms which are same, those are basically the d term. Similarly, for d 2 and its whole equivalent d 7 and d 3 and d 2 and its hole equivalent d 8 and d 3 and its hole equivalent d 7 are also can be paired up. So, if we have the d 2 d 8 configuration, d 2 d 8 we have the corresponding ground term as 3 F. Similarly, if we have the d 3 d 7 the ground term is again F, but of different spin multiplicity.

So, we will be dealing with only the d term and the F term, only difference for these different electronic configuration is that their different spin multiplicity. So, all together in this diagram in these two diagrams we will be handling 4 plus 4 8 different electronic configurations. So, out of 9 electronic configurations we will be handling 8 together. Only odd man out is the corresponding d 5 electronic configuration which cannot be handled by this diagram because this d 5 situation is little bit complicated and it can have two different situations like that of our high spin configuration and the low spin configuration. So, we will be handling if it is d 1 d 9 and d 4 d 6 electronic configuration with a d term. So, we will have for this qualitative aspects or qualitative picture what we can have.

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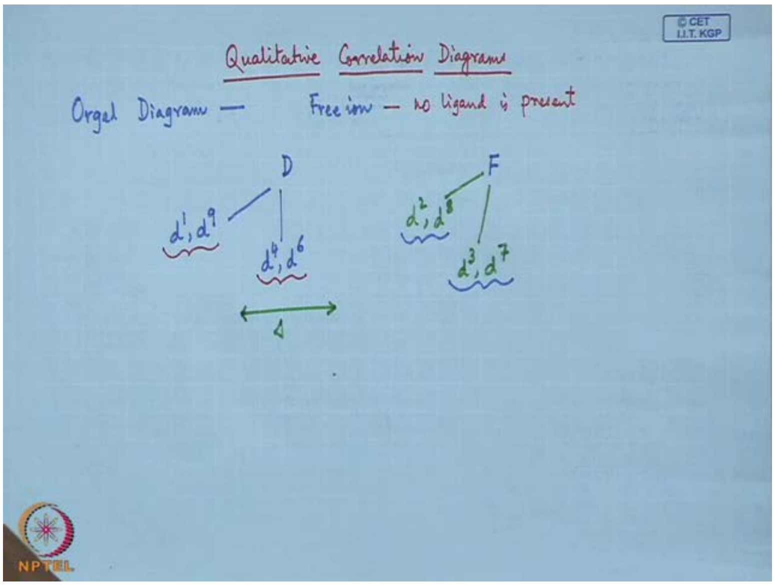

Qualitative Correlation Diagrams

Orgel Diagrams — Free ion — no ligand is present

So, qualitative correlation diagrams we can draw and those diagrams basically we are calling them as Orgel diagram and here we are just looking for a particular term. How we are getting those terms and those are basically the corresponding free ion terms where no ligand is present. So, you do not have any ligand around these middle ions.

So, this particular term is for d 1 and d 9 situation, this d term we are getting and then the corresponding one we will be getting for the other one that means d 4 and d 6. These are their corresponding whole equivalents. So, that means they are also pair wise they are related. If we know about d 1 you will immediately you can say that no the other one will also be d 9. Similarly, these two are the corresponding d 4 and d 6.

Similarly, for F we can have the corresponding d 2, the next one d 1 and then d 2, d 2 and d 8 and for this is d 3 and d 7 the next one. So, here also we have the corresponding generation for the hole equivalents and the F term. So, how these two terms basically can split in terms of its corresponding crystal field. So, if we have the crystal field for these two term, how these two terms can be splitted. So, in one such diagram where we have the F D term, D term for these first four ions and we will be getting this for one is for the d 1 electronic configuration and it is hole equivalent, in another case it would be found the d 4 and d 6 electronic configuration.

So, only thing is and only difference is that the doublet and the triplet, these are the two cases. So, D will be like the D orbitals can be splitted into E and T 2. So, D will be splitted into E and T 2. So, in one case E will be the ground state, in another case T 2 will be the excited state. So, in other case the triplet is the ground state and the doublet is the excited state. So, this is the two different cases. So, that means we have the D term and Orgel diagram tells us that how this D term will be splitted in these two different electronic configurations and this corresponding splitting.

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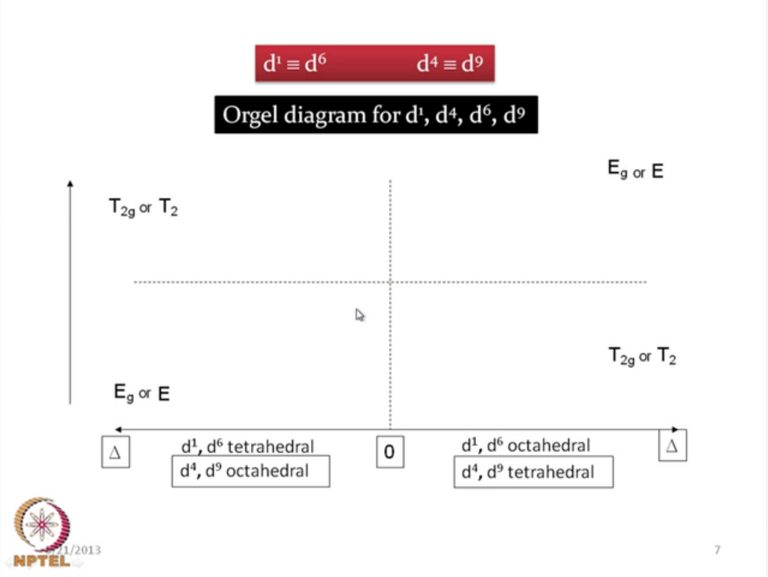

$d^1 \equiv d^6$ $d^4 \equiv d^9$

Orgel diagram for d^1, d^4, d^6, d^9

So, for d 1 and d 9 and d 4 and d 6 we can have. So, they have the corresponding equivalence that means d 1 will be equivalent to d 6 and d 4 will be equivalent to d 9 for in terms of the corresponding splitting. So, we can have these four ions that means d 1 d 9 and d 4 d 6 and we can have the corresponding energy values in this particular axis and this d 4 d 9 they are equivalent. So, d 4 d 9 on the left hand side and d 1 d 6 on the right hand side and again we see that there is a relationship between the splitting of the octahedral field with respect to the tetrahedral field because of the orientation of the different orbitals, what we have seen earlier.

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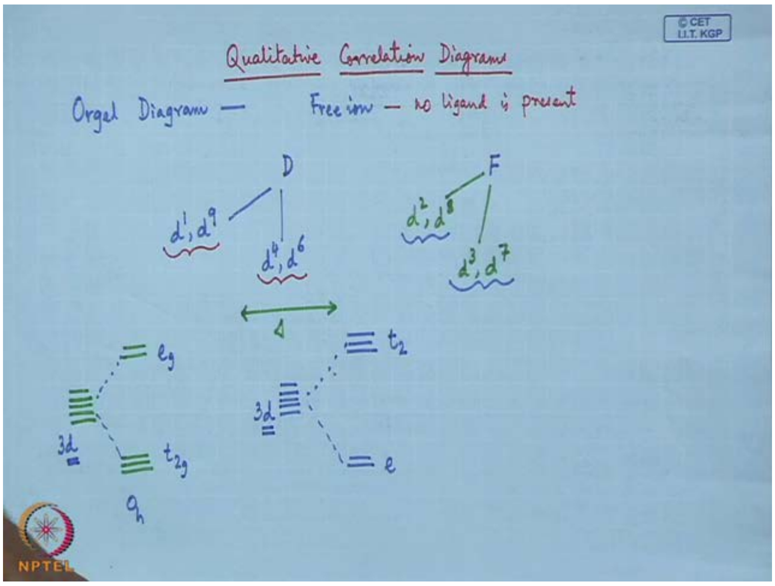

Qualitative Correlation Diagrams

Orgel Diagrams — Free ion — no ligand is present

That in case octahedral splitting if we can have the corresponding five orbitals we have and these are being splitted in a triplet and in a doublet form in an octahedral field. This is the corresponding t 2 g set and this is the e g set because of the relative orientation of the different orbitals belonging to the t 2 g set and other orbitals which are belonging to the e g set. And they are facing differently those orbitals towards that of our ligand field.

So, if we go from an octahedral field to a tetrahedral field we will see that the splitting is opposite. So, we will have the e set as the ground state and the t 2 set as the excited state. So, same thing is happening when we have instead of these are say 3 d levels, these are 3 d levels so these are that d orbitals. Now, instead of d orbitals if we have the d states so they have the similarity. So, if these are the octahedral one then the other one will be in the tetrahedral field of the different electronic configurations on the left and on the right.

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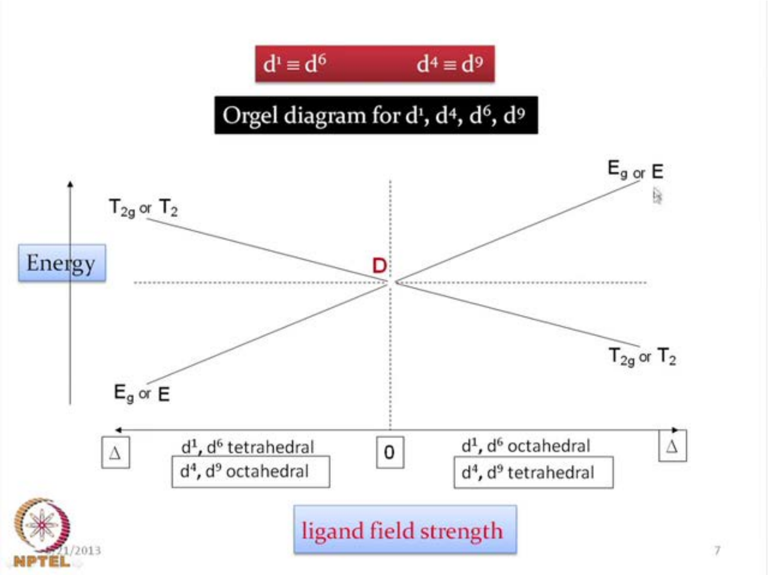

$d^1 \equiv d^6$ $d^4 \equiv d^9$

Orgel diagram for d^1, d^4, d^6, d^9

ligand field strength

So, we will be plotting this energy with respect to the corresponding ligand field strength. So, energy in this axis and ligand field state in the x axis and the corresponding term. The term what we will be utilizing for the splitting this can come as the corresponding term over here and this is our D term. So, D will be splitted for d 4 and d 9 system in the octahedral field as E g as the ground state and T 2 g as the excited state or E as the ground state for d 1 and d 6 tetrahedral or t 2 as the excited state when g subscript is missing for tetrahedral symmetry.

Similarly, on the right hand the D will be splitting in opposite fashion. In opposite fashion what these splitting is for octahedral this d 1 and d 6. So, T 2 g will be the ground state and E g will be the excited state. So, this is for the similar D orbitals what we find that the T 2 g is the ground state and E g is the excited state and without the g subscript we have the corresponding levels for the tetrahedral field.

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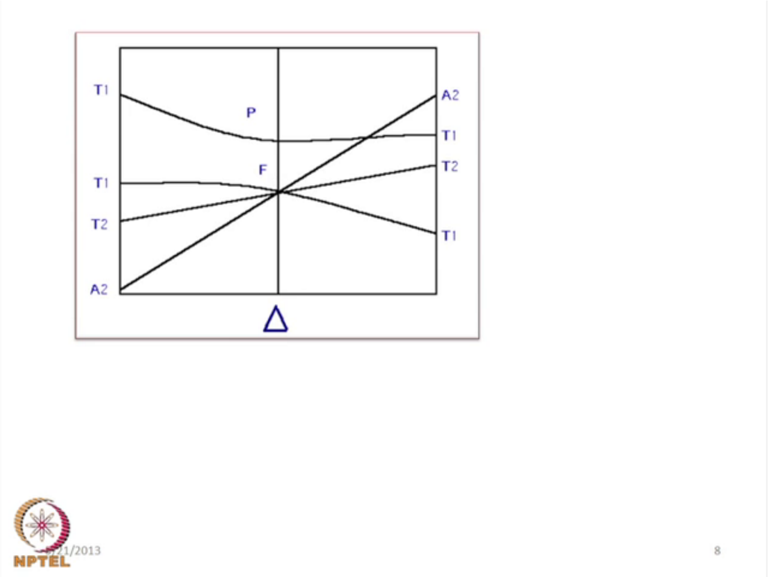

Now, we see that the second one for the F term. So, if we have these F terms which is for the d 2 and d 8 and d 3 and d 7 will be generating the corresponding F term. And F term what we have seen that a particular F term when it is being placed in a crystal field it will be splitted into say if it is placed in an octahedral crystal field.

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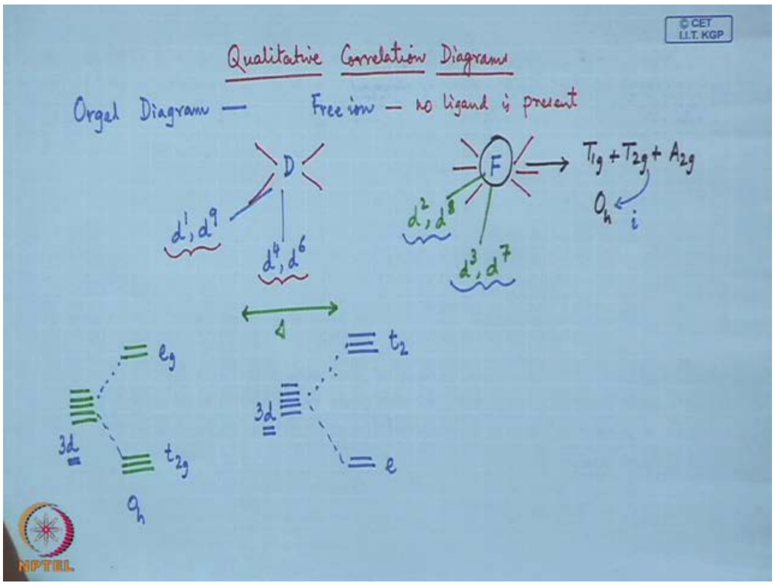

So, it will be splitted into T 1 g plus T 2 g plus A 2 g. And this g subscripts are basically for the octahedral symmetry because i is present and we will drop these g subscripts when we will be talking in terms of the corresponding tetrahedral symmetry. So, whenever we have the F term whether it is in for d 2 or d 8 electronic configuration or d 3 or d 7 electronic configuration they will have the corresponding splitting. So, again like the splitting of these D levels what we have seen on the left and on the right. Similarly, here we will have the splitting on the three levels, on the left and splitting in three levels on the right also.

So, we have this delta value. So, this F term is being splitted for A 2, T 2 and T 1 on the left and the reverse that means T 1, T 2 and A 2 on the right. And at the same time whenever we have a F term another P term is also there, which is the excited state. The first excited state in case of this corresponding d 2 and d 8 electronic configurations what we have seen, that c F term is the corresponding ground state term and its first or immediate excited state is the corresponding 3 P term.

Similarly, for d 3 and d 7 electronic configuration the 4 F term is the ground state term and 4 P is the first excited state immediately after this particular term. So, with respect to these delta values the P term will also change its energy like this with respect to this corresponding transformations from T 1 on the left and T 1 on the right. Only difference is that here it is not crossing any of the terms that means these two particular term, these two T 1 terms are basically repelling each other. These two are also repelling each other. So, they do not have such crossing, but this T 1 term can cross this A 2 term. So, what is happening this at particular, this particular lambda delta value that mean this particular crystal field value is there for crucial and above, which we have a corresponding cross over because before this particular crystal field we have the A 2 is the ground state and T 1 P is the excited state, but after this in the, when the delta value is high we have the T 1 P is the ground state and A 2 is the excited state.

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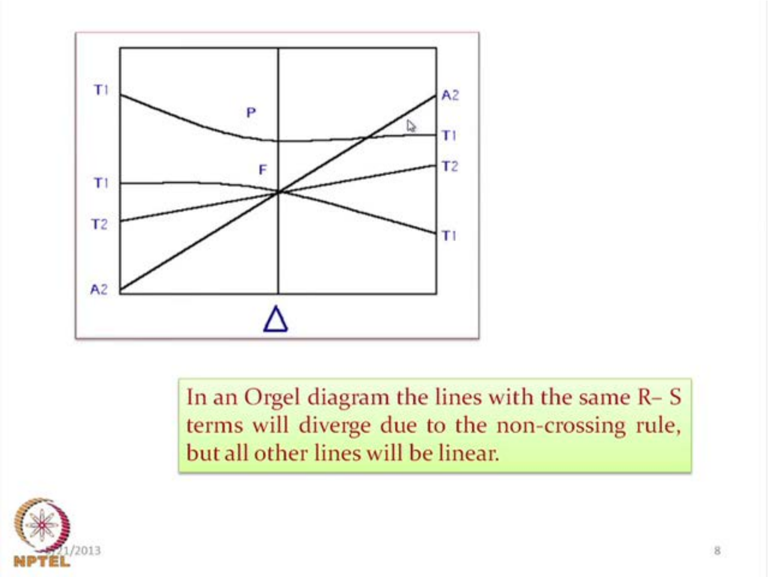

In an Orgel diagram the lines with the same R- S terms will diverge due to the non-crossing rule, but all other lines will be linear.

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So, what we find in this diagram is that in an Orgel diagram the lines with same R S term will diverge due to the non crossing rule. Since, they are not able to cross in some position so we have the non crossing rule, but all other lines will be basically linear. So, these two basically are deviating from the linearity because we have the T 1 term. So, the lines for T 1, one is originating from the P term and another is originating from the F term. So, they basically diverge due to non crossing rule because they will not cross so they will repel each other and they will just have the divergence. But the other lines in Orgel diagram what we will find that other line that means the line for T 2 and the line for A 2 these two are linear. So, we will have the linear line as well as the bend line in this particular diagram.

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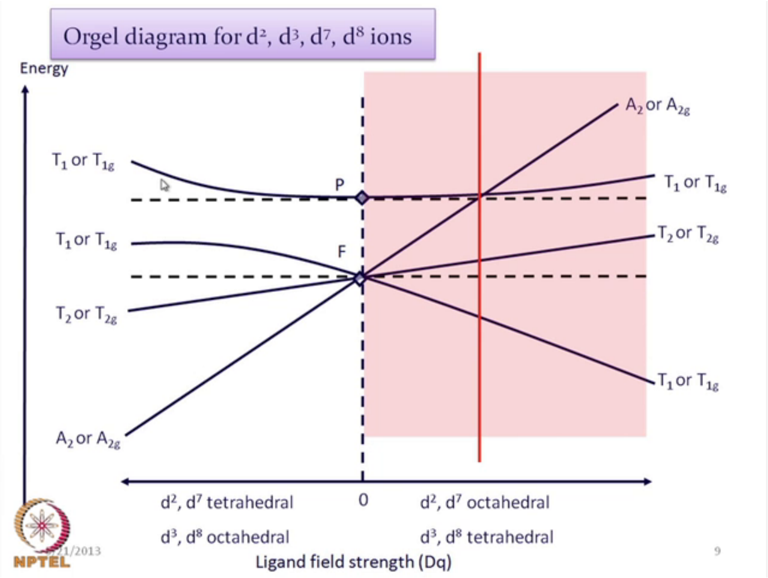
Orgel diagram for d^2, d^3, d^7, d^8 ions

So, we get this particular situation for this situation, for all four that means d 2, d 3, d 7 and d 8 where we have this F term, what we have seen just now. And since this is not crossing and the red line is the corresponding critical line, which will designate as the weak field case and the strong field case. So, in all octahedral situation, these will be leveled as g and in tetrahedral situation, they are all simply leveled as A 2 T 2 etcetera. Similarly, on the right hand side, we have the g leveling and the non g leveling; and these two things that means, what we can have for the P and F term. If these are the two horizontal line we can draw, so that this is deviating from the horizontal line, it is coming down and reaching P, and then again it is deviating. Similarly, when F is splitting for this T 1 so it is going up, but it is deviating this particular value, and this T is basically simply deviating from this horizontal line.

So, these are basically the levels depending upon the corresponding electronic configuration. So, if we have a d 3 and d 8 electronic configuration for the different situation where we have the F term, we can simple say that we can have the transitions from A 2 g to T 2 g, A 2 g to T 1 g and A 2 g to T 1 g P. So, these are the three basic transitions what we will see that in electronic spectrum we will find one, two and three transitions involving these diagrams which we can predict from simple Orgel diagram.

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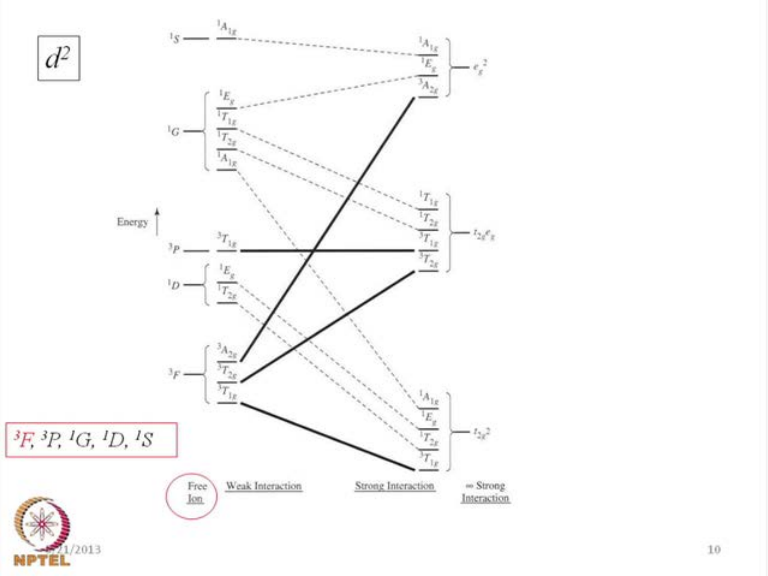

So, for a case of d 2 what we will find that in case of this d 2 electronic configuration what we have seen that we can have five different states and five different terms due to the corresponding Russell Saunders coupling, we can have two triplet states and three singlet states. And among these two triplet states which are 3 F and 3 P, we have the 3 F as the ground state and the immediate excited state is 3 P and all other. Then what we can go for this corresponding correlation diagram because we are slowly approaching from this diagram for Tanabe Sugano through the Orgel to the Tanabe Sugano diagram.

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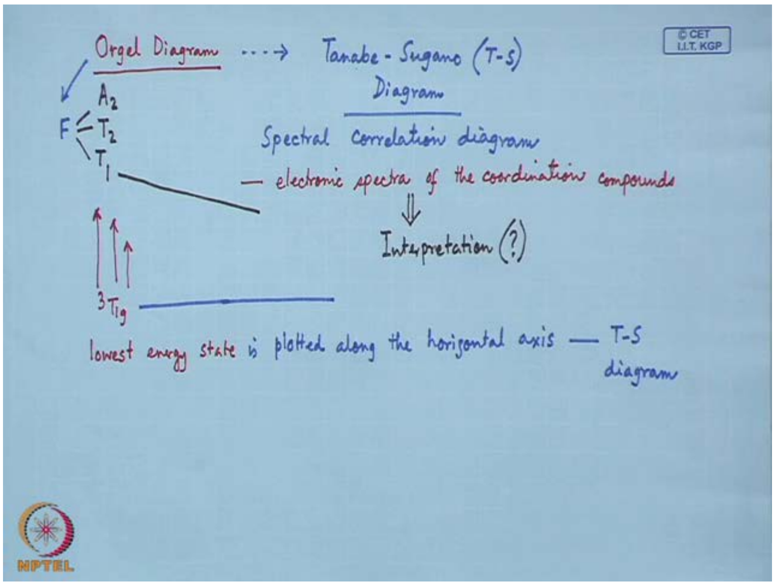
Orgel Diagram ---> Tanabe - Sugano (T-S) Diagram

Spectral correlation diagram

— electronic spectra of the coordination compounds

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Interpretation (?)

lowest energy state is plotted along the horizontal axis — T-S diagram

So, we were talking in terms of the corresponding Orgel one. So, next we will just proceeding towards the goal where we will find that how Orgel diagram can give us some information's about to draw for some other correlation diagram which is Tanabe Sugano diagram or T S diagram.

So, Tanabe Sugano diagram… So, this diagram basically will tell us that this is also a spectral correlation diagram spectral correlation diagram and this particular one is very much useful in the interpretation of the electronic spectra. So, we are still with the interpretation of the different electronic spectra of the coordination compounds of the coordination compounds. So, this electronic spectra of the coordination compounds when we are having so how we can interpret? So, interpretation is very much important. How we can go to their interpretation basically and that gives us some important. So, apart from this diagram what we have found in case of the Orgel diagram. So, we have seen that a particular state whether it is D or F in this diagram, in this Orgel diagram and when this particular state is getting splitted we have the corresponding term that means if the F is giving rise to three terms which is A, T and T. One is T 2 another is T 1 and another is A 2. So, these are the three terms we are having and if we see that the energy how the energy of this particular T 1 term will change with respect to the strength of increasing crystal field.

So, as we change these we just basically see that it is going down to down as we go towards and some infinitely strong crystal field strength. So, this is not basically going towards their corresponding thing that is is go down and down, but in this particular diagram which is different from this Orgel diagram in the basis of that identification that this particular one the lowest energy state which is very important. That means whether our lowest energy state is 3 T 1 g, if this is the lowest energy state then we will have the transitions from this state. This state we will be talking about the different transitions.

So, depending upon its corresponding value for this transition we try to have this as a typical horizontal line instead of this slope line. Line with some slope can be converted to some horizontal line. So, this lowest energy state is basically plotted along the horizontal axis that gives us our T S diagram.

So, how we get these correlations that we can find out from this diagram simply. So, for d 2 electronic configurations we have found out that we have 3 F, 3 P, 1 D, 1 G and one is electronic states. And interestingly in terms of the energy values of these free ion terms this 3 P term though it is a triplet state it has the higher energy compare to its 1 D term.

So, F is the ground state then D, then P, then G and S. And we all know that F can undergo splitting in terms of its irreducible representation in o h crystal field or o h symmetry, the group theoretical symbol or the notation we can get the corresponding irreducible representations of this particular 3 A values in terms of the 3 A 2 g, 3 T 2 g and 3 T 1 g. Similarly, these are the corresponding free ion terms and due to this weak interactions we can have very weak splitting or the terms what we get from here to there and since this is F term and we all know that F can be splitted in terms of the two triplet and one singlet that means, the total number of term value is equal to 7. Similarly, D into two terms E and T one triplet and one doublet and one doublet, P will remain as again a triplet term, G can be splitted in these values and S can remain as the corresponding 1 A 1 g term.

So, how we correlate this particular thing is that in strong interaction case what we can have in the strong interaction state, we have the corresponding values as the corresponding electronic configurations. What we can have in our hand as the t 2 g, the t 2 g e g and the corresponding e g 2 electronic configurations. So, what we have that if we have the 3 F term which is true for say vanadium 3 plus which is a D 2 electronic configuration.

So, this sevenfold orbital degeneracy which will not be present in this particular form and that cannot persist in the octahedral crystal field. So, it will split into three new electronic states. So, these are the three new electronic states we can generate from the free ion 3 F term. And therefore, after the splitting we have the corresponding states where the 3 T 1 g has three folds orbital degeneracy as well as threefold spin degeneracy. Similarly, this also will have the same and this has one fold orbital degeneracy, but having threefold spin degeneracy; so altogether if we consider this 3 F term.

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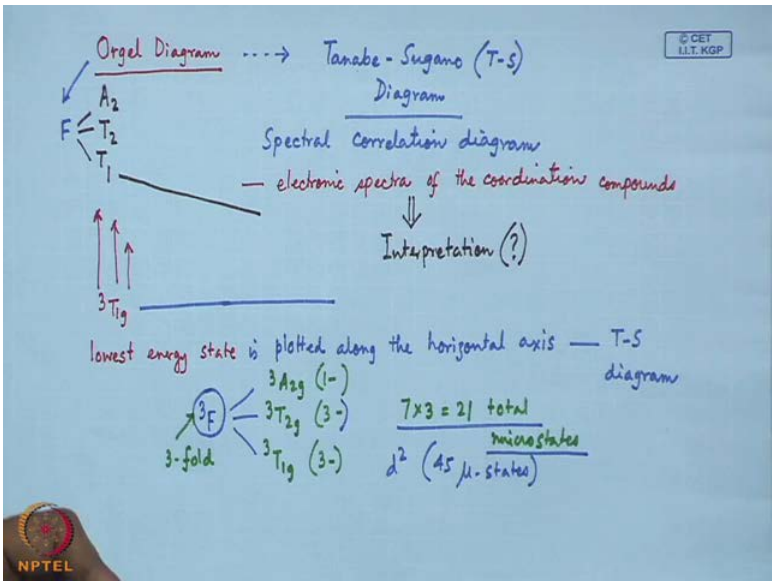

Orgel Diagram ---→ Tanabe - Sugano (T-S) Diagram

$F \begin{cases} A_2 \\ T_2 \\ T_1 \end{cases}$

Spectral correlation diagram

— electronic spectra of the coordination compounds

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Interpretation (?)

$^3T_{1g}$

lowest energy state is plotted along the horizontal axis — T-S diagram

^3F: $^3A_{2g}$ (1-), $^3T_{2g}$ (3-), $^3T_{1g}$ (3-)

3-fold

$7 \times 3 = 21$ total microstates

d^2 (45 μ-states)

We have this 3 F, which is splitting into three; and this splitting gives us 3 T 1 g, 3 T 2 g and 3 A 2 g terms. So, the spin is threefold, but the orbital here is threefold, this is threefold and this is one fold. So, all together we have 3, 3, 1 7 into 3, so 7 into 3 is equal to 21 total micro states we can get out of this particular term. So, in d 2 electronic configurations, we have all together 45 micro states.

So, only this particular term the 3 F term can account for this 21 micro states and we will be considering these micro states nicely for these transitions in this Tanabe Sugano diagram where we see that the triplet degenerate levels are most important for these transitions. So, next day we will still continue with these diagrams for these actual transitions with those electronic spectra.

Thank you very much.