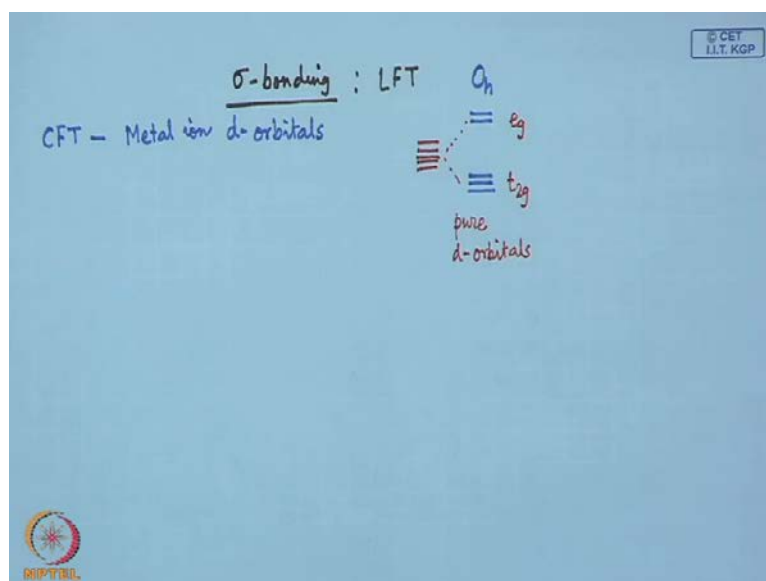


**Coordination Chemistry**  
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**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Lecture - 33**  
**Sigma Orbitals**

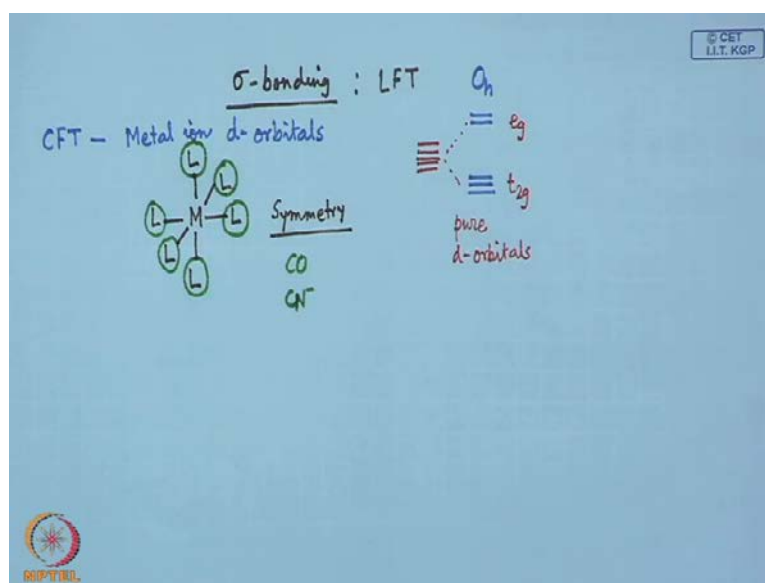
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Good evening everybody. So, today will start with the sigma bonding. In case of the corresponding theory what we have started to discuss with the ligand field theory. So, the basic proposition what we have seen earlier in case of crystal field theory were we have chosen the corresponding splitting and the interaction of the metal ion d orbitals metal iron d orbitals we had and these metal iron d orbitals are within the crystal field of the different ligands. If they are in octahedral field will find that we can have the corresponding splitting of these orbitals were we have the 5 orbitals in the p splitted condition to two sets one is e g and another is t 2 g.

But these were our pure d-orbitals of the different metal irons which are engaged in bonding with that of our legend systems.

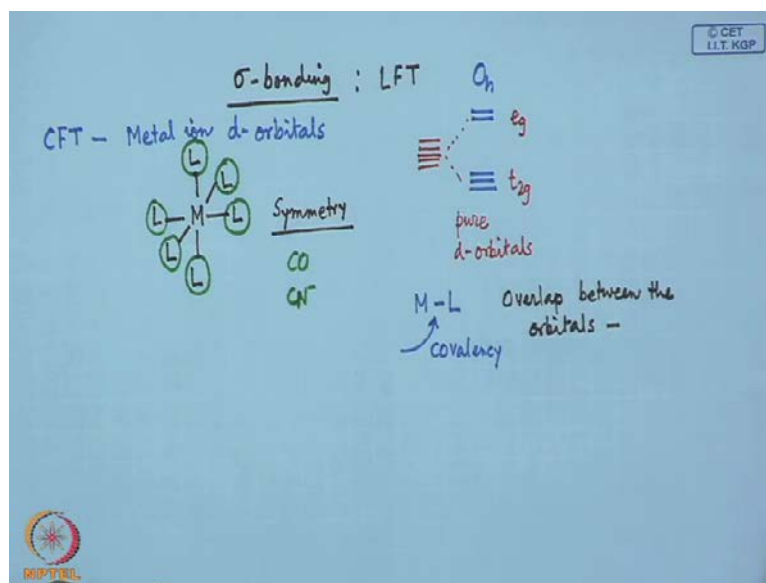
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So, if we have one central metal iron which is interacting with the 6 ligands in octahedral geometry. So, we have a spherically geometry. So, symmetry or the symmetrical arrangement of the different ligands are coming into the picture and how they are surrounding the corresponding metal iron that in the symmetry of the placement of the ligand system can so the what type of splitting.

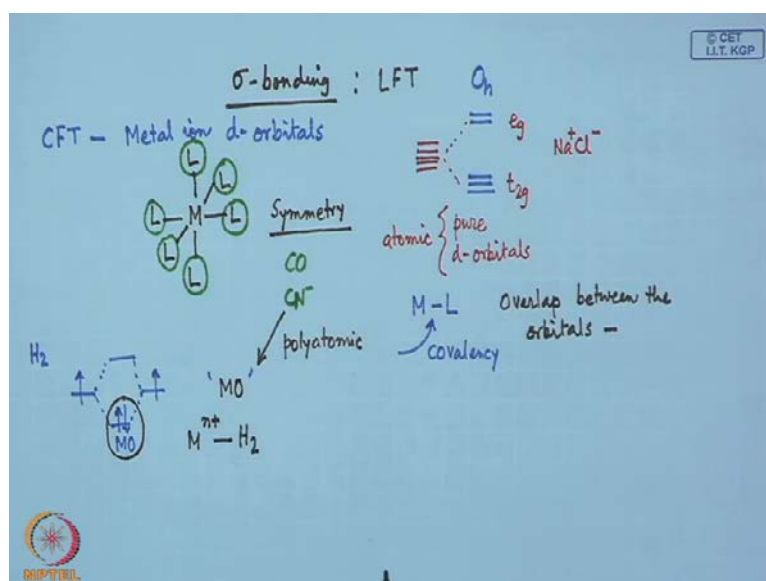
We can have weather we have a typical octahedral geometry or the tetrahedral geometry or square panel or square pyramidal geometry that basically we are getting from the information that what type of crystal field we are imposing due to the presence of these many ligand systems. But, this is not everything because this cannot explain nicely the corresponding position of the ligands in the spectrochemical series such as carbon monoxide or c n minus so to know the corresponding position of these ligands in the spectrochemical series.

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We have to consider something that we must have some interaction between metal and ligand. So, we should not talk about anything were the pure metal ions are informed only for these sort of arrangement and the placement of the different number of unpaired electrons which were present in the  $t_{2g}$  level and the  $e_g$  level only. But, the symmetry level remains the same because we are having the same crystal field in octahedral geometry. So, if we have some covalency between the interaction of the metal ion and the ligand. So, we should have some good overlap between the orbitals, that means the orbitals of the metal ion and orbitals of the ligand.

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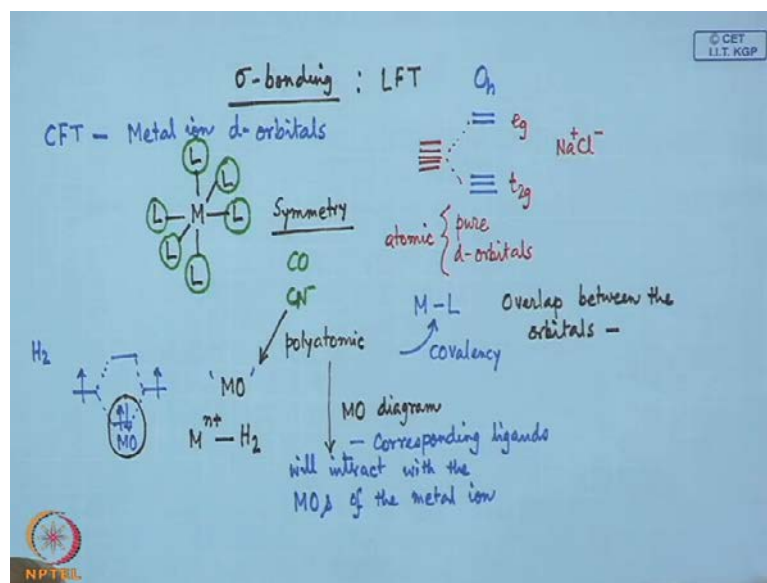


As a result what happens when we consider something, that means we are not talking in terms of the corresponding atomic orbital because these d-orbitals splitting for these systems in terms of the crystal field theory is that, we are having this pure d-orbitals means these are the corresponding atomic orbitals. So, if we just simply consider, instead of having so many atomic orbitals which are only undergoing splitting and due to that splitting which is very much similar to the splitting of different energy levels, we see in case of sodium chloride crystal lattice.

If we consider that the molecular orbitals are coming slowly into the picture so the individual molecular orbitals if we are talking with some ligand which is polyatomic in nature. So, if they are polyatomic that means individual atomic orbitals are losing their character and for a polyatomic system, we should also have a molecular orbital arrangement that we all know from the simple arrangement of the hydrogen molecule. So, for the hydrogen molecular what we can have that we know that for hydrogen molecule also. we can have the molecular orbitals like this one is the bonding molecular orbital and another is the anti bonding molecular orbital.

So, the molecular orbital picture for the hydrogen molecule also tells us that these two electrons for the hydrogen molecule it is present in a level where we have a bonding molecular orbital.

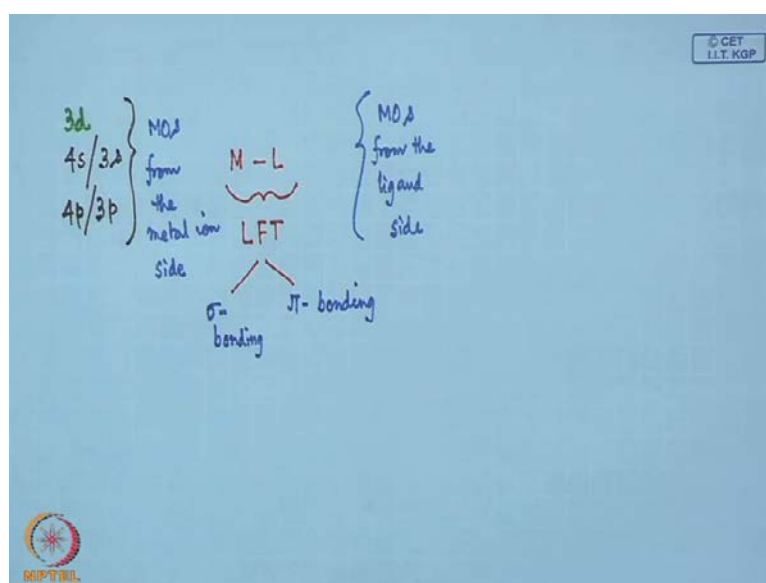
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So, if this bonding molecular orbital can be utilized now for some interaction with the metal iron say if  $M^{n+}$  is interacting with the  $H_2$  molecule then what we should consider we should the corresponding molecular orbital of the hydrogen molecule and then some combination or the some corresponding molecular orbitals on the metal iron.

So, these poly atomic systems like carbon monoxide as well as  $CN^-$ . We have the typical molecular orbital picture or molecular orbital diagram this molecular diagrams we must have for the corresponding ligands. First we must have the corresponding molecular orbital diagram from the ligands and instead of showing some interaction that means these molecular orbitals from the ligand side can show some interaction with the corresponding molecular orbitals from the metal side. So, they will interact will interact with the molecular orbitals of the metal iron. So, metal irons should also provide some molecular orbital instead of the typical atomic orbitals like the p or d-orbitals.

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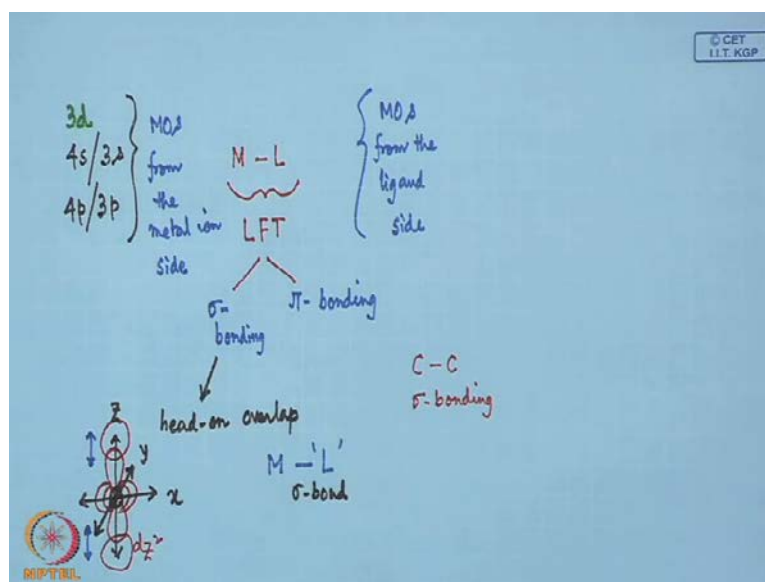
So, we should know the corresponding molecular orbitals from the metal side at the same time. So what happens there, therefore, that while talking about the crystal field theory we have the 3 d orbitals. Now along with these 3 d orbitals we should have the other orbitals that mean the 4 s orbital or in some case we can have also the 3 s orbital or 3 p orbital or 4 p orbital. So, the depending upon the energy of these orbitals and there's availability for the system. So, these orbitals can give us the corresponding molecular orbitals from the metal side from the metal iron side. So, these can have some level for

these at the same time we should have the corresponding molecular orbitals from the ligand side.

Now, these two basically when they interact we should consider this interaction between the metal and the ligand in terms of the corresponding field which will consider is coming from the ligand only instead of crystal like lattice. We should have now the ligand field and the treatment for these ligand field parts for the metal ligand interaction or some amount of covalency which can be utilized for describing the spectroscopic parameters the magnetic movement and all other thing will be treated in terms of the corresponding ligand field theory. So, when we consider these ligand field theory and when we are talking about the corresponding molecular orbitals so will find that the two different types of interactions.

We can have, when we talk in terms of the simple molecular orbitals for the covalent molecules like carbon monoxide or any other thing that we can have the head on overlap for sigma bonding and side on overlap for phi bonding. So, will have both sigma bonding and pi bonding for this.

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So, the entire spectrochemical series, what we can have we can now explain part by part the presence of these ligands within that particular big spectrochemical series that what are the ligands which can. So, good sigma bonding affinity towards the metal centre and

what are the other ligands which can show some pi bonding affinity which is dominating also to the metal centre.

So when we consider the sigma bonding parameter we must have some head on overlap. So, we should have the corresponding metal ligand overlap which can be considered as a head on overlap that means we have the corresponding axis what we considering as the x y and z axis. So, if it is said this x and this is y and the metal is sitting over at the centre of these cartesian axis. Now, we can have the corresponding ligands. So, if we have some ligand which we earlier we have seen in case of the corresponding crystal field theory that we have the corresponding d z square orbital. And if this d z square orbital can interact in an head on fashion such that the formation of the C-C sigma bond which we know that how C-C sigma bonding can take place due to the head on overlap from the corresponding hybridized orbitals from the first carbon atom to the corresponding hybridised orbital of the second carbon centre.

So, if we have now just simply we can place the corresponding orbitals the molecular orbital available from the ligand side. So, if this head on overlap is perishable or can take place we can have sudden amount of head on overlap and the amount of overlap that means the magnitude of overlap that we quantum mechanically we can chit them as the overlap integral can also tell us about the interaction that what type of interaction we are having from the ligand which is showing a direct sigma overlap with the metal orbital of d z square symmetry. So, how this one is interacting with the metal iron and what are the orbitals basically we are talking when in terms of the corresponding sigma bond that means we can have when we have the two carbon centres. We all know that that corresponding overlap because they are of same type.

So, there is no question of having one particular atom serving as a donor atom and another atom serving as an excepted atom and this particular situation they are basically sharing these orbital and electrons are occupying those particular bonding orbitals to give us the corresponding bond between these two carbon centres as a sigma bond. But, in this particular situation when the sigma bonding interaction will take place will find that weather this overlap is taking place between the corresponding donation from the ligand to the metal centre or at some time will find that the ligand can also function as an acceptor or by acceptor species which is excepting the corresponding electron density

from the metal side. So, both these two things can happen and for that particular purpose we should know the corresponding energy level for these sigma bonding interactions.

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## LFT: $\sigma$ -Bonding



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So, what we find that if we have the corresponding theory for the ligand field what we are getting corresponding to the typical sigma bonding interactions between that corresponding metals orbitals and the ligand orbitals which are in a particular cartesian axis. And head on overlap is taking place between the metal orbital and the ligand orbital and that also depends on the number of electrons available on the bonding orbitals, which is available from the metal side and which is available from the ligand side.



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## LFT: $\sigma$ -Bonding

$\Gamma_{\text{red}}$  reduces to  $A_{1g} + E_g + T_{1u}$



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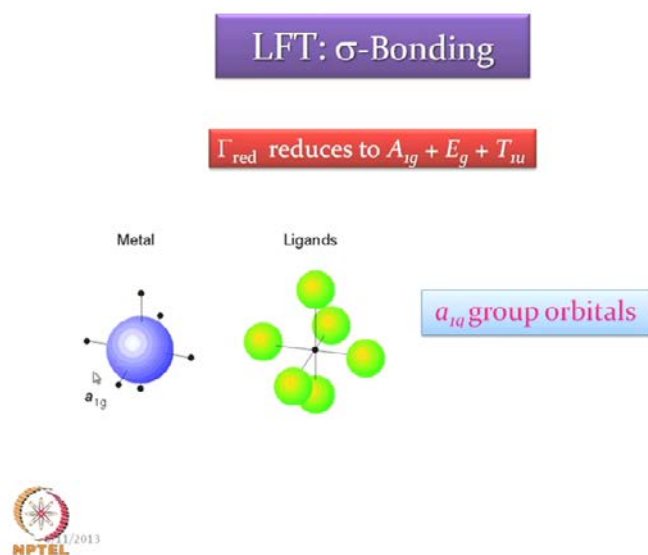
So, in our previous class what we have seen that from group theoretical notation, if we have the corresponding correctable for the octahedral symmetry we can get from all like all other spectroscopic treatments we have the corresponding gamma ready read thing that means the corresponding reducible representation for the sigma bonding. And this reducible representation can be reduced to three symmetry terms which is  $A_{1g}$ ,  $E_g$  and  $T_{1u}$  terms in an octahedral symmetry.

So, the point group which is  $O_h$  can immediately tells us that we have the corresponding molecular orbitals available from the metal side as well as from the ligand side are of these symmetry levels. So, when we have consider in case of only crystal field theory we have seen that the pure d-orbitals which are not the corresponding molecular orbital because, that was not a molecular orbital treatment. We have the two levels from the metal side as the pure d-orbitals which are informed. We have the  $e_g$  set and the  $t_{2g}$  set. Likewise, if you see that when you consider for the ligand field theory for sigma bonding we are not getting any term from the correctable as in it is irreducible representation of the point group of  $t_{2g}$  symmetry.

So, that means that  $t_{2g}$  level for the orbitals what we now know very well that these are the corresponding orbitals which are of symmetry were the orbitals are pointing towards the intermediate cartesian axis that means  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ . Those symmetry levels are not coming for the reducible representation for sigma bonding that means those

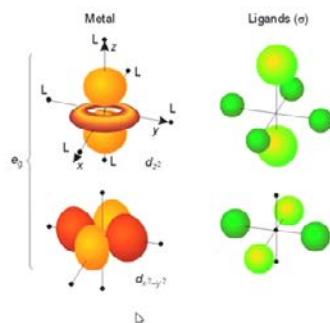
orbitals will not participate in sigma bonding in ligand field theory. So, only the e g orbital that means the d z square and d x square minus y square orbitals will be available for some amount of sigma bonding with the ligand symmetric orbitals.

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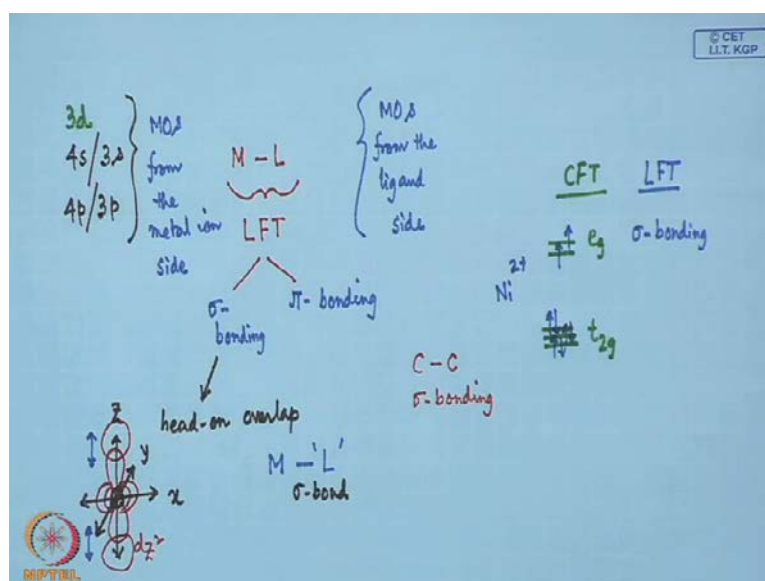
So, the first one what we have seen that what we have the  $A_{1g}$  group orbitals so is  $A_{1g}$  totally symmetric level for these group orbitals. So, the symmetry group orbitals for the salk orbitals the symmetry adopted linear combinations in a one g symmetry can give us the corresponding matching orbitals of the metal side which is  $A_{1g}$  that means is a typical spherically symmetric one which is the corresponding 3 s or 4 s orbital and from the ligand side. Also we have the corresponding level that means if we use 6 ligand orbitals and these 6 ligand orbitals are available for sigma bonding that means the corresponding symmetry level for the p x, p y and p z which is available for overlap with the  $A_{1g}$  symmetry of the metal orbital. Then we can say that the  $A_{1g}$  group orbitals will look like this. So, this is the corresponding pictorial representation of the ligand group orbitals which is symmetry level or we can also consider then as the salk orbitals. Therefore, the corresponding salk orbitals from the ligand side will have a corresponding pictorial representation like this and which is available for hundred percent overlap with the metal orbitals available. And which is typically some kind of head on overlap and with the ending of with some sigma bonding interaction of  $A_{1g}$  symmetry.

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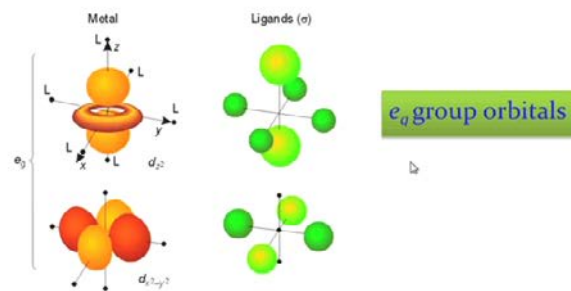


Then, the other group of orbitals which will find that this is the typically the availability of these two orbitals which we have seen in case of crystal field theory that  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals what we have seen in crystal field theory that we have these two levels and the  $t_{2g}$  set of orbitals. So, we have the  $e_g$  and the  $t_{2g}$  level. So, we are having so many properties related to something there we have seen that if the metal ion is a  $3d^8$  system for the bivalent nickel  $2+$  having 6 electrons in the  $t_{2g}$  level and two electrons which remain unpaired in the  $e_g$  level. So, these two electrons when they are available, now we

find in terms of the corresponding ligand field theory that the corresponding symmetry level is matching for sigma bonding for these e g orbitals.

So these two orbitals only can show some sigma bonding interaction if they for the nickel 2 plus ion with the corresponding ligand molecular orbitals in terms of the corresponding crystal field theory and these two orbitals will show only the sigma bonding interaction to the corresponding ligand system. And as a result what will find that if there is some kind of this metal ligand interaction and the covalency that can only the explain in terms of the involvement of the e g orbitals for sigma bonding in these interactions.

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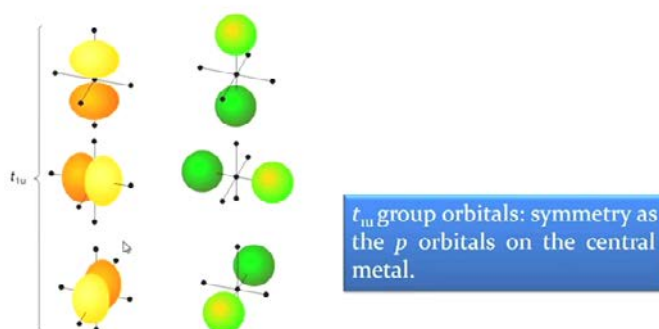


So, these two orbitals basically therefore, the d z square and d x square y square orbitals. We know they have the corresponding loops along the z square axis and a symmetric circular low along the x and y axis. So, we have the corresponding electron distribution available along the z axis. So, we have the corresponding ligand symmetry orbitals which will only faze from these two as well as these four.

So, we have one type of sign for these two level loops along the z axis and for other of different sign from other four axes which are the positive side of the x and negative side of the x and positive y and negative y side. Similarly, for the x square y square only we need these four corresponding loops which are symmetry matched from the ligand and sides. So, this is typically the corresponding set that means the e g set of ligand group

orbitals which are available because we have the positive loop from x axis and the negative loop from the y axis. So, this is the corresponding matching orbital matching symmetry level from the ligand side. So, we have the corresponding e g level or e g group orbitals available for this interaction between the metal and the ligand. So, after A 1 g we have the e g group of orbitals which are available for this interaction.

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Next we have the  $T_{1u}$  group orbitals the  $T_{1u}$  group orbitals which are having symmetry at the  $p$ -orbitals on the central metal iron. So, now we are talking something which we have not discussed in case of crystal field theory because we have not consider the corresponding  $p$ -orbitals for any kind of interaction between the metal and the ligand in crystal field theory. But, it is not the true picture or the right picture for explaining the metal ligand interaction to explain nicely the corresponding amount of interaction between the metal and the ligand and to explain the entire spectrochemical series. We should also utilize the  $p$  orbitals so these are the corresponding  $p$  orbitals along  $p_x$ ,  $p_y$  and  $p_z$  so this particular set having a symmetry level of  $T_{1u}$ .

Because, which is not symmetric with respect to inversion and the corresponding matching orbitals from the ligand side which are facing directly towards the corresponding  $p$  orbitals with this is the only situation only opportunity what we see. That the corresponding ligands what is available is giving the corresponding  $p$  orbitals for interaction if it is an oxygen donor or oxygen atom of the water molecule or nitrogen

donor from the big ligand system or nitrogen donor from the ammonia molecule. Then we all know that this nitrogen and oxygen can provide nicely the corresponding p-orbitals for interaction to the metal centre. But, previously what we are seen that these electrons present in this p-orbitals of the different ligands are providing the corresponding crystal field environment along the metal centre.

That we are not talking anything in terms of the corresponding overlap of the p-orbitals of the ligand to that of the p-orbitals of the metal side so this is the first time what we are considering that p-p interaction can take place during complex formation. So, in terms of the ligand field theory the corresponding p-p interaction is permissible for the strengthening the corresponding metal ligand interaction and providing some energy level for the T<sub>1u</sub> set. That means the p orbitals on the metal atom or the ion which can be utilized for interacting with the ligand orbitals to give us a corresponding head on overlap and this head on overlap can provide us the corresponding sigma bonding interaction.

So, apart from this d-orbital and s-orbitals, we have these p-orbitals also which are engaged in sigma bonding. So, what you see that in case of a sub by tell if we have one a sub by tell of A<sub>1g</sub> symmetry then 2 d orbitals of e<sub>g</sub> symmetry and 3 p orbitals of T<sub>1u</sub> symmetry. Therefore, all together 3 plus 2 plus 1 that means 6 orbitals is available from the metal side for interaction. Similarly, in terms of the corresponding Salk that means the symmetry adopted linear combination of the different available orbitals on the ligand atom are also 6 in number that means 6 plus 6 twelve orbitals are involve for the corresponding molecular orbital formation for sigma bonding.

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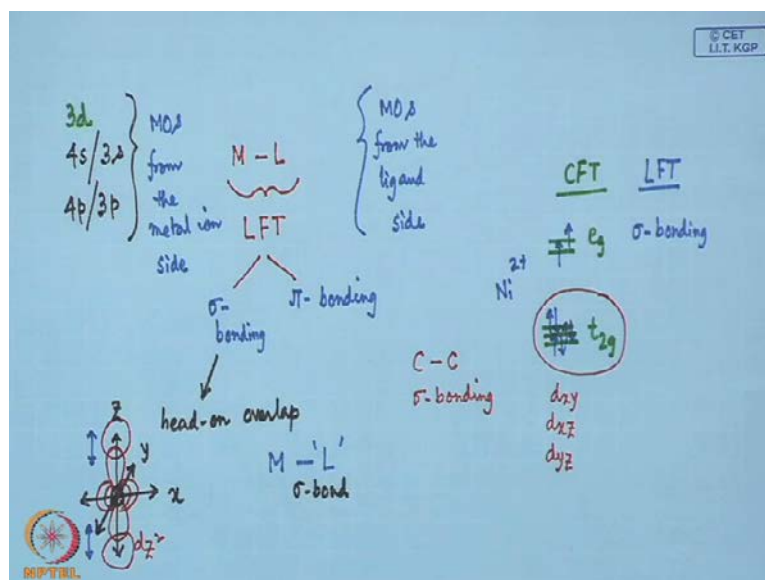
Since the ligands don't have a grouping with  $t_{2g}$  symmetry, the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals on the metal ion will be non-bonding when  $\sigma$  bonding is considered.



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Then we see that the other set what we do not utilize for sigma bonding that means in case of crystal field theory what we have seen that  $t_{2g}$  set of orbitals.

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So, this  $t_{2g}$  set of orbitals what were you were having and in that particular case we are having the electrons available from these  $t_{2g}$  levels and this  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals will not have any matching symmetry from the ligand side for sigma bonding. Therefore, these  $t_{2g}$  set of orbitals will not show any kind of sigma interaction with that of our ligand group orbitals or ligand sides. Therefore, these orbitals will be there but,

they basically show something what will find when we have the typical molecular orbital diagram in terms of this ligand field that these orbitals will not show any bonding interaction with that of the corresponding available ligand orbitals. So, what we see that.

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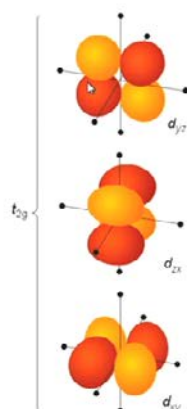
Since the ligands don't have a grouping with  $t_{2g}$  symmetry, the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals on the metal ion will be non-bonding when  $\sigma$  bonding is considered.



Since this ligand do not have a grouping with  $t_{2g}$  symmetry. That means from the ligand side we are not getting any such  $t_{2g}$  symmetric orbital and the corresponding orbitals from the metal iron side or the metal side when we are having some complexes in 0 oxidation states such as nickel tetra carbonyl or chromium hexa carbonyl that  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  and  $d_{yz}$   $xz$  and  $yz$ . This is  $xz$  orbitals on the metal ion will be nonbonding when sigma bonding is consider so when these 3  $xz$ ,  $xz$  and  $yz$  this is the  $xz$ . We will consider then as nonbonding because we do not have the corresponding matching orbitals available from the ligand side.



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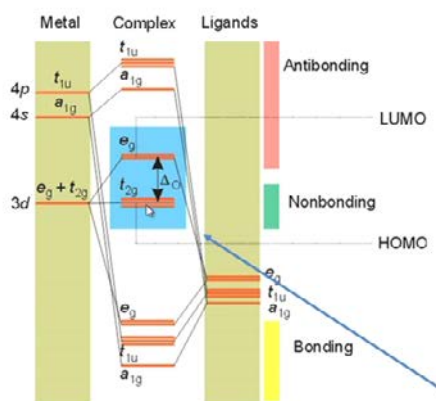
Since the ligands don't have a grouping with  $t_{2g}$  symmetry, the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals on the metal ion will be non-bonding when  $\sigma$  bonding is considered.



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So, we will have only the set that means the  $t_{2g}$  set what we have seen in case of crystal field theory. We are talking so much about the occupancy of the  $t_{2g}$  level but, we see now that unfortunately these three orbitals will remain as a standby and since we do not have some matching orbitals corresponding to these we do not have any kind of sigma interaction with these orbitals.

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So, now we have all these bonding orbitals in our hand. So, we can construct like constructing the corresponding molecular orbital picture what we can draw for simple

oxygen simple nitrogen simple carbon monoxide or simple CN minus. So, this particular drawing is also similar to that of our drawing in terms of the molecular orbital formation were the available orbitals the atomic orbitals which are available from the metal side are the 5 d the 4 s and 4 p orbitals. Because if we consider that some of these lower level s and lower level p-orbitals are also involve but, they are all field and they will not so any kind of interaction with these orbitals.

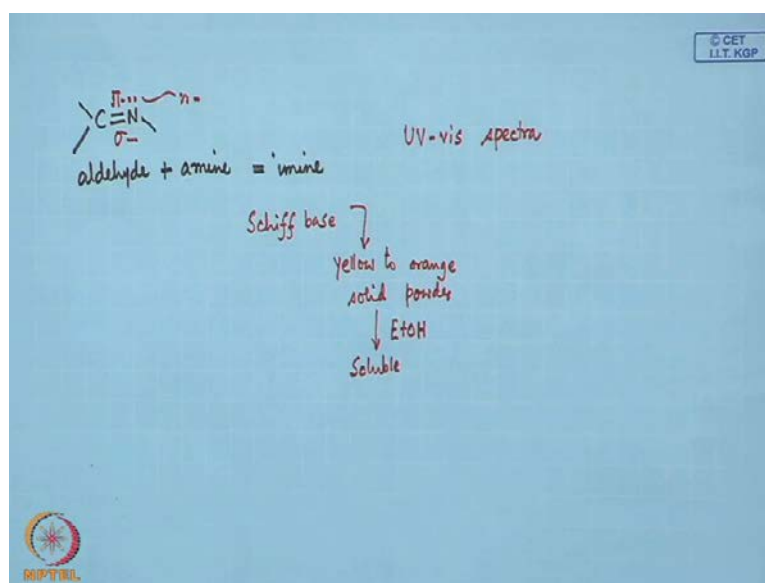
So, in essence what we find that these are the 4 s and 4 p orbitals which we are having were the symmetry level is A 1 g and the T 1 u. And we have the corresponding symmetry level from the ligand side also and as result this interaction what we are getting over here is the typical interaction were the ligand orbitals are of higher energy. Because these are above the corresponding energy from the 3 d level these are 4 s and 4 p. So, these two are of higher energy and these two higher energies basically giving rise to some of these atomic orbitals which are of high energy. And when they are interacting with the ligand side of A 1 g and T 1 u symmetry, these four orbitals we are getting corresponding ligand field related molecular orbitals of A 1 g symmetry and T 1 u symmetry. Since these two are basically giving a bonding part and the anti bonding part.

So, the bonding part will have the energy close to the ligand side that means the presence of 4 s and 4 p levels will not change the corresponding energy level much from that of our individual atomic orbitals which were present from the ligand side. So, only thing that due to this interaction we have some amount of stabilization and that stabilization is basically stabilizing these two sets of orbitals as they are corresponding bonding molecular orbitals in terms of the corresponding sigma bonding interactions. So, this yellow shaded line for the bonding part of the molecular orbital diagram is coming from these four orbitals from the ligand side. Then we have the available e g symmetry from the d orbitals that means the d z square and d x square minus y square. These two orbitals when interacting with the corresponding e g symmetry orbitals from the ligand side they provider e g bonding level as well as e g anti bonding level. So, what we find that whatever we have that we have the empty level as the e g level which is anti bonding in nature but, the e g symmetric bonding level is lower in energy. That means which is a typical task to understand that whatever we have consider earlier for the crystal field interaction the crystal field theory providing the corresponding crystal field splitting and we had consider so many things in terms of the crystal field stabilization energy. And the

corresponding stabilization in terms of this type of splitting which is delta octahedral but, here we find that the e g bonding level is farther most stabilized that means whatever molecular orbital picture.

We can have in terms of the ligand field theory that e g level will have the corresponding strong bonding interactions which are stabilized in this particular level only available orbitals of that symmetry is the anti bonding e g level that means the e g star level. So, we have only the excepter level available which is the e g star level or the e g anti bonding level. Similarly, if we go of farther we will have the corresponding anti bonding orbital for A 1 g symmetry because it is interacting with 4 s and the anti bonding orbital of T 1 u symmetry. That means T 1 u star which is of T 1 u symmetry. So, they are of much higher energy levels.

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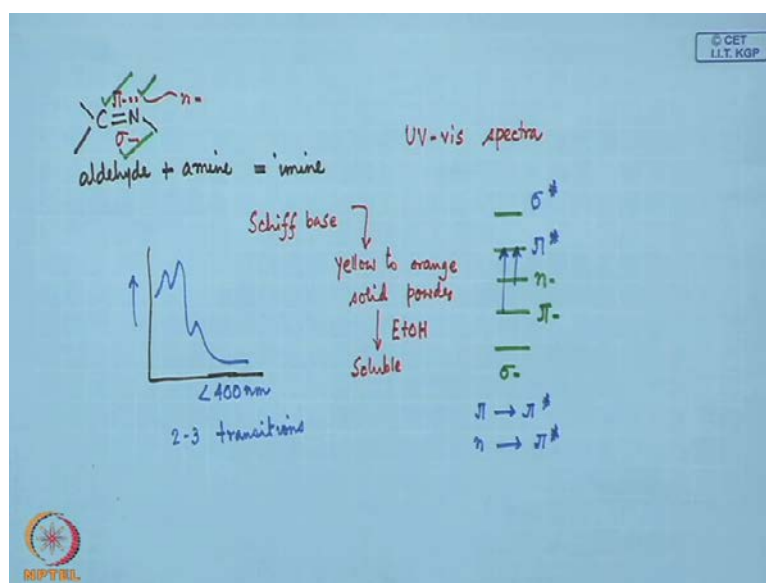


So, what we find that in this particular situation like getting the corresponding transitions in the spectroscopic parameters what we have seen in invisible spectra of simple molecules like carbon monoxide or any in functions. What we have discussed earlier also that if we have this corresponding sick base formation that means between an aldihyde and the amine giving rise to the formation of the amine that means C double bond N.

So, if we have this particular situation and the chromoforic group because these are most of the cases solid yellow compound. Then we can isolate in solid state and this yellow to orange colouration of this is due to the presence of this corresponding electronic

transition involving one sigma bond one phi bond and the electrons which are available on the nitrogen as the n electron. So, we have the sigma electron we have the n electron and we have the pi electron. So, when we are talking about the invisible spectra of these compounds such that any sick base, if we have and they are yellow to orange solid powder and they can be isolated through synthesis say in ethanol and these compounds are also soluble an ethanol.

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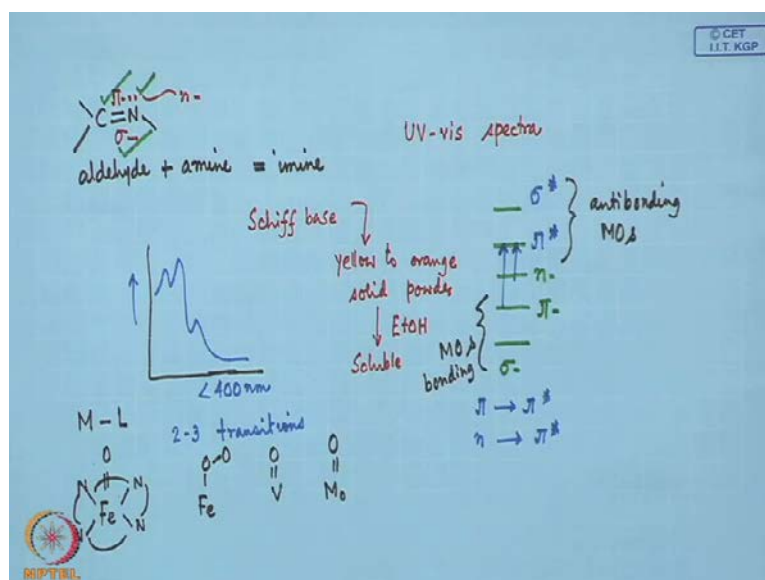
So, if we take an ethanolic solution of these sick bases and learn the corresponding invisible spectra we get some of these bands some characteristic bands close to the ultraviolet and the visible region that means less than 400 or 450 nanometre. So, if we have a multiple feature like this for the absorption and these electronic transitions are taking place due to the presence of some levels what we have considered earlier as these 5 distinct levels.

So, when we have this sigma bonding interactions for these atomic orbitals of the carbon atom and the nitrogen atom we have the corresponding sigma bonding level with those electrons which are occupying in the sigma level. Then we have the corresponding pi electrons for little bit weaker interactions between the corresponding pi symmetric orbitals available from carbon side as well as from the nitrogen side giving rise to corresponding pi level. Then what is available is the corresponding nonbonding electron that means the electrons which are not involved in any kind of bonding on the nitrogen

atom. Then we have the corresponding, because this is typically nonbonding level. Then after that we have these are as anti bonding orbital. So, we have the corresponding phi anti bonding orbital as the phi star and the corresponding sigma anti bonding orbital as the sigma star. So, during these electronic transitions if it has 2 or 3 transitions, in most of these cases we have two to three transitions and mostly they are some time they are very high intensity transition. That means the Charles transfer transitions what we have discussed earlier in this particular classes.

So, what we have see that we have basically two well intense transitions. We can consider one is pi to pi star transition, another is n to pi star transition so during these invisible spectroscopic transitions for simple organic molecules.

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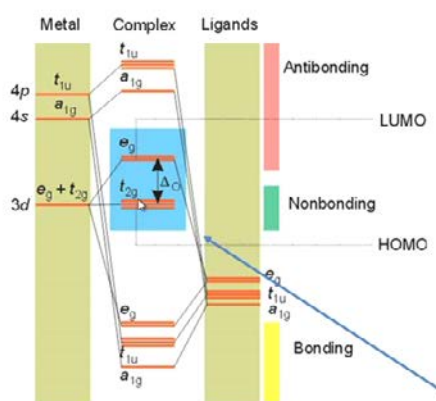


What we see that we can have these two transitions involving two of these that means these are related to the bond formation between carbon and nitrogen. When we are trying to make the corresponding Schiff base from the aldehydes an amine that these are the corresponding bonding molecular orbitals and we have the corresponding anti bonding. Also, these are the corresponding anti bonding molecular orbital so the same sort of ordering also will see during the interaction only thing that we are now having instead of carbon nitrogen bond formation we are having.

Now, metal ligand interaction and sometime this metal ligand interaction can also be the multiple interaction what we see. That in case of several are an oxo compounds which

we get in biological system. Also that we can have the iron, oxygen also we can talk about the corresponding iron oxygen multiple bonds or the iron binding in haemoglobin such as in mioglobin also. And also we can have the double bond with vanadium and the double bond with molybdenum. Also, these all basically gives us the same sort of interaction what we see in case of this corresponding sick base formation. So, the energy ordering for this sigma pi n pi star and sigma star will also be the same. If we go for the corresponding bonding, nonbonding and anti bonding levels for these molecular orbital picture involving this metal-metal centres

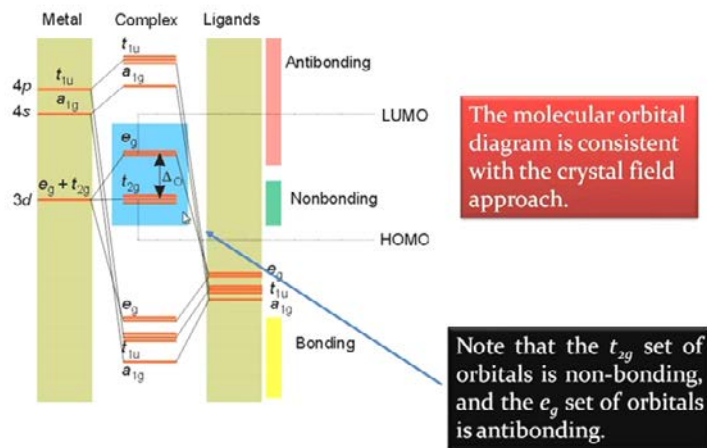
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So, in this particular case this particular part that means 3, 2, 5 and 6. These are the 6 bonding orbitals in our hand and what we had seen that all together we have 5, 1, 3 that means 5, 6, 9 orbitals. And 9 plus 6 from the ligand side so 15 orbitals we are having for sigma interactions. So, 6 of them are binding therefore, the equal number should also be there as anti bonding. So, this is e g star A 1 g star and T 1 u star and three will remain as nonbonding the same sort of ordering. What we have seen just now for sick base ordering for the different levels will have also the bonding level. We have the nonbinding level and we have the anti bonding level involving 2 plus 1 plus 3 of 6 orbitals. So, as a result what we see that we can have all sorts of transitions possible from there but, likewise for the sick base molecules the transition from these n to pi star. So, if we consider that this is the n orbital and this is the corresponding pi star orbital. So, this is the most a important area were we have the energy gap is less. So, we have the

corresponding transition corresponding spectroscopic transition. We can have or the electronic transition, we expect in the visible or n i r region. So, energy gap between this transition from the  $t_{2g}$  to  $e_g$  level is less and we expect the corresponding transition would be in the visible or n i r region. And what we have been seen in case of the corresponding simplified what is an of this ligand field theory as the corresponding crystal field theory? Were we see that this particular crystal field theory is basically giving us some levels were we have the  $t_{2g}$  level and we have the  $e_g$  level and we have the corresponding transition for these  $t_{2g}$  level to the  $e_g$  level.

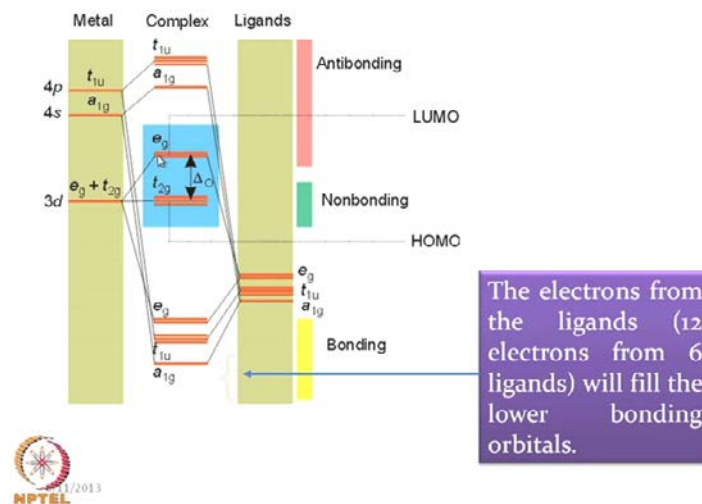
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So, what we see that the corresponding level that the molecular orbitals. What we are getting and the molecular orbital diagram is consistent with also the corresponding crystal field approach. Because only this part this blue shaded region this blue shaded region is matching with that of our crystal field approach well we have two energy levels. One we are considering as the  $t_{2g}$  level and other as the  $e_g$  level. We have the corresponding crystal field splitting parameter of delta octahedral due to the levels. Do levels but, the here the  $t_{2g}$  level. Due to this interaction in terms of the corresponding ligand field interaction is r i as the corresponding nonbonding levels. So, the nonbonding levels electrons from these nonbonding levels which will be available for the anti bonding  $e_g$  level or the  $e_g$  star level for the transition. So, this  $t_{2g}$  set is present as the nonbonding and the  $e_g$  set of orbitals are the anti bonding.

So, our transition is very much similar to that of our  $n-2$   $\phi$  star transition also. What we have seen in case of the crystal field theory and this particular part is still there for the transition in the ligand field diagram also.

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So, we have the thing that this is the homo level that means the highest occupied molecular orbital because we are talking in terms of the corresponding energy level for all these as well as these nonbonding level. So, the metal iron or the metal atom giving the electrons which are occupying the  $t_{2g}$  level will serve the purpose. As the corresponding homo level or the highest occupied molecular orbital level which is highest in energy and the  $e_g$  is giving the corresponding  $e_g$  star level which is the corresponding lowest unoccupied molecular orbital.

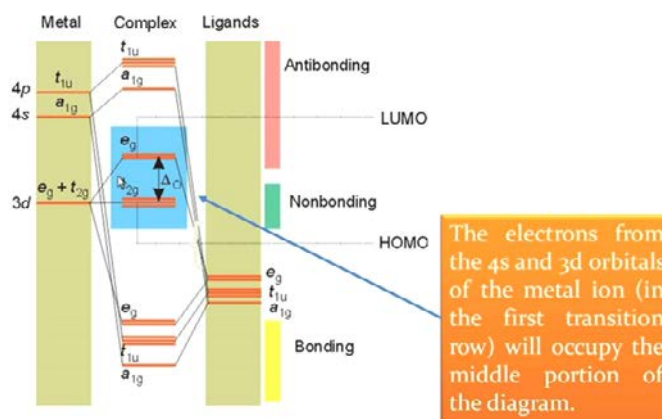
So, we have the corresponding Homo, Lumo gap and we basically due to this sort of interactions. We basically modify the corresponding homo, Lumo gap and interestingly what we can see that we do not had any control for the energy level for this  $e_g$  level. What we have been considering for the corresponding crystal field interactions that we are talking that since we have the crystal field splitting we have the stabilization for the  $t_{2g}$  level and destabilization for the  $e_g$  level. Because of the head on interaction from the  $e_g$  orbital that means the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals and they are getting destabilized and that is why they are of higher energy. But, it is not the fact the fact is that the  $e_g$  level. How the  $e_g$  level is involved in sigma interaction with the  $e_g$



level from the ligand side. So, if our energy for this e g level from the ligand side are different our stabilization energy for the e g level as well as the destabilized level of the e g star will also be of different energy that means the metal ligand overlap from the e g orbitals of the ligand side do control this particular energy gap. It is not the entire crystal field which will be responsible for giving us the corresponding crystal field and we are talking in terms of some interaction from the ligands which are giving our strong interaction will have bigger splitting if we have the metal iron in the plus 3 or plus 4 oxidation state will have bigger interaction. But, as most of the cases what will find that thus stabilization of these e g level from the ligand side. How it is stabilizing the corresponding bonding level bonding e g level will tell us the corresponding gap between these e g and the e g level t 2 g level and the e g level. So, what we see that the electrons from the ligands with we are having the 12 electrons from the 6 ligands.

So, ligands are providing all together 12 electrons and per electron we are having 2 electron because we are considering the ligands as 2 electron donor whether it is the oxygen atom of the water or nitrogen of the ammonia molecule. So, all 12 electrons will come to occupy these 6 orbitals and they are all filled. Due to these interactions what we are getting thus these are filled by the ligand orbital. So, the ligand orbital because they are of low energy compare to the metal ions. So, what will happen in the next state the metal iron orbitals? That means the t 2 g level will be filled from the metal orbital so the pure metal orbitals they are of only the metal d-orbitals are filled in the t 2 g level and we are having only the corresponding p-orbitals which can be consider as the p star level from the ligand side or the e g star level which will be our good acceptor level.

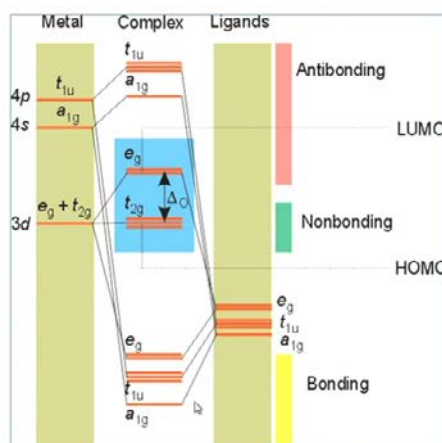
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So, we just basically level the entire part for these donor and the acceptor level and we have filled this particular level as the 12 electrons from the ligand side and the electrons from the 4s and 3d orbitals of the metal side in the first (( )) rough will occupy this middle portion of the diagram is basically when you consider that that e<sub>g</sub> and t<sub>2g</sub> level it is the 3d electrons not 4s. Only there is a 4s also the 4s is of higher energy it is the three d level of electrons which will occupy these levels that means if we have for nickel 2 plus. So, will truly speaking when nickel is interacting with ammonia or water molecule. So, all the 12 electrons which are coming from the ammonia and the water molecule will filled up these 6 levels and the nickel electrons which are 8 in number. They will occupy these numbering t<sub>2g</sub> level and the anti bonding e<sub>g</sub> star level. So e<sub>g</sub> star level will have two unpaired electron.

So, the property for this is basically a typical numbering level and this Lumo level will tell us all these properties related to the nickel 2 plus.

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CFT doesn't take into account the overlap of ligand and metal orbitals

MO energy levels of a typical  $O_h$  complex



So, when we have these bonding anti bonding and non bonding level and we just simply say that the interaction between the homo level and the Lumo level. What we have ignore in case of the crystal field theory that crystal field theory does not take into account the overlap of the ligand and the metal orbital. So, this is the principle drawback of this particular theory were we are not talking in terms of the overlap of the ligand and metal. But, this is not the true and the most realistic picture in our hand, because we should have the metal and the ligand overlap and the ligand orbitals particularly these 6 orbitals from the ligand side which are functioning as a bonding orbital.

So, the strength of the metal ligand bonding or the strength of the metal complex or the metal iron complex is purely depending on this sort of interaction were we have the 6 orbitals of  $A_{1g}$ ,  $T_{1u}$  and  $E_g$  symmetry for the as this blue shaded, yellow shaded region as the bonding level. So, this sort of bonding basically now we see in terms of the ligand field theory that the bonding interaction is basically stabilizing the metal complex and whatever other spectroscopic magnetic and other interactions we should have is coming from the nonbonding and anti bonding interactions. And we have the corresponding nonbonding level as our homo level.

So, homo is our non bonding level and the Lumo is the anti bonding level and these two levels are basically characteristic though for these stabilization in terms of the corresponding number of electrons and they are transfer from one level to the other. But,

the typical thing that means the bonding for these metal complexes are basically due to the bonding from ligand orbitals. So, this particular picture the entire molecular orbital energy level diagram for a typical octahedral complex can now explain the availability of these orbitals how they are interacting with the ligand group orbitals which are symmetry level. That is why they are also known as eg and t<sub>2g</sub> the symmetry group orbitals and how this energy levels are available for these different types of characteristics and the properties.

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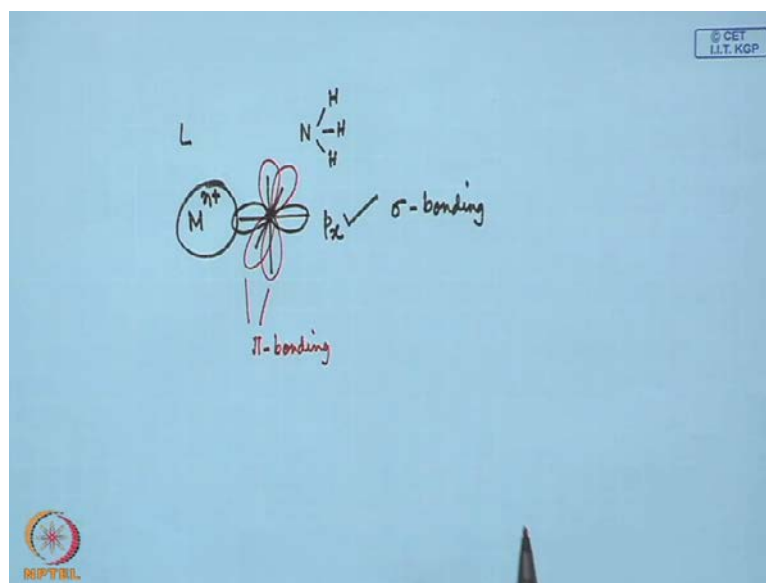
### Considering $\pi$ -Bonding

To obtain  $\Gamma_{\text{red}}$  for  $\pi$  bonding, a set of cartesian coordinates is established for each of the ligands.



So, next we can consider in our next class that how will consider the corresponding pi bonding interactions. So, whenever we have these corresponding pi bonding interactions. So, if we have the ligand and if we have the ammonia molecule in our hand and we will find that from this ammonia molecule we will having.

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The three orbitals available one is  $p_x$  another is  $p_y$  and another is  $p_z$ . So, one we have utilize say  $p_x$  orbital we have utilize overlap with the metal iron. So, already we have considered this one particular orbital. So this  $p_x$  is gone for sigma bonding so next will consider the corresponding orbitals which will be available as the corresponding  $p_y$  and the  $p_z$  which are not utilized for sigma bonding. So, these two orbitals will give us the corresponding pi bonding in this metal complex. So, next we will see how this bonding also can support some of these properties of these ligands in the metal complexes.

Thank you very much.

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