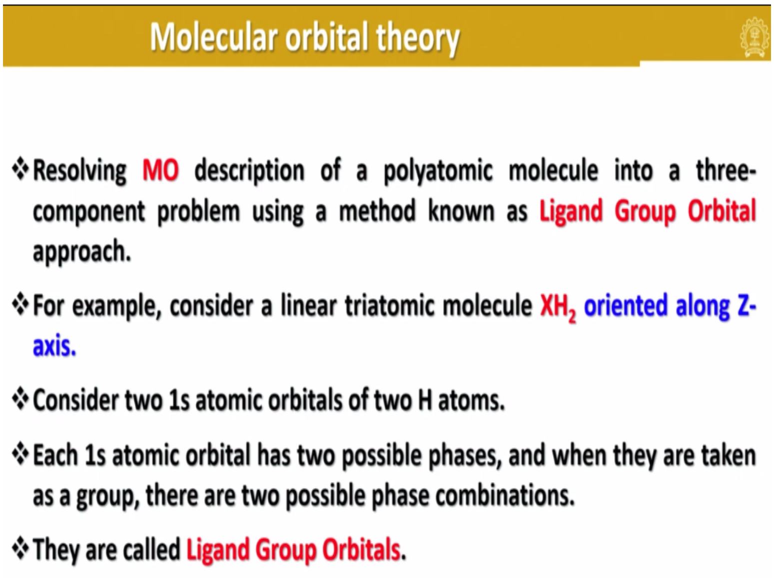
Advanced Transition Metal Chemistry – Ligand Field Theory
Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 18
Ligand Field Theory (LFT)

(Refer Slide Time: 00:31)



Molecular orbital theory

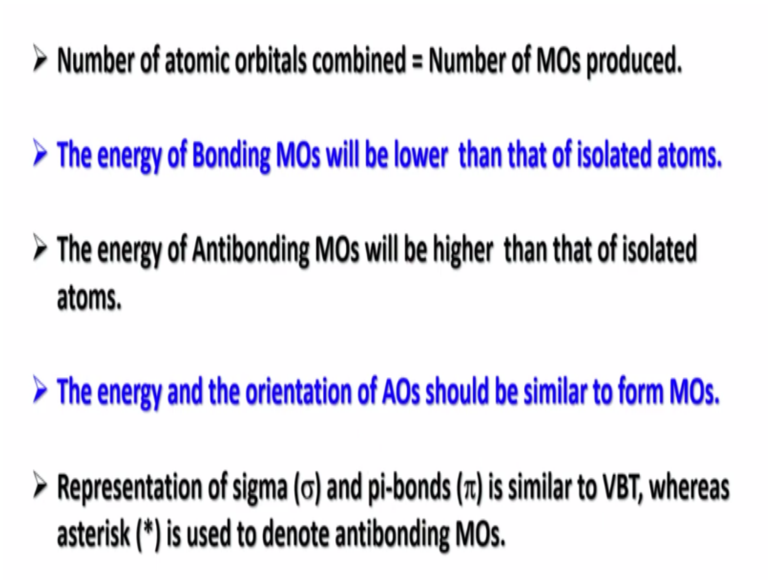
- Resolving MO description of a polyatomic molecule into a three-component problem using a method known as Ligand Group Orbital approach.
- For example, consider a linear triatomic molecule XH_2 oriented along Z-axis.
- Consider two 1s atomic orbitals of two H atoms.
- Each 1s atomic orbital has two possible phases, and when they are taken as a group, there are two possible phase combinations.
- They are called Ligand Group Orbitals.

Once again, I welcome you all to MSB lecture series on advanced transition metal chemistry. This is 18th lecture in the series. In my previous lecture, I had initiated discussion on ligand field theory, let me continue from where I had stopped. As I mentioned in my previous lecture, before I begin using ligand field theory to explain bonding for coordination compounds, let me make you familiar with molecular orbital theory so that understanding of ligand field theory would be very easy.

Here, resolving molecular orbital description of a polyatomic molecule into a three-component problem using a method known as ligand group orbital approach. For example, when we write molecular orbital diagram for simple diatomic molecules or hetero diatomic molecules, it is very easy. I am sure you are all familiar with writing your MO diagrams for molecules such as hydrogen, N_2, O_2 or even CO.

But however, when we want to write molecular orbital diagrams for polyatomic molecules it is very appropriate to consider a set of orbitals called ligand group orbitals. For example, let us consider a triatomic molecule such as water oriented along the z axis. So, here consider two 1s atomic orbitals of two hydrogen atoms and each 1s atomic orbital has two possible phases. And when they are taken as a group, there two possible phase combinations, we essentially call them as ligand group orbitals, whether we have 2, 3, 4 or many, so we can go for this ligand group orbital concept.

(Refer Slide Time: 02:06)



- Number of atomic orbitals combined = Number of MOs produced.
- The energy of Bonding MOs will be lower than that of isolated atoms.
- The energy of Antibonding MOs will be higher than that of isolated atoms.
- The energy and the orientation of AOs should be similar to form MOs.
- Representation of sigma (σ) and pi-bonds (π) is similar to VBT, whereas asterisk (*) is used to denote antibonding MOs.

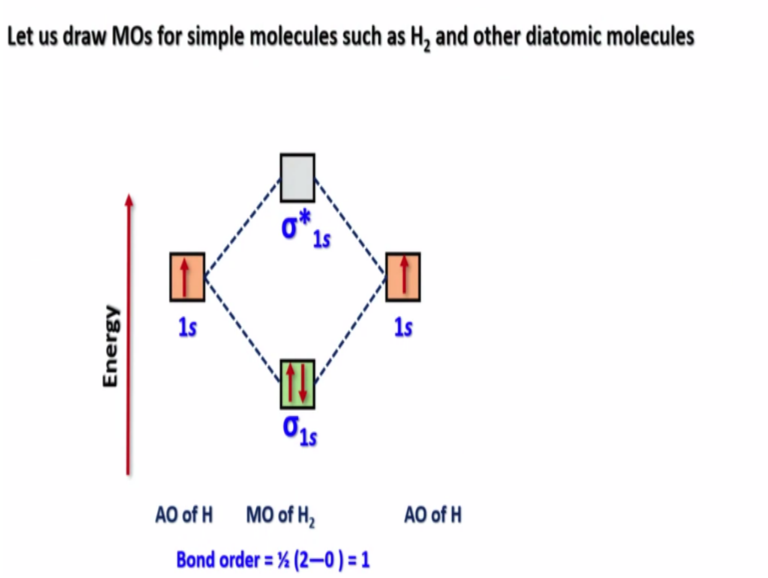
Now, once again the number of atomic orbitals combined is equal to number of molecular orbitals produced. The energy of bonding molecular orbitals will be lower than that of isolated atoms. The energy of antibonding molecular orbitals will be higher than that of isolated atom and they are almost close to the one of the atomic orbitals which is higher in energy compared to the other one, in case if we are considering two atoms having different relative energies.

The energy and the orientation of atomic orbitals should be similar to form molecular orbitals. For example, if we take p_x, it has to interact with p_x only, p_x cannot interact with p_y orbital. Representation of sigma and pi bonds is similar to what we use in valence bond theory, sigma bonds we use Greek symbol "σ" and pi we are using "π" whereas antibonding irrespective of whether sigma or pi we put star (*) as a superscript at the end or on the right side of that symbol.

So, while filling molecular orbitals similar to atomic orbits Aufbau and Pauli's exclusion principles and Hund's rules should be followed, and higher the bond order, you should remember stronger is the bond. And bond order is nothing but the number of electrons in the bonding molecular orbitals minus number of electrons in antibonding molecular orbitals divided by 2.

The bonding and antibonding molecular orbitals for core electrons cancel each other. As a result, there is no net contribution from core electrons towards the bond formation in a molecule, as a result, what happens there is no net contribution for bonding and that can be ignored. Only molecule orbitals diagram shows MOs created by combining atomic orbitals of valence electrons are very important. That means the emphasis is given for valence orbitals and or valence electron orbitals.

(Refer Slide Time: 04:09)



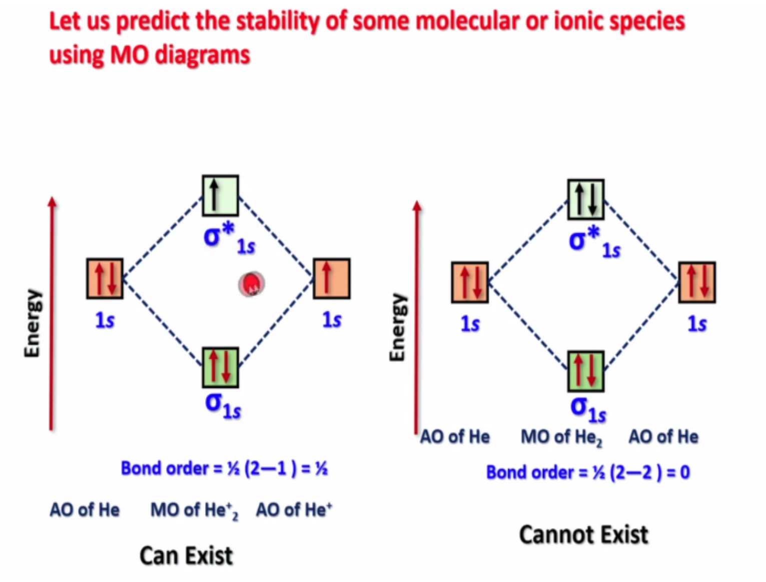
Let us draw MOs for simple molecules such as H_2 and other diatomic molecules

Bond order = ½ (2—0) = 1

Now, let us draw MO diagram for simple molecule such as H_2 and also for other important diatomic molecules for better understanding. So, now if you take, you know, two hydrogen atoms are coming with 1s, one electron each and their energy is similar. So, they are in the same line, same energy. So, when they combine together, they generate two molecular orbitals; one is bonding, one is antibonding, and two electrons are occupying the bonding here and here it is empty.

So, if you calculate the bond order 2 – 0 by 2 = 1, so bond order is 1. So thus, we have a one bond between H and H. That means molecular orbital theory very nicely predict the multiplicity of the bond and also once you know the bond order, you can tell whether the strong bond exists between them or weak bond exists between them; how molecule is stable.

(Refer Slide Time: 05:02)



Let us predict the stability of some molecular or ionic species using MO diagrams

Bond order = ½ (2—1) = ½

AO of He MO of He^+_2 AO of He^+

Can Exist

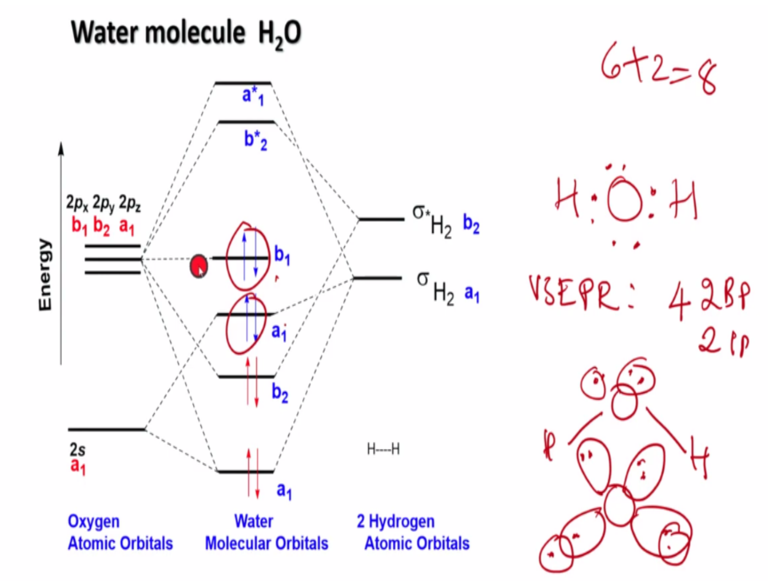
Bond order = ½ (2—2) = 0

Cannot Exist

So, now let us consider a couple of more molecules. Let us try to write MO diagram for helium, diatomic molecule, so helium molecule, having He_2 molecule. So, now, it is completely filled, 1s orbital is there, so 2 electrons are here and 2 electrons are here in this one for He_2. So, then if you try to form molecular orbitals, we have sigma has two electrons, sigma star also two electrons, so net bond order is 0. So, that means if the bond order is 0, then the molecule cannot exist.

So, simply you can say He_2 cannot exist. How about He_2^+? When you consider He_2^+ we are considering one He with 2 electrons, one He is positively charged cation with one electron. In this case what happens? Two electrons are occupying the bonding orbitals and one is occupying antibonding. So, net bond order is half, yes there is a possibility of the existence of He_2 cationic species. So, this also again tell you whether a particular molecule can exist as a diatomic species or not.

(Refer Slide Time: 06:14)



So, now let us try to write MO diagram for water molecule, it is very interesting. So, this is how; do not worry much about Mulliken symbols, if you have not understood does not matter. What is important is water molecule means oxygen, oxygen is coming with s^2p^4, 6 electrons are coming and then H_2 means, as I said ligand group or once if you consider H_2. So, 2 hydrogens are there, we are getting 2 electrons.

So, 2 electrons and 6, 8 electrons are there. If you place the 8 electrons, we are placing in this fashion, 2 electrons here, and 2 electrons here, 2 electrons here and 2 electrons here. And these two electrons, and these two electrons are responsible for making two OH bonds, whereas these two pairs of electrons are essentially the loan pairs based on oxygen, let me show you from Lewis dot structure and also from valence bond theory.

So, we write like this according to Lewis dot structure. What we do is to we have 6 + 2, 8 electrons are there. Out of 8 electrons what we are using here? We are using here 2 electrons here, we are using 2 electrons for making bonds and remaining 4 electrons I am putting here to complete the octet. In VSEPR theory, we have four pairs of electrons or steric number according to VSEPR.

We call it as steric pair. So, we have four pairs here. Out of four pairs, what happens two are bonding and two are lone pairs, bonding pairs and two are lone pairs, that means we write something like this here and then here, we have two electrons. So that means we have two pairs of electrons there and these two pairs of electrons can be seen from here, this one and then if you go for hybridization concept valence bond theory oxygen undergoes sp^3 hybridization.

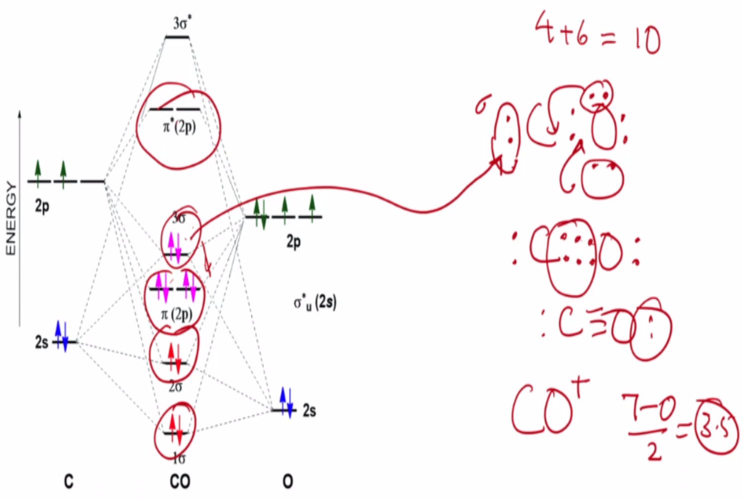
And when it goes sp^3 hybridization, it has two sp^3 hybrid orbitals with one electron each and two sp^3 orbitals with two electrons each, and this will interact with hydrogen so that water molecule is formed here. Again, these lone pairs are there. These lone pairs can be seen from this one here. So, the question is have you come across any example where water acts as a bidentate ligand? We know that water can bind readily as aqua and then which lone pair, one of the lone pairs, so this lone pair is responsible for making water as a ligand.

And how about the second pair? It cannot, see it is literally deeply buried, it cannot give readily and when you make an attempt to give this one what happened the OH bond goes and it becomes hydroxo species. When it becomes hydroxy species, it acts as a bridging ligand. And if you see in the literature or somewhere, neutral water molecule is not acting as a bidentate ligand because second pair is not readily available.

Although you can see the lone pair is there, because it is lower in energy and it is not readily available for bonding. When, we make an attempt using a base or an acid, in that case what happens we are cleaving one of the OH bonds, as a result it becomes hydroxo species and then that can bridge two metal centres. So that means this information does not come from valence bond theory, but molecular orbital theory can explain some of these important properties.

(Refer Slide Time: 10:08)

CO molecule



Now, let us look into carbon monoxide. Carbon monoxide is a very interesting molecule and when I floated my course on main group elements, I did discuss about carbon monoxide and a lot of students wrote to me asking you about the stability of CO molecules when you remove an electron and all those things. I must have told answer to a lot of students and still continue doing it. So, let me clarify those doubts with the CO molecule.

Of course, I will be discussing more such interesting aspects as this course progresses. Let me write MO diagram for CO molecule here. If you just look into CO molecule; carbon here and oxygen is here and oxygen as once again comes with 6 electrons and carbon comes with 4 electrons, we have a total of valence electrons 10. Out of 10, basically what happens here, 2 electrons are here, 2 electrons are there and here 2 electrons, 2 electrons and 2 electrons.

So 2, 4, 6, 8 10 are there. If 10 are there, how do you consider carbon monoxide bond order there is a question. So, for that one let me write again, Lewis dot structure here. For that one before Lewis dot structure I write, let us count valence electrons. We have 4+6, 10 electrons are there and out of 10 electrons first utilize a pair of electrons to make a bond and then 8 electrons are there. First, I should satisfy the octet of the most electronegative atom, in this case is oxygen, so I should write here,

Now, 8 electrons have been utilized, a pair of electrons are left, I put here a carbon. So, if you see these electrons here, so this pair of electrons are responsible for making carbon monoxide as a neutral sigma donor ligand. So, this is a sigma donor pair of electrons. Now, the octet of carbon is not satisfied, it has only four electrons there. Then what happens? Carbon monoxide pleads with oxygen whether it can donate a pair of electrons and place it in between so that both of can enjoy octet satisfaction.

In that case oxygen agrees and it puts here and another pair it puts here, as a result what happens we see a triple bond between carbon monoxide and oxygen. So, now the triple bond is there. So, these triple bonds are responsible for giving bond order of 3 here. So, these electrons are coming from this space and this one, and this one if you see that is because of this one. So, this one, it looks like, it remains nonbonding.

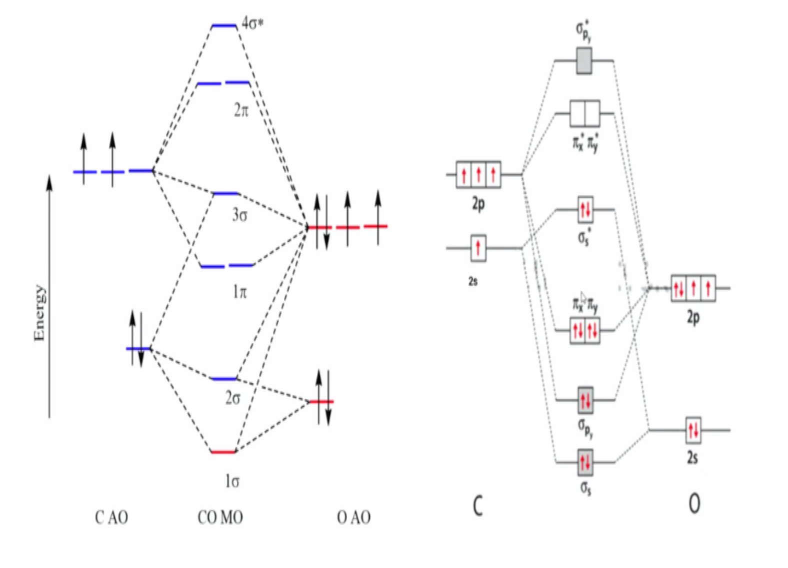
And several books propose several types of molecular orbital diagram, nevertheless, it is nonbonding, but it is a little lower in energy but still we are considering what happens these 6 electrons are responsible for making the C triple bond out of 3. And for example, if you remove one electron to generate CO^+ then what happens, the energy of this one further drops and comes little lower. So, in that case what happens?

We have to consider that also as bonded, in that case what happens the bonded will be a 7 – 0 by 2, 7 electrons are there, bond order 3.5. So that means CO^+ bond order increases and this is how you can give a correct answer for CO^+ versus stability of CO molecule. So, there should not be any doubts about that one. So, this is nonbonding and this nonbonding; this is we are talking about. This is how one can understand CO and what will happen.

And of course, here next when it acts as a pi-acceptor, metal electrons will be going to this one. When the metal electrons go, more and more electrons are going to pi star, then what happens? The bond order would start decreasing and eventually sometime what happens this triple bond will almost become a double bond. As a result, we have multiple bonds between metal to carbon. I will be discussing all those things in detail.

And in fact, you should remember the fact that carbon monoxide can take anywhere between 0.2 to 1.2 electron density into its pi star. So, accordingly you can see the strengthening of metal to carbon bond to the same extent weakening of carbon to oxygen bond of carbon monoxide.

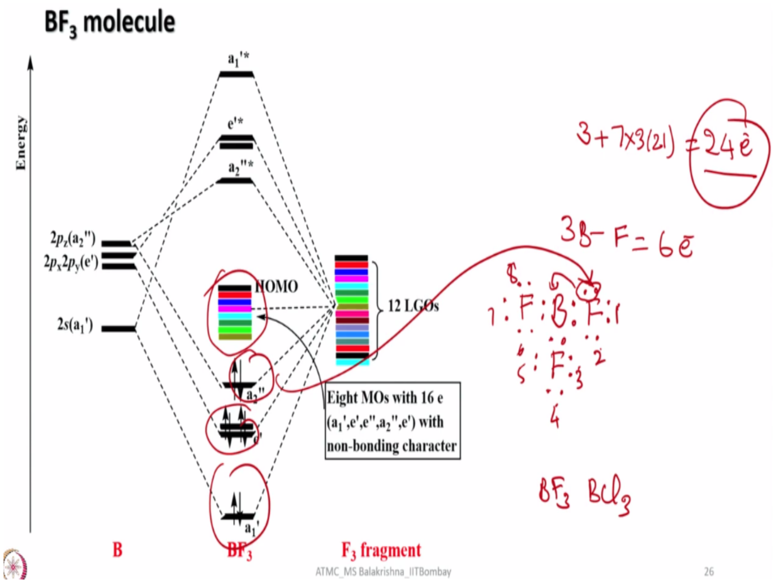
(Refer Slide Time: 14:13)



So, yeah, this another one I showed you. So, this is how another carbon monoxide MO is shown. And I have also come across these kinds of things and here they are predicted as antibonding, yes, if it is antibonding then you had to consider these things, at bonding this also you should consider, then 8 – 2 it becomes 6 and after removing one electron what happens its sigma bonding becomes lower, then it becomes 7.5.

This also holds good, but this is not appropriate. And because for bonding purpose it should not be considered deeply buried dots and lone pair, that is the reason probably I believe it is not the right one. The right one is the one I wrote here. This is the most appropriate MO diagram for carbon monoxide.

(Refer Slide Time: 14:59)



BF$_3$ molecule

Eight MOs with 16 e (a$_1$',e',e'',a$_2$'',e') with non-bonding character

Let us look into another interesting molecule BF$_3$. BF$_3$ we have 3 electrons in the valence shell of boron and then we have three fluoride ions are coming or three fluorine atoms are coming with 7 electrons each. That means in order to construct this one I should consider four valence orbitals of boron that is 1s and 3p. Similarly, I have to consider four orbitals from each fluorine atom so that we should have 12 ligand group orbitals will be there.

That is the reason, to understand them, I have given different colours, it does not mean anything. There are no ligand group orbitals having the similar properties, but to distinguish I have just given different colour so that you can count, it would be very easy. So, 12 group orbitals are there. That means now what we have is, so 3 electrons are coming from boron and then 7 into 3, 21 are coming from; the total 24 electrons are there.

So, this molecular orbital diagram should account for these 24 electrons. Let us see how it happens. So, you can see here the filled ones, 2 electrons here and then 4 electrons and 6 electrons. So, these 6 electrons represent three B—F bond formation. These electrons here and this one would represent three BF bonds. So, that means you have utilized 6 electrons, are there. And what is this one here?

This one is essentially coming from one of the lone pairs of fluorine atom, let me show you using Lewis dot structure here. So, boron is there and I write something like this and utilise 6 electrons for making three BF bonds and then whatever the electrons left, I should satisfy the octet I will start writing like this. At the end you can count whether my writing is correct or not. So, now if you count totally we have 24 electrons there.

So, 24 electrons are there, but boron has only 6 electrons, is electron deficient and as I said Lewis acid. So, now the question comes, if you have BF_3 and BCl_3; F is a more electronegative atom, so then when we compare the Lewis acidity, strictly speaking according to periodic properties BF_3 should be a stronger acid and BCl_3 should be relatively weaker compared to BF_3, it is also stronger acid.

But, when you look into actual properties, BCl_3 is a stronger Lewis acid compared to BF_3, then how to explain that one? Here, what happens? You are talking about 2p orbitals and 2s orbitals, again also here 2p and 2s. So, orbitals are of same size, as a result overlapping is efficient, and since the energy of 2p is same and then basically what happens a pair of electrons from one of the fluorine atoms will be donated here.

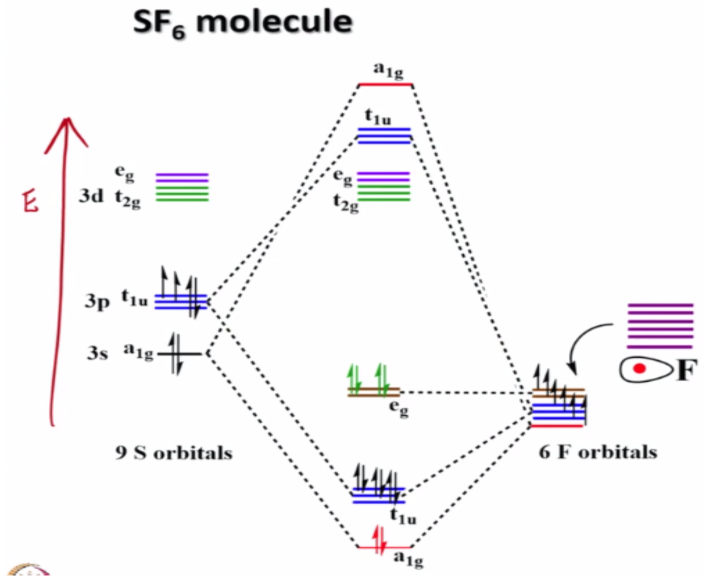
So, that means, now what happens, octet is satisfied by this pair of electrons shown here. So, this happens, whereas why it do not happen in case of BCl_3? BCl_3, we are considering 3p orbitals and because of the orbital mismatch, this overlapping of 3p electrons with 2p orbital is not effective, as a result what happens? Still boron remains electron deficient, as a consequence BCl_3 is much more stronger Lewis acid compared to BF_3.

So, again this can give you a very satisfactory answer about these trends or properties so that probably you may not understand valence bond theory. Of course, if you use valence bond theory also you can write. If you use valence bond theory, then we have to talk about sp2 and then keep the p orbital empty, that empty p orbital would take electron from one of the fluorine atoms. So, this is how you can explain in case of polyatomic molecules.

Now, we have utilized 8 electrons, 2 for back donation from fluorine to boron and remaining electrons will be, so 16 electrons are there. Those 16 electrons are 1, 2, 3, 4, 1, 2, 3, 4, 5, 6, 7, 8. That means these 16 electrons remain as nonbonding here, they are nonbonding electrons, 16 electrons are accounted. That means 16, 18, 20, 22, 24; all 24 electrons are accounted. So, this is how you can explain without any problem the bond formation and the existence of BF_3 molecule.

And you can also predict and tell you about its Lewis acidic nature with respect to BCl_3. This shows superiority of molecular orbital theory over other bonding concepts that we use.

(Refer Slide Time: 20:06)



So now let us look into another interesting molecule SF_6. Before we shall focus our attention on this MO diagram, I will show you this one with valence bond theory. Of course, SF_6 when you look into it, Lewis dot structure cannot explain because we have here 12 electrons. It shows only about octet, that means beyond 8 it does not believe. So, that means BF_3 also you cannot explain, where electron rich atoms more than 8 electrons are there Lewis dot structure cannot tell.

But partially to an extent Lewis structure is true that is proved by molecular orbital theory. If you look into valence bond theory, what happens you can see clearly here we have 3s, we have 2 electrons are there and 3p we have four electrons there, we have 3d orbitals there which are empty, yes I can utilize them very similar to outer orbital complex like sp^3d^2. I can make six sp^3d^2 orbitals and then put these fluorines coming with 12 pairs of electrons.

Because once all the electrons are taken out, they become F– and each one will be given 2 electrons that means 6 electrons will be coming to sulphur, so sp^3d^2 will be completed. So, this is how valence bond theory predicts the geometry of SF_6 as octahedral and it say sp^3d^2 hybridization system. But if you look into this MO diagram here, the energy of 3d is too high, I forgot to put here energy, energy is too high.

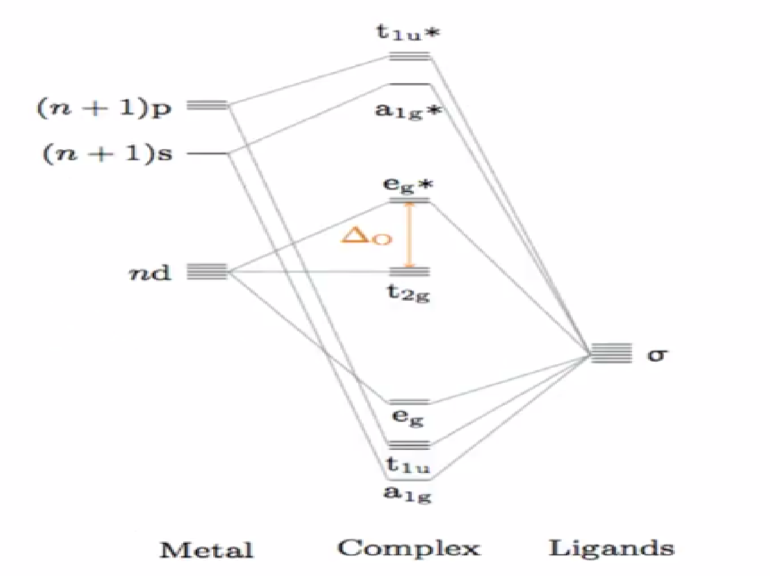
That means nowhere you can see the participation of e_g or t_{2g} with F orbitals. So, instead how it is explained, you can see 6 fluorine atoms are coming with 12 electrons, already we are having here 6 electrons there, that 6 and 6; 12 should be accounted. And here if you see a pair of electrons is there and then pairs of 6 electrons are 3 pair and then these 8 electrons, we see here are fine. And then we have another two pair of electrons here that is coming from fluorine.

They do not find suitable orbitals from sulfur and as a result they remain nonbonding. So that means SF_6 solely stabilized with only 4 pairs of electrons, then what it is, then it is a hypervalent molecule. Such molecules we call it as hypervalent molecules and 6, 8 electrons are there that makes octet satisfied, obtaining Lewis acid and then 4 electrons are there and these four electrons means two fluorine bonds essentially keep the electrons towards itself and make weak bonds, in this case, because of the very high energy of d orbital.

So, they are not participating in bonding, they are called hypervalent molecules. Similarly, if you consider sodium hexafluorosilicate Na_2SiF_6 that is also hypervalent molecule. Then how it is octahedral geometry: What happens, it is highly symmetric, what happens this is like almost dynamic process, they keep changing, as a result what happens it looks very stable and the stability comes because of kinetic stability.

So, for example, if the moisture or something tried to attack, there is no vacant site on sulfur. As a result, what happens? SF_6 appears more stable compared to SF_4. Nevertheless, when you heat it and get it off two fluorine atoms, it is vulnerable for hydrolysis. So, SF_6 is a hypervalent molecule and it never employs 3d orbitals in this bonding scheme.

(Refer Slide Time: 23:46)



So, let me stop at this stage. And now with this information on molecular orbital theory, let me switch over to ligand field theory. Of course, ligand field theory is more or less molecular orbital theory, but it has crystal field theory component has also taken, mixing of orbitals that valence bond theory is also taken. So, let me discuss more interesting chemistry based on ligand field theory in my next lecture.