Main Group Chemistry
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Lecture – 11
Structure and bonding aspects: MO Theory

Once again, welcome to MSB lecture series on main group chemistry in my previous lecture. I was discussing about molecular orbital theory and its utility in explaining bonding in simple diatomic molecules such as H 2 to second row p block elements. I told you about how 1 can use MO diagrams to explain bond strength, and bond distance and all those things, by just looking into the number of electrons present in bonding orbitals and number of electrons present in anti bonding orbitals.

So, that will give you some magnitude of bond order based on bond order, bond strength, and bond enthalpy can be accessed. So, now before I proceed further for hetero diatomic molecules or poly atomic molecules let me write MO diagrams for F 2 molecule.

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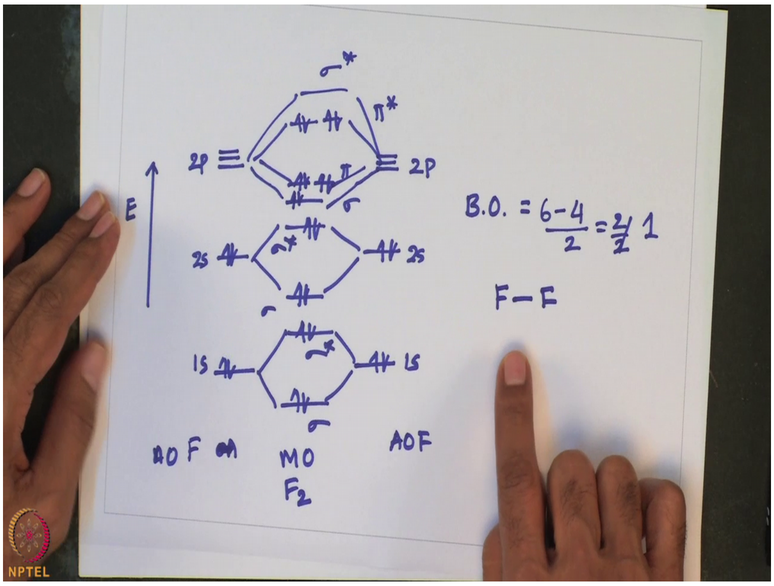

Always remember to write r O to show energy, and here 2p and another 2p from another fluorine atom, then we have 2s 2s and then we have 1s we have 1s. So, here we will make bonding and anti bonding sigma, and sigma star, we have 2 electron here 2 electron here. So, this shows the core electrons do not contribute to the bonding. So, because here the bond order is 0 that is a reason most of the cases we ignore the writing MO diagrams for core electrons.

Now, it is for so, the again sigma and sigma star again we have 2 electron each. So, now, what we have is sigma pi pi another sigma. So, that is sigma star here it is pi star, and here it is pi and it is sigma so now, we have here 5 electrons are there 1 2 like this and now another 4 electrons will come here. So, now, let us look into the bond order this is F atomic orbital, and here atomic orbital of F and MO for F 2.

Let us look into the bond order equals here, this are cancelled no point in counting here. So, we shall count here 2 4 6 minus 4 in anti-bonding so, divided by 2 will give you 2 by 2 1 so, between F and F there is a single bond. So, we should be able to write MO diagram and also depict the bond over here. So, we have a single bond between 2 fluorine atoms in F 2.

So, when we write for a hetro diatomic molecule that results in the formation of a polar covalent compound in these kind of polar covalent compounds bonding molecular orbitals or closer in energy to the atomic orbitals of the more electronegative atom. And also the anti-bonding molecular orbitals will be closer to the energy of atomic orbitals of least electro negative atom for example, I am taking 2 atoms of the same elements then if you take this 1 whether you consider bonding or anti bonding molecular orbital, they are at equidistant from both the energy of both atomic orbitals in the free state or isolated state.

But if I take something like this 1 with low electro negativity higher in energy, and other 1 with more electro negativity lower in energy. So, when they are combined; obviously, when we generate molecular orbitals the bonding molecular orbitals will be closer to the 1 which is more electro negative and; obviously, another anti bonding molecular orbitals will be closer to the atomic orbitals of least electro negative atom something like this.

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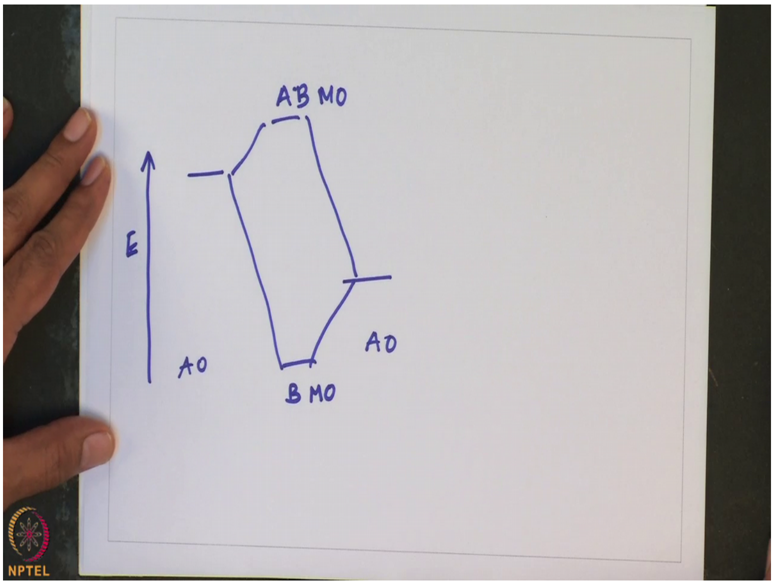

For example if I consider 1 here less electro negative another 1 is more electro negative atomic orbital, and here atomic orbital and if I constitute molecular orbital something like this. So, this is the bonding molecular orbital and this is anti-bonding molecular orbital.

So, here you can see this 1 would be much closer to the energy of isolated atomic orbitals having least electron negativity. So, this 1 should remember always when we write a diatomic molecule or for a covalent compound we should consider the electro negativity and accordingly we should write then energy. So, that is the reason I am telling you we should be extremely careful in always mentioning this arrow, and that mentions about that indicates the energy of the orbitals. Now let me consider 1 such molecule that is NO we have N and ON is little less electro negativity compared to oxygen let me write the MO diagram.

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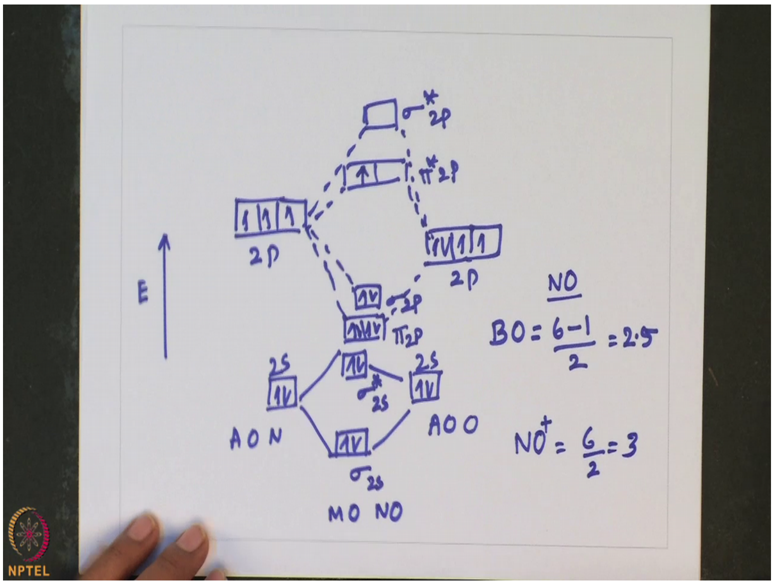

So, here I am considering 2p atomic orbital of nitrogen and little lower in energy 2p atomic orbital of oxygen. And then I am considering here 2s 2s. So, this will give so, this sigma and sigma star of 2 s is completed. So, now, first what we have is here pi 2p and then we have sigma 2p, and then we have pi star 2p and sigma star 2p. So, now we have here 3 electrons 2s to 2p 3 here we have 2s 2p 4.

So, like this now, we have to arrange this 7 electrons. So, this 2 are filled this 2 are filled. So, we have 1 electron that comes here it comes to the pi star anti bonding orbitals. So, let us look into this is MO for NO. Let us look into the bond order bond order equals we have 6 electrons here and 1 electron here, so this is 2.5. So, bond order of NO is 2.5 that is the reason NO has a tendency to loss the loan electron present in anti-bonding orbitals to get extra stability once if you remove that 1 it becomes NO plus when it is NO plus we do not have any electron in this is for NO.

Similarly, if you remove this electron so, it will be NO plus NO plus will be 6 by 2 it will be 3. So, N O bond is getting stabilized that is the reason and this NO legend as a tendency to act as a cationic legend by eliminating the electron present in the anti-bonding orbital; that means, about the character about the reactivity and properties of molecules can be predicted simply by writing MO diagrams and looking into the electronic arrangement in the bonding and anti-bonding orbitals ok.

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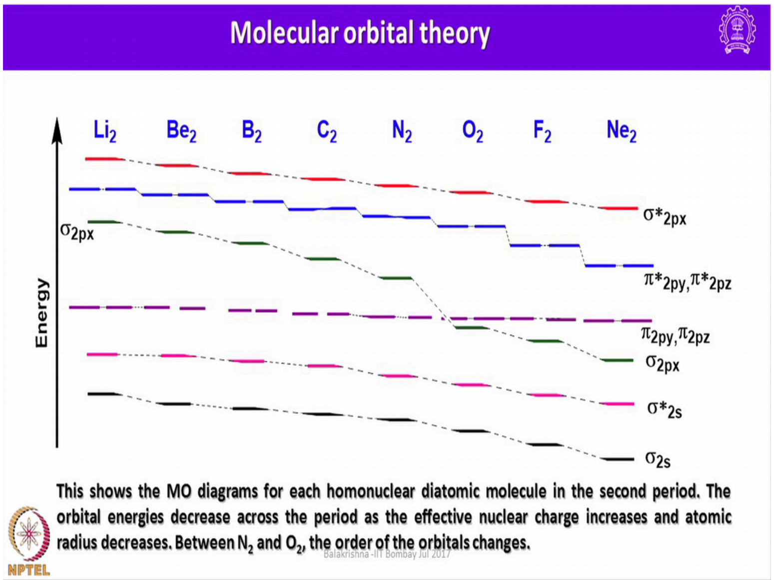

Molecular orbital theory

This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.

So, this diagrams what I have shown shows the relative energy of various atomic orbitals, and when they form diatomic molecules especially I have given here for second row elements, how that is changing gradually. We can see as we move from left to the right of the periodic table the electro negativity studily increasing as a result what happens electrons are coming more and more close to the nucleus, because of the increased effective nuclear charge as a result what happens the shells in which the electrons are present are also orbitals are also pulled more closer towards the nucleus.

In this context what happens the energy studily drops you can see here from starting from lithium to neon energy studily dropping at N2 it crosses here, you can see here this sigma will be lower in energy compared to 2 that is p z will be lower in energy that, then this will be in higher energy, this is what exactly happens that is reason I wrote 2 different diagrams for molecules up to nitrogen, and nitrogen onwards oxygen fluorine and neon and the trend changes the sigma p will be sigma 2p will be lower in energy compared to pi 2 p. So, this 1 should remember and also this diagrams is there in most of the textbooks you can just have a look at it ok.

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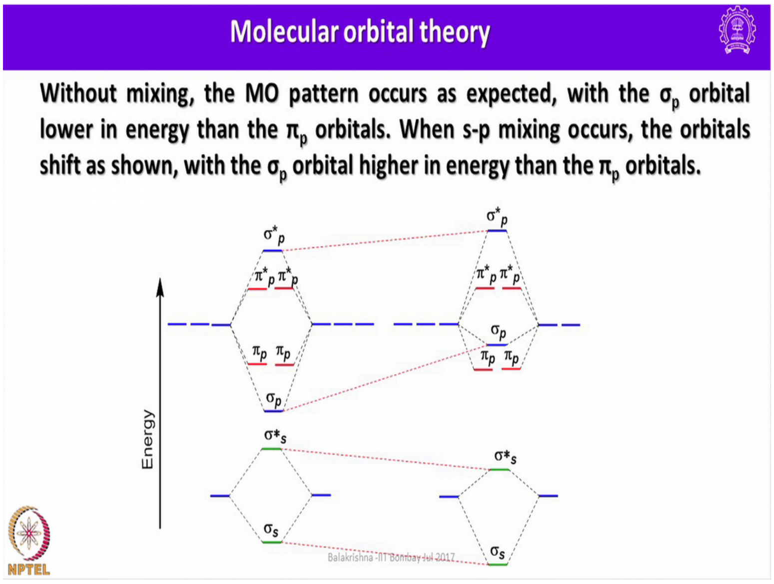

Molecular orbital theory

Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the π_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

So, in this 1 just I have shown here as the electro negativity increases, as the orbitals comes more and more towards the nucleus there is a possibility of mixing of atomic orbitals even before the molecules being formed. So, here without mixing MO patterns occurs as expected here. I have shown MO diagrams with mixing without mixing the first 1 is here without mixing you can see here without mixing is similar to what I wrote for several molecules, in my last lectures and also here due to the mixing basically what happens the s p mixing occurs the orbitals shift is shown here.

So, sigma orbital will be higher in energy than the pi p orbitals as a result you can come across some sort of mixing and more refined molecular orbitals. In fact, show mixing of s as well as p z while the formation of sigma orbital and also. Similarly p x p y do not mix with s orbital. So, I will show you some more MO diagrams where we can visualize how this mixing occurs prior to the formation of molecular orbitals with this so, let me write MO diagrams for water molecule. So, in water we have 2 hydrogens having 1s electron each will be combining with oxygen to form 2 OH bonds from VSEPR theory. As well as valence bond theory we know the fact that oxygen in water is tetrahedral with 2 lone pairs and 2 bonded pairs, and the shape of water molecule is bent or v shaped ok.

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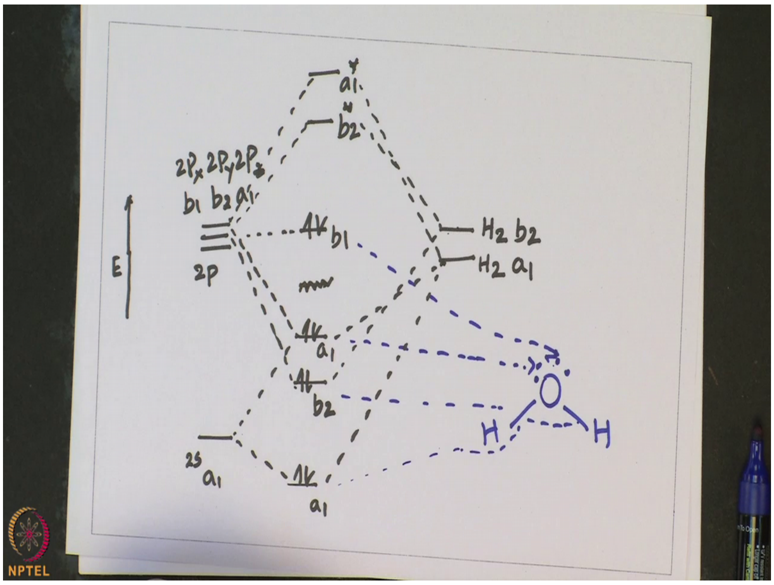

So, here I am considering 2p orbitals of oxygen, and then here I am considering 2s orbitals here, legend group orbital we are considering and here 1 and another 1 here, and of course here we call this H 2 bonding and H 2 anti-bonding. So, this is with a 1 symmetry this is with b 2 symmetry and this are all called mulliken symbol at present you may not be familiar with what is a 1 what is b 2, how this mulliken symbols are given for that 1 should have the knowledge of group theory perhaps, when you study group theory. And when you go for understanding the spectroscopy futures of coordination compounds I am sure you will understand mulliken symbols right.

Now I am not go into dig deep into the mulliken symbols simply we should remember here, we have mulliken symbols for this 1 this is for bonding H 2 we have a 1 and anti-bonding we have b 2. And now we are considering of course, here we have 2p x 2p y and 2p z. So, for this also 2p x is called as b 1 symmetry and 2p y as b 2 symmetry, and 2p z as a 1 symmetry. And of course here, s always as a 1 symmetry. And now we are considering here we have total of 2 electrons are coming from 2 hydrogen atoms, and now we have here 6 electrons are coming from oxygen ok

So, let me write them here so this is a 1 and this is b 2 and this is a 1 this is not there ignore this one, this is b 1 and this is b 2 and this is a 1 so, this 2 are anti-bonding. So, here now I start filling so total we have to this is not there. So, what we have is 6 electrons here plus 2 8 electron are there we start fill those things 2 electrons are here, and 2 are here, and 2 more are here and 2 more are here. So, now, let me start connecting this 1.

So, we have to connect now the similar ones a 1 so, a 1 and of course here also a 1 is there it should be connected now b 1 is there. So, b 2 is from here we should connect to this 1 and b 2 is also here, it should be connected. And now b 1 we do not have any so, it remains as non-bonding b 1 the corresponding we do not have it remains as nonbonding. So, now, b 2 is connected here, and a 1 is connected here, and then a 1 is connected here, and b 2 is connected here ok.

So, now let us look into these diagrams here this represents this 2 electron here, and this 2 electron represent, the presence of 2 OH bonds. And then these 2 electrons and these 2 electrons represent the 2 lone pairs present on oxygen atom in water molecule for example, if I write something like this I can simple correlate this one to this one of this bond, and this one to one of the other bond.

And then we have 2 lone pairs, so one of this 1 will be represent this lone pair, and another 1 represent this lone pair. So, this is how you can clearly write the MO diagram for even a triatomic molecule like water of course, 1 can also write for poly atomic molecules, that I will be considering in in a few minutes time hope you have understood how to write the MO diagram for water molecule. Now other we discussed NO plus as a stronger NO bond, because bond order is 3 whereas, in simple N O where due to the presence of 1 electron in the anti-bonding orbital it as a bond order of 2.5.

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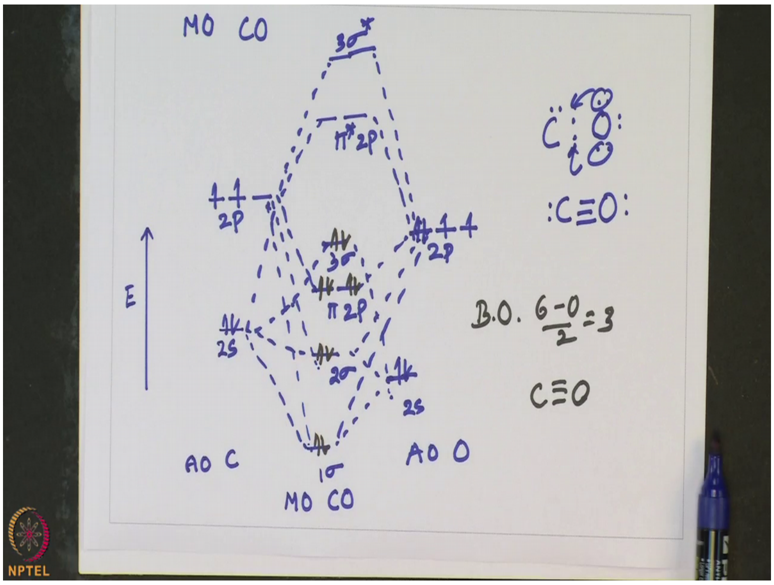

Now, let us consider another important molecules such as CO, MO for CO molecule MO diagram for CO molecule. So, here we have carbon and oxygen; oxygen being a more electro negative, its energy both 2s and 2p energy will be relatively lower compared to the energy of 2s and 2p so, we have to keep that in mind always. So, here let me write 2s for C atomic orbitals of carbon. And then I write here for 2p and then relatively lower level I write for oxygen and also 2s for oxygen atomic orbitals of oxygen here, and here we have 4 electrons in this case we have 6 electrons ok.

So, first there will be I am showing you the mixing now both 2s and 2p they mix, and just remember with which orbital 2s is mixing and what is a nature of that bonding whether it is a sigma bonding or pi bonding. So, here let me write relative energies one here, one here so here it is sigma equal to 1 sigma here 2 sigma and pi 2p and 3 sigma pi star 2p and 3 sigma star. So, this another way of representing.

So, now this 2 has to be connected here and then this also it connected this one and this also shows connection with both, and then this also shows connection with this one whereas, this 1 there is no connection from 2p, because 2s will not participate in pi bonding, but 2s can correspond to this one. So, like this let me start writing the electrons here, and then here to 4 and then here we have total 6 electrons.

Now, the bond order this is for MO for CO I will show you again. So, 2p we have 2 electrons, and 2p we have 4 electrons it is little lower in energy, and then we have 2s orbital and 2s orbital here both have 2 electrons. Now 2s has symmetry for sigma all sigmas interact with 2s, it is head on entry and overlapping. So, here all are connected whereas, pi does not connect with 2s. So, it shows on the interaction of this 2p orbitals of carbon as well as oxygen to form. Now we have total of 4 plus 6 8 electrons are there they are filled here 2 4 6 8 ok.

So 8 electrons are there now let us look into the bond order 6 minus 0 by 2 this is 3. So, this represents very clearly 3 bonds between carbon and oxygen out of which 1 is sigma and 2 are pi that can also be seen here, same information we got from valence bond theory and also when we look into Lewis dot structure. This is how we wrote initially so here the total number of 10 electrons. So, here this 2 are coming here and this 2 are coming here in order to give octate for both so as a result we had this kind of situation. So, here these 2 lone pairs on carbon makes carbon monoxide, a soft Lewis base, and here you can see triple bond is there same information we are also getting from carbon monoxide MO diagram ok

So in my next lecture, so I would discuss about more interesting molecules such as carbon dioxide and BH 3 BF 3 and also hexa coordinated sulfur compound, sulfur hexa fluoride very interesting. And also we can make an analogy of the geometry and the structure information we get for a (Refer Time: 25:08) 6 for MO diagram to the what we have predicted is octahedral geometry from valence bond theory using hybridization concept. Let us consider those two things and whether any difference is there are when a whether any abnormally is there, we shall look into those things in my next lecture until then have a pleasant chemistry of reading.

Thank you.