Main Group Chemistry
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Lecture – 09
Structure and Bonding aspects: Mo Theory

Welcome to the lecture series by MSB on the chemistry of main group elements, in my previous lecture spoke about the Valence Bond theory essentially based on hybridization concept and it is utility in main group compounds to understand structure and bonding including the geometry and shape. Today let me continue the discussion on structure and bonding and proceed to another important theories that is molecular orbital theory, before that let me say about the limitations of valence bond theory and of course, we saw valence bond theory using hybridization concept very effectively explains the geometry and shapes of most of the molecules of main group compounds and to an extent transfer metal compounds as well.

But; however, there are some serious limitations of application of Valence Bond theory as far as coordination compounds are concerned and too an extent in case of main group compounds as well what are the limitations let us look into those things and proceed to the next molecular orbital theory concept. The major limitation of Valence Bond theory is it does not explain the colour of the compounds that is spectral properties and also it does not explain fully the magnetic properties.

For example the temperature dependence of magnetic properties and all those things are not fully explained and it only gives an idea about calculating spin only magnetic movement values and in general Valence Bond theory gives more emphasis for localized bonding concept. So, in view of this one molecular orbital theory was proposed and it takes all the best parts of Valence bond theory, Vsepr theory, Crystal field theory and made it very refined theory to explain almost all aspects concerned with the main group as well as trans metal compounds and the reactivity as well.

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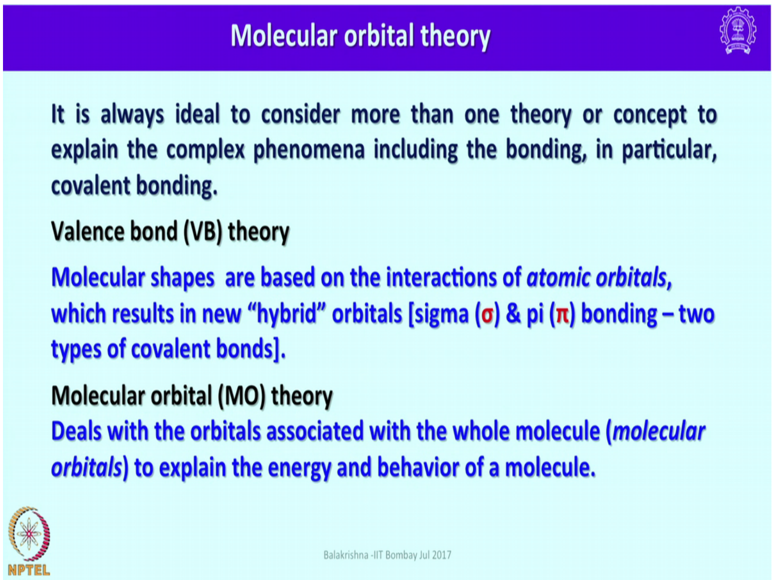

Molecular orbital theory

It is always ideal to consider more than one theory or concept to explain the complex phenomena including the bonding, in particular, covalent bonding.

Valence bond (VB) theory

Molecular shapes are based on the interactions of *atomic orbitals*, which results in new "hybrid" orbitals [sigma (σ) & pi (π) bonding – two types of covalent bonds].

Molecular orbital (MO) theory

Deals with the orbitals associated with the whole molecule (*molecular orbitals*) to explain the energy and behavior of a molecule.

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Let us start look into those things keeping in whatever I mentioned about the previous structure and bonding concepts we came across it is always ideal to consider more than one theory or one concept to explain the complex phenomena that occurs in a molecule in particular bonding. According to Valence bond theory molecular shapes are essentially based on the interaction of atomic orbitals, which results in new "hybrid" orbitals and which can explain both sigma bonding as well as pi bonding.

Whereas Molecular orbitals theory essentially deals with the orbitals associated with the whole molecule that is we call it as molecular orbital that results due to the combination of atomic orbitals of the atoms that are combined to make a molecule.

To explain the energy and behaviour of a molecule this is the major difference between the valence bond theory and molecular orbital theory.

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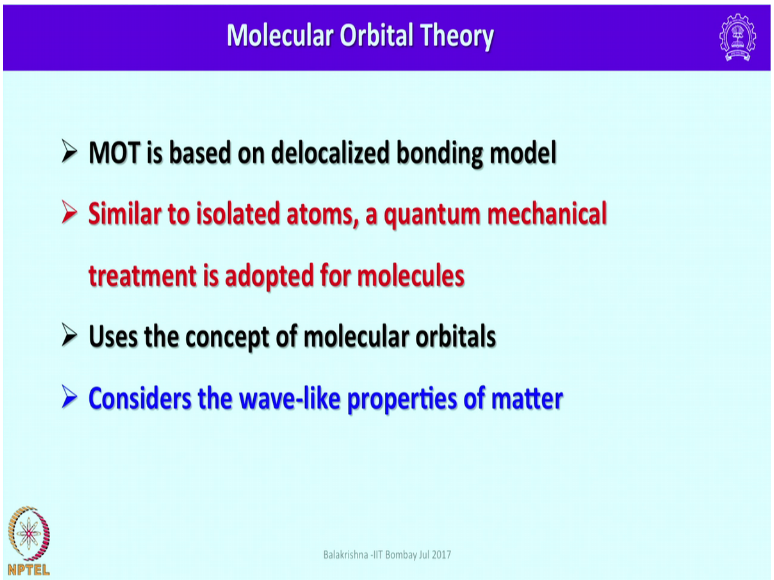

Molecular Orbital Theory

- MOT is based on delocalized bonding model
- Similar to isolated atoms, a quantum mechanical treatment is adopted for molecules
- Uses the concept of molecular orbitals
- Considers the wave-like properties of matter

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And Molecular Orbital Theory is based on delocalized bonding model that is very very important and similar to isolated atoms a quantum mechanical treatment is adopted for molecules as well uses the concept of molecular orbitals and here considers the wave like properties of matter.

So, let us look into the themes of molecular orbital theory a molecule is considered on a quantum mechanical level.

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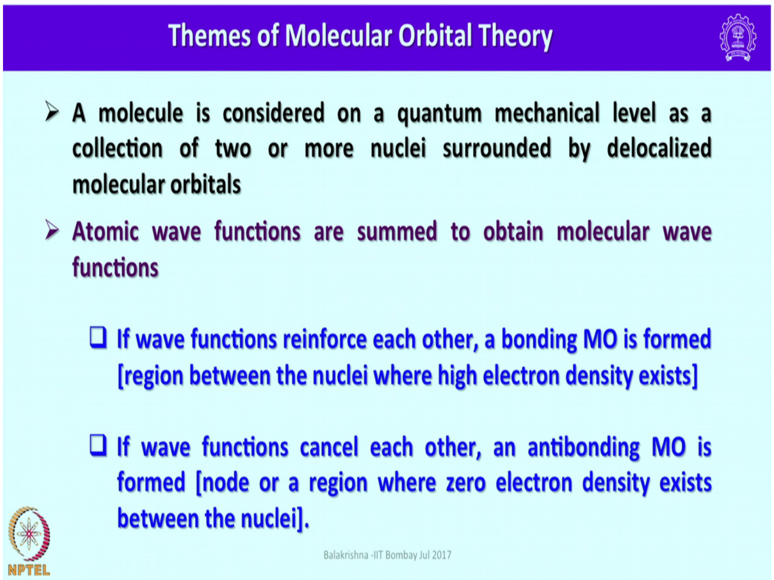

Themes of Molecular Orbital Theory

- A molecule is considered on a quantum mechanical level as a collection of two or more nuclei surrounded by delocalized molecular orbitals
- Atomic wave functions are summed to obtain molecular wave functions
  - ☐ If wave functions reinforce each other, a bonding MO is formed [region between the nuclei where high electron density exists]
  - ☐ If wave functions cancel each other, an antibonding MO is formed [node or a region where zero electron density exists between the nuclei].

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A molecule is considered on a quantum mechanical level as a collection of 2 or more nuclei surrounded by delocalized molecular orbitals generated as a consequence of mixing of atomic orbitals; that means, atomic wave functions or some to obtain molecule wave functions.

If wave function reinforce each other, that is couple each other, a bonding MO bonding molecular orbital is formed; that means, the region between the 2 nuclei where high electron density exist in molecular orbitals that is called bonding molecular orbitals. If wave functions cancel each other, an antibonding molecular orbital is generated; that means, in a node or a region where 0 electron density exits between the nuclei is also referred to as antibonding molecular orbitals.

We should remember when atomic wave functions are summed up we get bonding molecular orbitals, when the atomic wave functions are subtracted in antibonding molecular orbital is generator.

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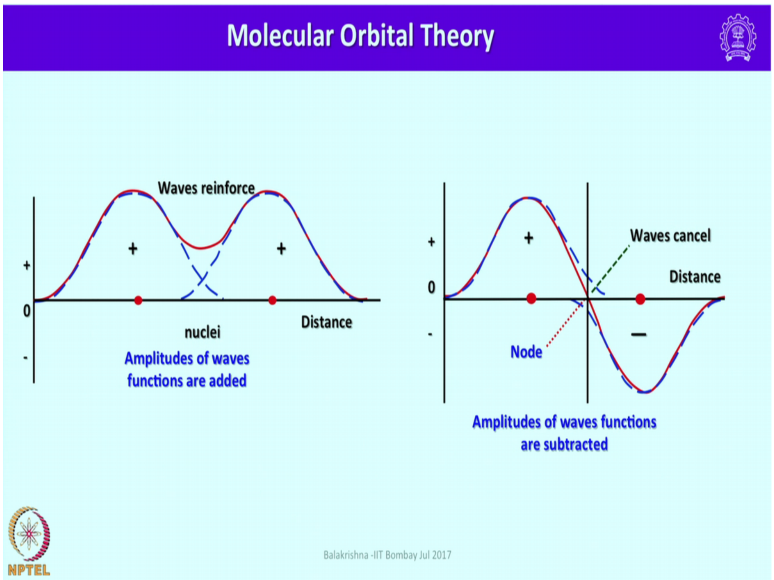

Molecular Orbital Theory

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You can see here in this picture in the first one you can see clearly this is due to the summation of that atomic orbitals here a bonding molecular orbital is generated. So, Amplitude of waves is wave functions are added here. So, Amplitude of wave functions of 2 nucleus interact in together is added where as in this case Amplitude of wave functions are subtracted. So, amplitude of wave functions are subtracted, this represent Antibonding molecular orbitals and this represent the bonding molecular orbital.

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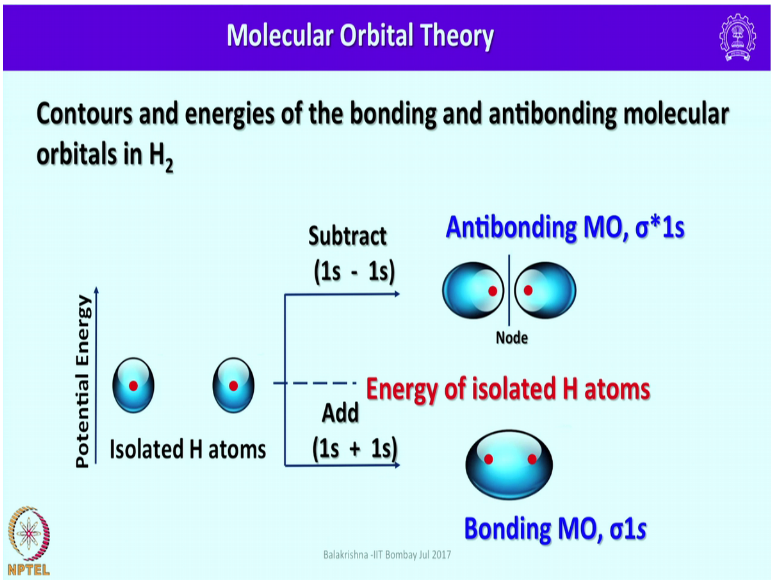

Molecular Orbital Theory

Contours and energies of the bonding and antibonding molecular orbitals in H_2

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So, let us look into the contours and energies of the bonding and Antibonding molecular orbitals of a simple diatomic molecules such as H2. So, here we are considering the 1s orbital of hydrogen atom. So, there interacting so; that means, here when you sum of the wave functions of both are atoms are added.

So, that and or they can be subtracted when they are added it generates the bonding molecular orbitals where the electron resides between these 2 nuclei whereas, here antibonding molecular orbital is generated and here a nodal region; that means, 0 electron density exist between the 2 nuclei and of course, when we combine 2 atomic orbital bonding molecular orbital always have much lower in energy where as the antibonding molecular orbital will be having higher energy than the energy of 2 atomic orbitals that are combined in generating these 2 bonding and anti bonding molecular orbitals.

For example if 2 atomic orbitals are here and you are generating 2 molecular orbitals one is bonding another is antibonding this will be much lower in energy than this 2 and this is higher in energy than this to draw mo diagram involving say 4 set of orbitals.

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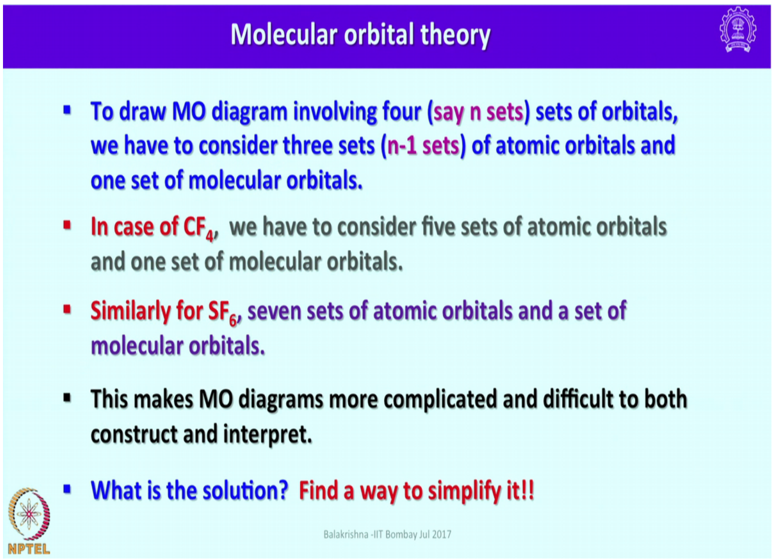

Molecular orbital theory

- To draw MO diagram involving four (say n sets) sets of orbitals, we have to consider three sets (n-1 sets) of atomic orbitals and one set of molecular orbitals.
- In case of CF_4, we have to consider five sets of atomic orbitals and one set of molecular orbitals.
- Similarly for SF_6, seven sets of atomic orbitals and a set of molecular orbitals.
- This makes MO diagrams more complicated and difficult to both construct and interpret.
- What is the solution? Find a way to simplify it!!

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We have to consider 3 sets of atomic orbitals and one set of molecular orbital for example, let us consider the case of CF4 or CH4 we have to consider here 5 sets of atomic orbitals; that means, 4 sets of atomic orbitals are coming from 4 fluorine atoms and 1 set is coming from carbon and then that generates 1 set of molecular orbitals.

Similarly, if you consider sulphur hexafluoride we have to consider 7 sets of atomic orbitals 6 from chlorine atoms and 1 from sulphur to generate 1 set of molecular orbitals. So, this makes MO diagrams much more complicated and difficult to both construct and interpret; that means, we find a solution to simplified it, how to simplify it.

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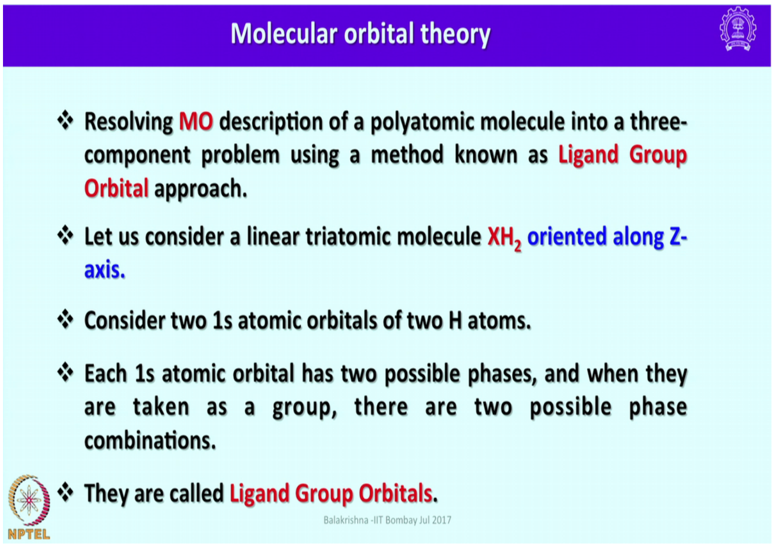

Molecular orbital theory

- Resolving MO description of a polyatomic molecule into a three-component problem using a method known as Ligand Group Orbital approach.
- Let us 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.

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So, resolving MO description in particular polyatomic molecules into 3 component problem using a method to known as Ligand Group Orbitals of course, Ligand Group Orbitals are extensively used in coordination compounds.

Let us consider a linear triatomic molecule having composition XH 2 oriented along z direction. So, consider 2 1s atomic orbitals of 2 hydrogen atoms each 1s atomic orbital has 2 possible phases and when they are taken as a group they are essentially 2 possible phase combinations their essentially leads to 2 possible phase combination essentially they are called Ligand Group Orbitals. So, this combination 2 possible phase combination that results is nothing, but Ligand Group Orbitals.

So, number of atomic orbitals combined is equal to the number of molecular orbitals generated or producer for example, if I am using 4 atomic orbitals and then I will be having 4 molecular orbitals out of which 2 maybe bonding, 2 will be antibonding the energy of bonding molecular orbits will be lower than that of the isolated atoms the energy of antibonding molecular orbitals will be higher than those of isolated atoms.

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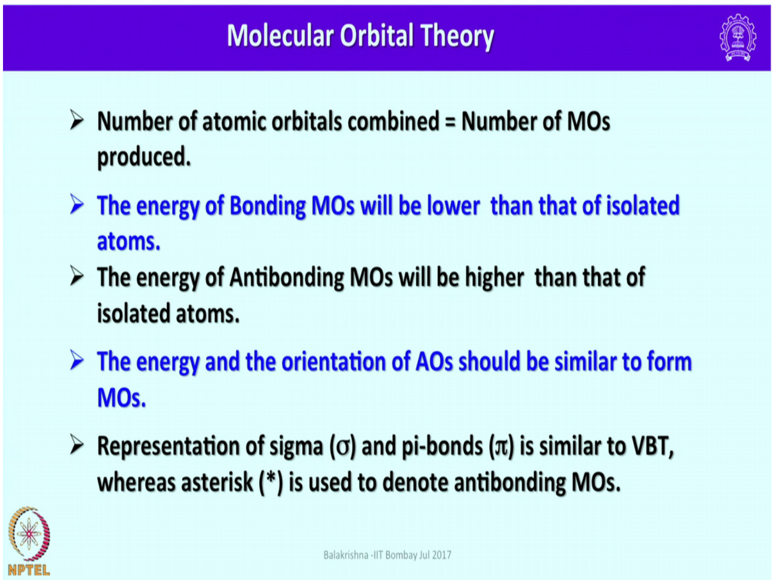

Molecular Orbital Theory

- 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.

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The energy and the orientation of atomic orbital should be similar to form molecular orbitals; that means, when we are combining 2 atomic orbitals from 2 isolated atoms their energy should be comparable.

For example energy should be somewhere here or there it should not be something like this in this case essentially effective molecular orbitals cannot be generated because the energy difference between these 2 combining atoms will be quite considerable. So, in that case actually there is no bonding takes place.

So, representation of sigma and pi bonding is very similar to valence bond theory whereas, in case of molecular orbital theory we are using asterisk that is star to denote antibonding molecular orbitals for example, if I say simply sigma it is bonding orbital and if I put a superscript star sigma star or pi star essentially they represent antibonding molecular orbitals.

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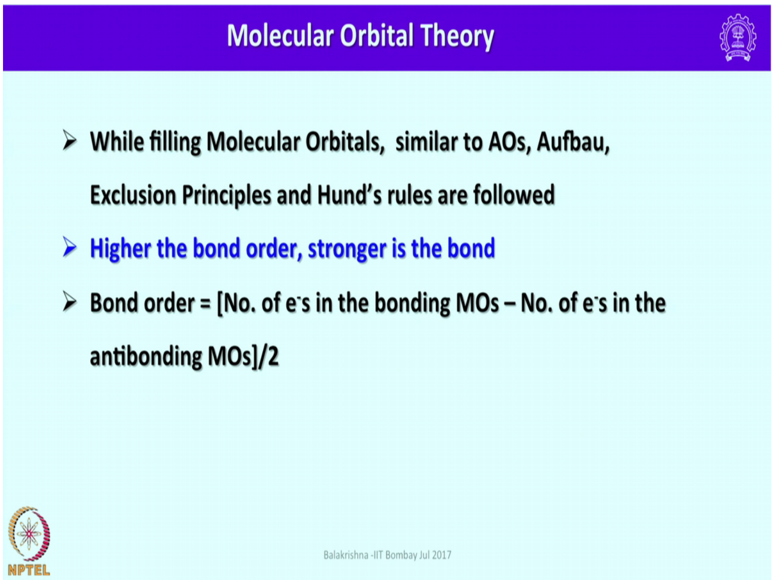

Molecular Orbital Theory

- While filling Molecular Orbitals, similar to AOs, Aufbau, Exclusion Principles and Hund's rules are followed
- Higher the bond order, stronger is the bond
- Bond order = [No. of e^-s in the bonding MOs – No. of e^-s in the antibonding MOs]/2

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While filling molecular orbitals they are generated as a combination of atomic orbitals similar to atomic orbitals, Aufbau and exclusion principles and also Hund's rules are strictly followed; that means, whatever the method we are following rules were following while considering the filling of the atomic orbitals of isolated atoms the same strategy is used while filling molecular orbitals with the electrons that are coming from the both the combining atoms.

So, higher the bond order stronger is the bond. So, bond order equals number of electrons in the bonding molecular orbitals minus number of electrons in the antibonding molecular orbitals divided by 2, bonding and antibonding molecular orbitals for core electrons cancel each other for example, if I take 2 electrons from one atomic orbital and 2 electrons from another atomic orbital.

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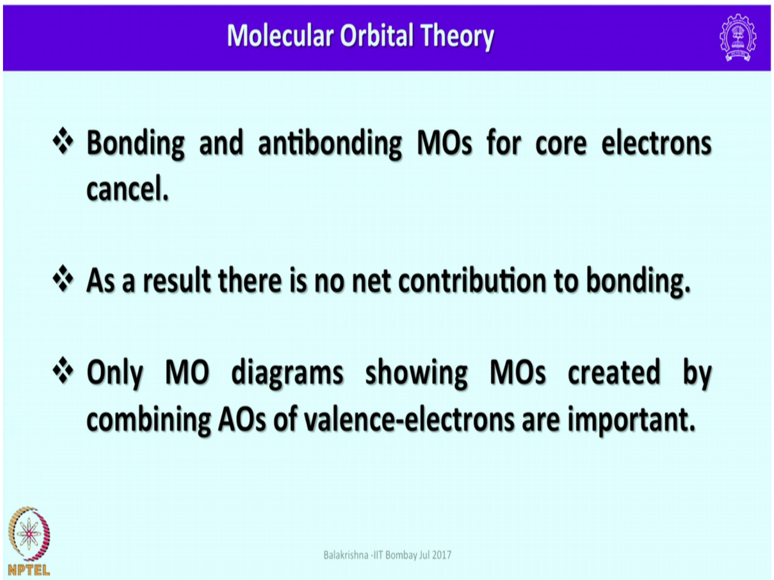

Molecular Orbital Theory

- Bonding and antibonding MOs for core electrons cancel.
- As a result there is no net contribution to bonding.
- Only MO diagrams showing MOs created by combining AOs of valence-electrons are important.

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And I generate 2 molecular orbitals one here, one here, both of them will be having 2 electrons each as a result net bond order is zero; that means, does not exist any bond that is what it says the bonding and antibonding molecular orbitals for core electrons cancel each other as a result we are not considering them towards net bonding in a molecules; that means, there is no net contribution coming from the core electrons.

Only MO diagrams showing molecular orbitals created by combining atomic orbitals valence electrons are very very important; that means, when we look into the reactivity of the molecule bonding bond strength we have to consider or give emphasis only for the atomic orbitals having valence electrons.

Let us draw MO diagram for simple molecules.

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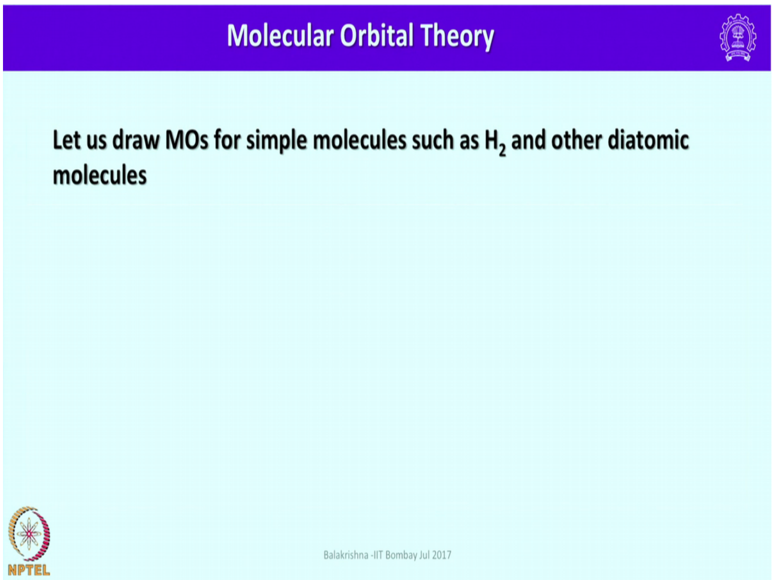

Molecular Orbital Theory

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

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Such as H2 and then we can continue writing for other higher poly atomic molecules let me start with the simplest diatomic molecule that is H2.

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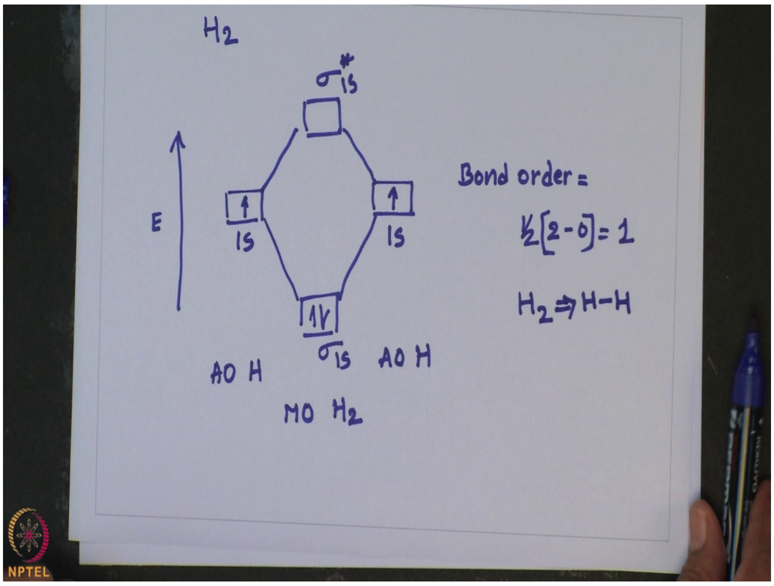

In case of H2 we are considering 2 hydrogen atoms having 1 electron each in their respective 1s atomic orbitals.

This is energy, here this is 1S and this is 1S we have 1 electron each. So, these 2 will combine together to generate 2 molecule orbitals. So, this is called sigma 1S this bonding molecular orbitals, this is atomic orbital of H, this is atomic orbital of H and this is molecular orbital of H 2. So, this is how one should write and now these 2 electrons will come here and bond take place and next here it is sigma 1S star this represent antibonding. If you calculate the net bonding in this one bond order equals half 2 electrons minus here 0 electrons equals 1. So, net bond order is 1, that 1 should write H2 molecule has H H. So, this is how one can write MO diagram for H2 molecule.

So, let us predict the stability of some molecular as well as ionic species using the same molecular orbital diagram.

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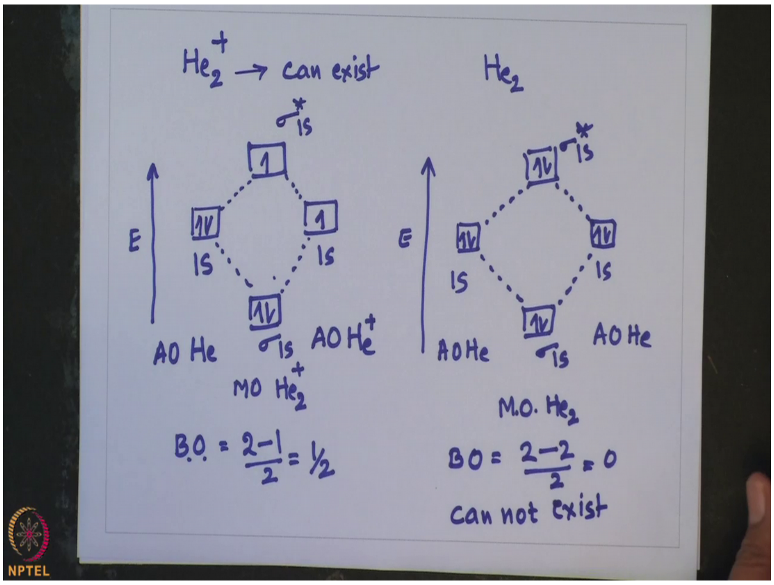

Now, I am considering He2 plus so; that means, I am considering He2 I am considering He2 plus; that means, we have 2 helium atoms one comes with 2 electrons and another one comes with 1 electron.

Of course always we should remember to write here one. So, here I am considering atomic orbital of helium here 2 electrons are there here, I am considering atomic orbital of helium plus; that means, 1 electron is removed. So, we have only 1 electron now I should consistent MOs. So, 2 atomic orbitals are combining to give 2 molecular orbitals one is bonding, one is antibonding and again same sigma 1s and sigma 1 s here. So, I am putting 2 electrons here.

So, now we are left with 1 electron this will go to antibonding. So, now, let us this is MO of He2 plus, now, let us look into the bond order equals 2 electrons here minus 1 electron divided by 2 here, it is half bond order is half; that means, this He2 plus can exist here if I have a question say predict whether He2 plus species exist are not since it has a net positive bond order it can exist.

Let us look into now He2, again here what I am doing is I am considering the both helium atoms having 2 electrons each another one here 1S. So, atomic orbital of He, atomic orbital of He and here I am writing MO molecular orbitals of He2. So, here 1S, here 1S, this is 2 electrons are there and 2 electrons are here. So, now, let us look into the bond order equals 2 here and 2 here by 2 equals 0.

So, cannot exist we can simply conclude that He 2 cannot exist. So, this is predict using simple MO diagrams whether a molecular can exist a molecular ionic species can exist are not.

So, let us continue with this exercise using MO diagrams predict whether Li 2 and Be 2 can exist are not.

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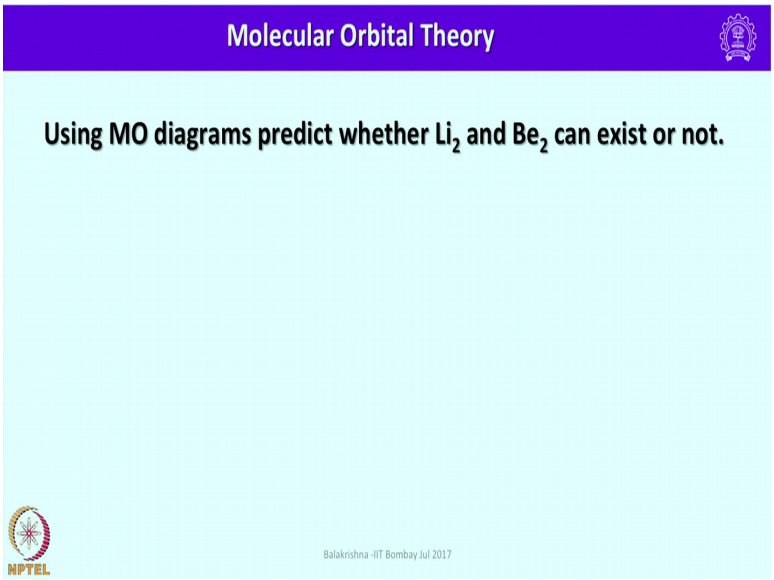

Molecular Orbital Theory

Using MO diagrams predict whether Li_2 and Be_2 can exist or not.

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The question is using MO diagrams predict whether Li 2 and Be 2 can exist or not.

So, let us look into now Li.

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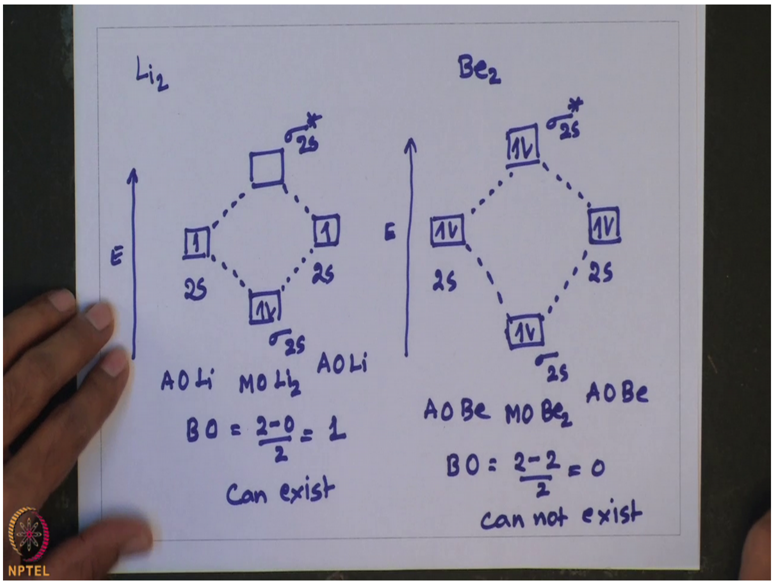

So, what we have is here the same exercise we should continue this is it represents energy we are now considering the valence shell of lithium having 1 electron in it 2S orbital and similarly we are also considering 2 such lithium atoms having 1 electron each and they combine together to form 2 molecular orbitals this is sigma 2S star where as this is sigma 2S.

So, we join them and in homo diatomic molecules the energy of both the atom that are combine will be having the same energy and these 2 will be equidistance from both the atoms this distance will differ depending upon the electro negative difference of 2 atoms that are combining those cases comes when we look into hetrodiambic molecules or poly atomic molecules. So, now, we have 2 electrons here and no electron here, this is atomic orbital of lithium, this is atomic orbital of lithium and this 1 is molecular orbital of lithium 2.

So that means, here if we calculate the bond order that is equals to 2 minus 0 by 2 equals 1, can exist. So, now, let us look into beryllium 2; that means, diberyllium molecule same exercise we should follow and in case of beryllium we have 2 electrons in the valence shell that is the electronic configuration is 1S2, 2S2 we have 2 electrons we are combining to make 2 molecular orbitals. So, this is sigma 2S star this is sigma 2S. So, this 2 electrons will come here another total up we have 2 electrons.

So, here atomic orbitals of beryllium atomic orbitals of beryllium and here MO molecule orbitals of beryllium 2 plus. So, now, let us look into the bond order equals 2 here minus 2 here divided by 2 equals 0. So, we can simple say beryllium diberyllium cannot exist. So, this is how we can easily write the electronic configuration from that one we can derive the molecular orbitals starting from the corresponding atomic orbitals and we can say we can talk about bond order and also we can conclude whether this molecule or ionic species exist or not.

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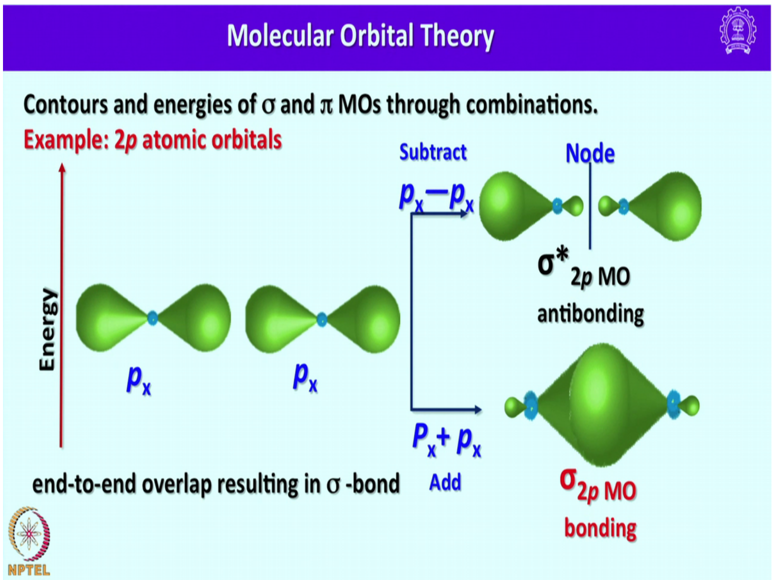

Molecular Orbital Theory

Contours and energies of σ and π MOs through combinations.

Example: 2*p* atomic orbitals

end-to-end overlap resulting in σ -bond

So, now I would show you the contours and energies of sigma and pi molecular orbitals through combination if you just look into the previous diagrams just I made box diagrams and I wrote actually how this electrons in a particular orbital interact while generating molecular orbital for example, I have considered 2 p atomic orbital in this case we can see the diagrams.

I have shown here 2 such 2 p x atomic orbitals are oriented in this from 2 atoms and here this is called end to end overlap or head to head overlapping essentially always this end to end overlap or head to head overlap results in sigma bond formation and again one can write bonding molecular orbitals as well as antibonding orbital. So, how this contours appears can be visualized from this diagram here you can see when the wave functions of both p x are added here it generates a sigma 2 p molecular orbital having the electron density residing at the middle of 2 nuclei.

Whereas in this case when you subtract it generates antibonding molecular orbitals that is sigma star 2 p where a node or 0 electron density exist between 2 combining nuclei. So, this is how one can show the contours and energy of sigma molecular orbitals in the next slide I will be showing you the pi hope it is clear for you. So, here 2 are combined together to generate bonding molecular orbital and at the middle where the bulge portion is there electron density resides there and in this one you can see a node is generated where there is no electron density this is sigma antibonding molecular orbital.

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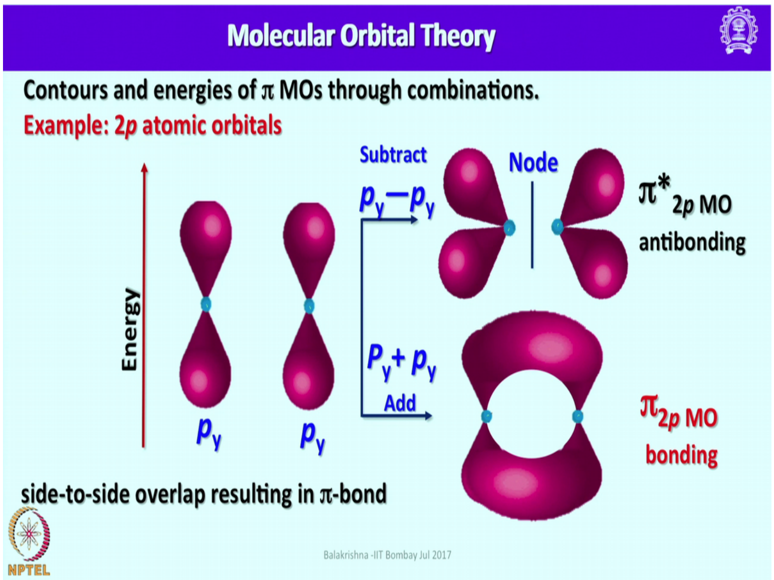

Molecular Orbital Theory

Contours and energies of π MOs through combinations.

Example: 2*p* atomic orbitals

side-to-side overlap resulting in π-bond

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So, since they are orthogonal to each other if you bring 2 atoms close to each other if p z is interacting you know head to head in that case remaining p y and p x orbital can have only the sideways overlapping so; that means, now side to side overlapping also results in covalent bonding and that we call it as pi bond we can see here when the wave functions of both of them are added here it generates a bonding molecular orbital of this shape here, this is called pi 2 p molecular orbital bonding.

Similarly, here electron density resides whereas, here a node is generated between the 2 combining orbital and this is called pi star 2 p molecular orbital antibonding. So, you can you can just differentiate between the sigma and the pi using these diagrams. So, these diagrams clearly show the contours and energies of sigma as well as pi molecular orbitals generated through the combination in different orientations.

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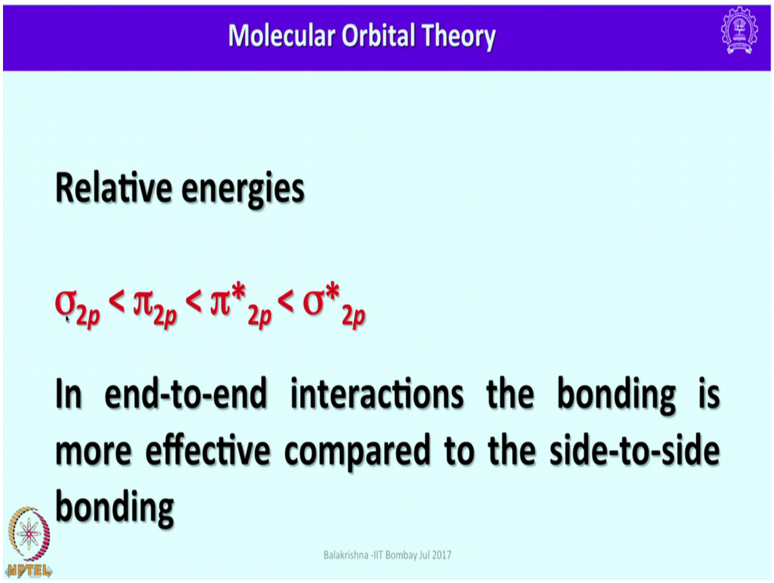

Molecular Orbital Theory

Relative energies

$\sigma_{2p} < \pi_{2p} < \pi^*_{2p} < \sigma^*_{2p}$

In end-to-end interactions the bonding is more effective compared to the side-to-side bonding

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So, let us look into the relative energies the relative energies will be in this order sigma 2 p is less than pi 2 p is less than pi star 2 p less than sigma star 2 p and there can be some variation in end to end interaction the bonding is more effective; that means, sigma bonding is much more stronger compare to the pi bonds the end to end interaction the bonding is in end to end interactions the bonding is more effective and bonds are much stronger compare to the side to side bonding.

So, relative mo energy levels for second row homo nuclear diatomic molecules I am going to write down now. So, that will give you some idea for example, let us consider diatomic molecular species of all elements in the second row of course, first one should write energy here.

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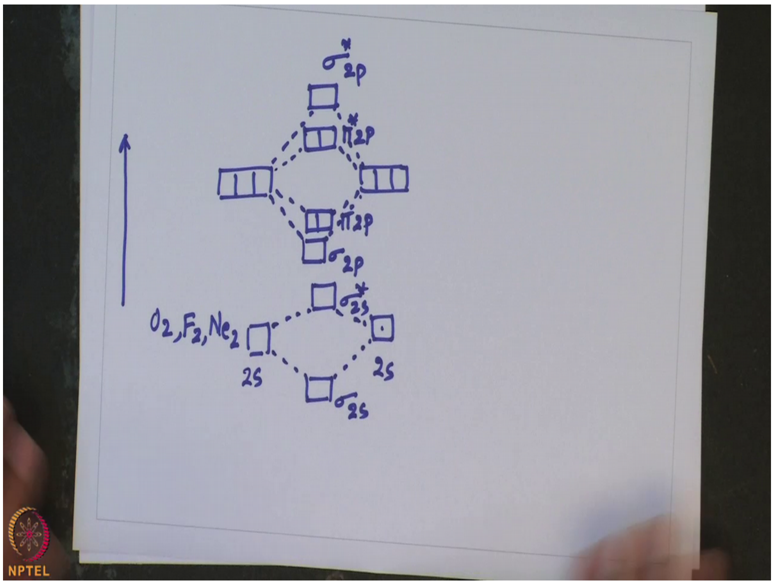

First I am considering O2 F2 and Ne 2. So, here what we have is 2 p and another 2 p since it is a diatomic homo diatomic molecules the energy should be same. So, here it is splits into sigma component as well as pi component we have here sigma and then we have here pi and similarly we have here sigma and of course, here sigma star 2 p and it is pi star 2 p and sigma 2 p and pi 2 p.

So, I can just show them like this because of lack of space I have brought them close to each other it does not mean that they are much closer in this one it is not according to some scale because I have to write mo diagram for 2S as well here we have sigma star 2S and this diagram holds good for diatomic species generated for oxygen fluorine and neon.

So, in my next lecture I will be discussing about the remaining second row elements such as boron, carbon and nitrogen that is B2, C2 and N2 what would happen in those cases whether they have similar energy order or there will be some difference and let me discuss all those things in detail in my next lecture. So, have a pleasant reading.

Thank you very much.