

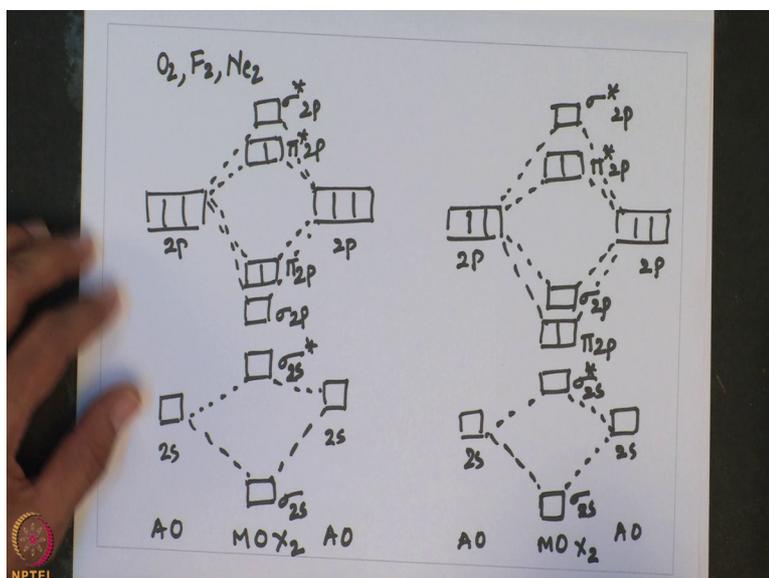
**Main Group Chemistry**  
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**Lecture – 10**

**Structure and bonding aspects: MO Theory**

I once again welcome you to MSP lecture series on main group chemistry. In my previous lecture I was discussing about molecular orbital, while discussing molecular orbital theory I wrote a general MO diagram for second row diatomic molecules for oxygen, fluorine and neon. Let me write now MO diagram for beryllium, carbon and nitrogen diatomic species that is B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub>. Since, I am going to compare the MO diagrams for diatomic molecules such as O<sub>2</sub>, F<sub>2</sub> and Ne<sub>2</sub> with B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub>. Let me write the MO diagrams for both here so that comparison becomes much easier.

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So, here in this case the lower energy 1 will be sigma 2p then we have pi 2p and then pi 2p, pi star 2p and then sigma star 2p. So, and then of course, we have 2 electron in 2s orbital, that also should be considered. This is sigma 2s anti bonding and sigma 2s bonding. So, like this we can write this is for 2s, this for 2s and this is for 2p and this for

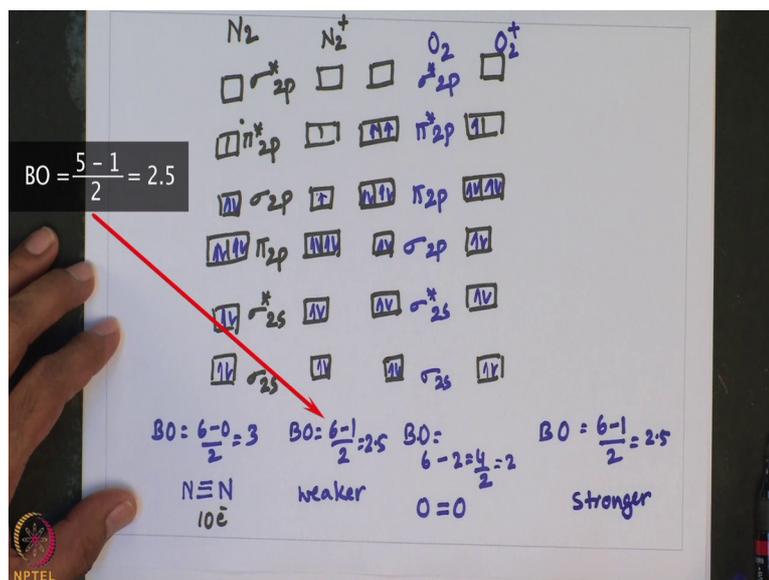
2p. So, this how one can write the MO diagram, this is atomic orbital and this is atomic orbital, this represents the diatomic species O<sub>2</sub>, F<sub>2</sub> and Ne<sub>2</sub> they exists or not that is a different issue, but one can write MO diagram in this fashion and keeping the energy of this in this order ok.

So, let me right now for carbon, boron and nitrogen, now little changes will be there just remember here sigma 2p is the lower whereas, here pi will be lower. Pi 2p will be lower and then sigma comes sigma 2p and then as usual here no change, a pi star 2p will be essentially same and here it is sigma star 2p. I can connect now, this is 2p this is 2p there is no change in the 2 s combination this is 2s, this is 2 s again this is these are all atomic orbital's; this is molecular orbital for diatomic species.

So, now you can see the difference, here in this case pi 2p is much lower in energy compare to sigma 2p whereas, in these cases; that means, in the heavier or more electronegative elements in the second row, the energy due to sigma 2p will be lower compared to pi 2p. Whereas, in the same row group 13, 14, 15 elements we have a opposite situation here pi 2p will be lower in energy compare to sigma 2p. Let us look into it why that happens, before I proceed for that one I pose a question here. So, that is we can explain the bonding properties of molecules are speak, ionic species. For example, let me consider N<sub>2</sub> and N<sub>2</sub> plus and O<sub>2</sub> and O<sub>2</sub> plus and let me look into the bond energy associated with these species and also the bond lengths that is N-N bond length or O-O bond length in these species and let us try to understand from alkali output diagram how to explain these properties.

First let me write for N<sub>2</sub> of course, now I am not going to write you know the order so simply I.

(Refer Slide Time: 06:15)



Let me write in the order here, sigma 2 s and then sigma star 2 s and then I have pi 2p and then sigma 2p and then pi star, pi star 2p and then sigma star 2p. So, this is for N 2 I am writing and N 2 we have total of 10 electrons in its valence shell that is 1 s 2, 2 s 2, 2p 3 so we have totally 5 electron from each nitrogen. So, we have 10 electrons, those 10 electrons have to be filled here 2 electrons will go here and 2 electrons will go here and 2 will go here and 2 will go here, now 2, 4, 6, 8 and this is it.

So, this is how you can show the filling order for N 2 and of course, if N 2 if I consider here between these we have 6 electrons, I can calculate the bond order this is for N 2, bond order equals 6 minus 0 by 2 equals 3 so; that means, the bond order is 3 that indicates there exist 3 bonds between 2 nitrogen atoms. So, now, let us look into N 2 plus, N 2 plus. So, N 2 plus we are having 1 electron less. So, here we have 10 electrons, 10 electrons we have in this case 10 electrons and then here we have 9 electrons. So, in the same fashion I will start writing the molecular orbital.

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Let me start filling, now this 9 electrons, 2 electrons here, 2 electrons here, 1 2 electron and 2 electron and here 1 electron because N 2 plus 1 is n 1 is n plus; that means, 1 nitrogen comes with 1 s 2, 2 s 2, 2p 3 electrons that is n, n plus comes with 1 s 2, 2 s 2, 2p 2 electron. So, we have total of 9 electrons, these 9 electrons have been placed here in

this fashion 1. So, 1 electron here so total we have 9 electrons so now if you look into the bond order equals  $5 - 0$  by  $2$  it goes to  $2.5$ .

So, here the net bonding is we have a  $2.5$  we cannot write fractional bond, but we can say bond is weaker. Similarly, I can write for  $O_2$  here,  $O_2$  and  $O_2$  you should notice the difference, this is essentially same and next we have this two are same  $1s, 2s^2, 2s^2$ . Now, we have  $\sigma_p$  here comes and then  $\pi$  comes here and this does not change and this is how it is. So, now, let me write them, this is  $\sigma_{2s}$  this is  $\sigma_{2s}^*$  and then here  $\sigma_{2p}, \pi_{2p}, \pi_{2p}^*$  and  $\sigma_{2p}^*$ .

So, now in case of oxygen we have  $1s^2, 2s^2, 2p^4$ . So, so total we have 12 electrons, we have a total of 12 electrons. So, these 2 electrons have you start placing here to here to here to here 6, 8, 10 and one electron here ok.

So, that means, 2 unpaired electrons are there because of this one you can say clearly oxygen is paramagnetic and it has 2 unpaired electrons. So, one can calculate the magnetic moment  $\mu$  using square root of  $2s + 1$  formula and this clearly indicates why  $O_2$  species is paramagnetic and here if you look into the bond order we have here  $2 + 6 - 6$  are there,  $6 - 2$  equals  $4$  by  $2$ ; that means, the bond order is  $2$  that indicates we have double bond between 2 oxygen atoms.

So, verification is correct, now let me write the MO diagram for  $O_2$  plus,  $O_2$  plus we have 1 electron less. So, let me start filling here, here we have 2 oxygen atoms are there one is oxygen with  $1s^2, 2s^2, 2p^4$  electronic configuration, another one is  $O_2^+$  with  $1s^2, 2s^2, 2p^3$  electronic configuration. So, we have one electron less, let me start filling them in the same order. So, they cancel each other, they are 4 electrons now. Now, you look into here  $2s^2, 2s^2$  here. So, we have added 10 electrons, the last electron will come here. So,  $O_2^+$  species is also paramagnetic whereas, here in the bond order if I calculate here bond order equals  $6 - 1$  by  $2$ , it is equal to  $2.5$  so; that means, bond is stronger, this is stronger, the bond order increases.

So,  $O_2^+$  will be much more stable compared to  $O_2$ . So, now, we wrote here this MO diagram and we know the stability using this one, with this let us look into the bond parameter side I told you what are those bond parameters for bond energy.

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	$N_2$	$N_2^+$	$O_2$	$O_2^+$
Bond Energy kJ/mol	945	841	498	623
Bond length (pm)	110	112	121	112
B.O	3	2.5	2	2.5
	Stronger	weak	weak	strong.

I am writing in kilojoules per mole and also I am writing bond length in Pico meters,  $N_2$  and  $N_2^+$  and then  $O_2$  and  $O_2^+$ . Let us compare these parameters now, let me start writing the values it is 945. So, kilo joules per mole and for this one 841 and then 498 and then 623 and in a bond length this is 110 Pico meter and here its 112 and here it is 121 whereas, here 112 ok.

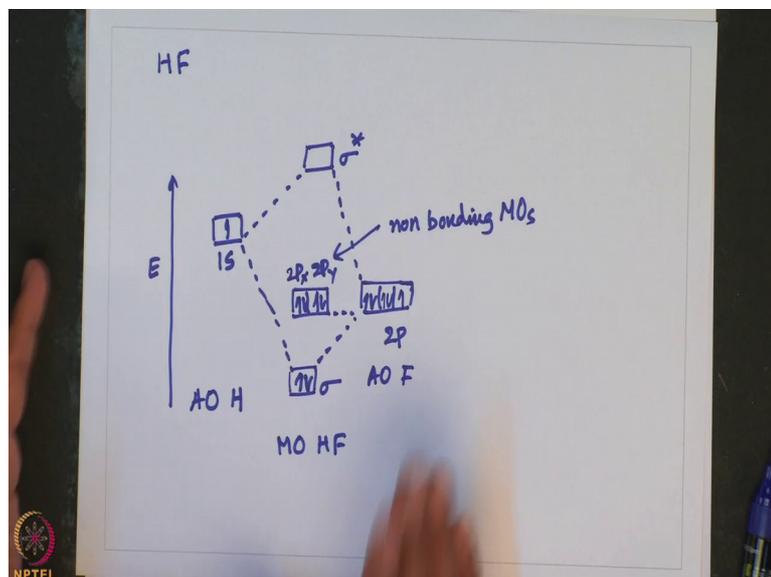
So, now we have to explain, I already showed you the MO diagram for  $N_2$ ,  $N_2^+$ ,  $O_2$  and  $O_2^+$ . In case of  $N_2$  bond order let me write here, bond order in a case of  $N_2$  it is 3, in case of this one it is 2.5, in case of this one it is 2, this one 2.5. That means, here strong bond 3 bonds are there weak and this is relatively, if I say this is weak this is strong. So, this information has come from molecular orbital diagram simply by writing, now if I compare you see 945 kilo joules per mole and bond length is shorter because you have bond order 3 a triple bond exist between n and n and its bond energy is 945 kilo joules per mole. Actually, single bond N-N bond energy is 160 kilo joules per mole, it is more than 3 times that is the reason is more stable of course; I will be giving you more details when I discuss the chemistry of group 15 elements and then the bond length is 100 and 10 Pico meter.

Now,  $N_2^+$  you can see bond order is 2.5; that means, bond order is reduced; that means, it is relatively weak compare to  $N_2$  that is reflected in its bond parameter 112 little longer 112 Pico meter and whereas, its bond energy has dropped from 945 to 841

kilojoules per mole and same analogy can be extended between  $O_2$  and  $O_2^+$ . In case of  $O_2$  the bond energy is 498 kilojoules per mole and here bond distance is 121, 121 Pico meter and bond order is 2. Now, when one electron is removed from anti bonding orbital and now the bond energy increases considerably from 498 to 623 kilojoules per mole and as a result the net increase in the bond order is from 2 to 2.5. As result the oxygen atoms come very close to each other,  $O$  and  $O^+$  come very close to each other as a result the bond distance shrinks and it is now 112 Pico meter. That means, the bond distance in case of  $N_2^+$  as well as  $O_2^+$  are essentially same. So, you can see how some of these properties can be readily explained simply by drawing the MO diagram and also the reactivity all those things one can extrapolate and understand better by practicing and knowing the MO diagrams for most of the molecules we come across ok.

So, let us look into some heteronuclear diatomic molecules. So, heteronuclear diatomic molecules it will be little different, what we should know is we should know the relative electro negativity of the 2 atom that are combining to make a diatomic species.

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For example let me consider HF, this always one should remember to write. So, let me put 1 s here, this is coming from atomic orbital of hydrogen. Now, if you look into the electro negativity difference between hydrogen and fluorine and there is a remarkable difference is there. So, energy of 2p orbital that is going to combine with one s atomic orbital will be much lower in energy so this will be somewhere here. So, this is 2p and

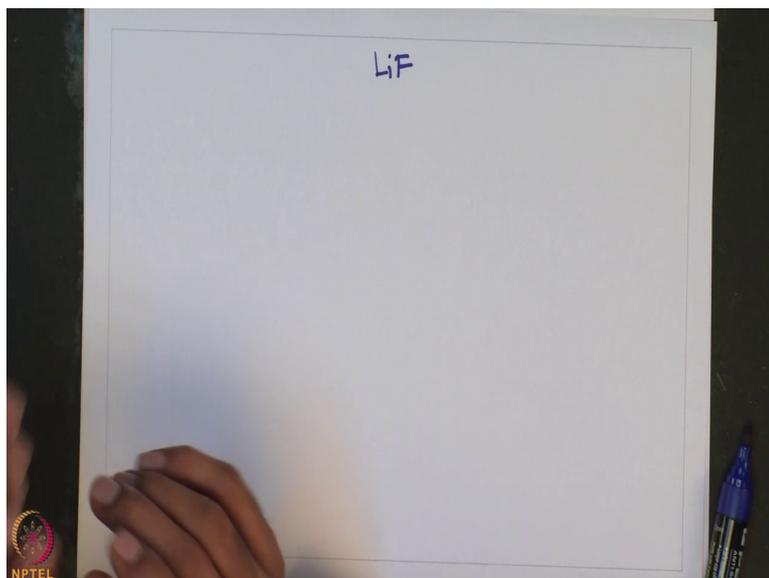
we have 5 electrons electronic configuration of fluorine is  $1s^2, 2s^2, 2p^5$ . So, it is in need of one electron to complete its octet.

So, it combines now, when it combines it generates 3 plus 1, 4 atomic orbitals are combined to generate 4 molecular orbitals out of this one, 1 is bonding here this is sigma and then here this is essentially nonbonding because for one let us say  $2p_z$  interacts with  $1s$  atomic orbital to form sigma bond, remaining  $2p_x$  and  $2p_y$  we do not have corresponding atomic orbitals from hydrogen. As a result they do not combine with any of the atomic orbitals, we can think of with hydrogen they remain just nonbonding. So, essentially they remain as nonbonding here, that is a reason there is no net change in the energy compared to the free fluorine atom and then here we have sigma star. Of course, I did not write here. So, here 2 electrons are there and this is essentially  $2p_x, 2p_y$ ; that means,  $p_z$  is combined with this one, this is sigma sigma star and these are essentially non bonding molecular orbitals atomic orbitals of fluorine and molecular orbital of HF.

So, this is how one can write the molecular orbital diagram for hetero nuclear diatomic molecule. Here, one should remember the electro negativity of  $1s$  is remarkably less compared to the electro negativity of  $2p$  they have much more lower energy. So, that when you are writing you should write in this fashion always more stacular interelements have lower energy for the corresponding atomic orbitals and we have a situation something like this and here 2 electrons are there and  $2p_z$  combines with one  $s$  to form a sigma bonding molecular orbital. Where one electron from this one, one of the electron from fluorine will be residing to generate bonding molecular orbital and then the 2 4 electrons from  $p_x$  and  $p_y$  do not have corresponding atomic from hydrogen. So, they remain non bonding molecular orbital and net number of molecular orbitals are still same here 1, 2, 3, 4, 1, 2, 3, 4; that means, that balancing should be there.

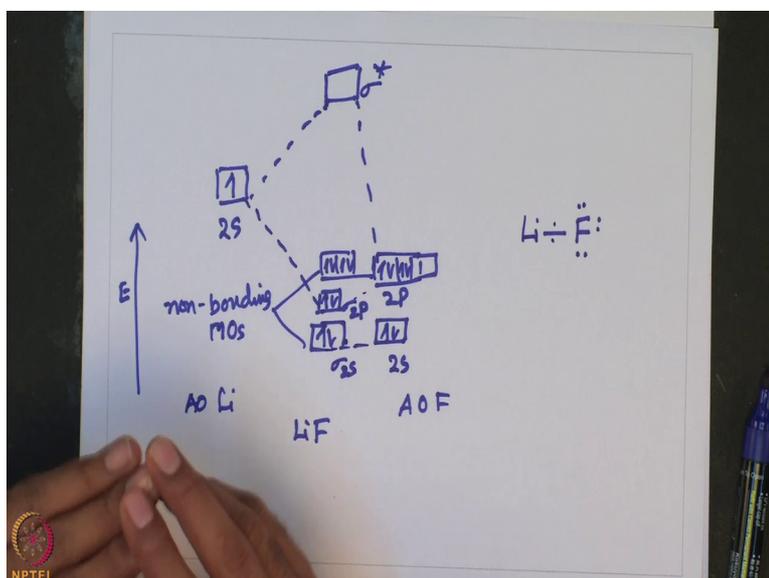
So, this is a simplest molecule you can think of as an example of heteronuclear diatomic molecule, one can extrapolate this one to other molecules as well. So, let us try to write for another diatomic molecule, heterodyne nuclear heteronuclear diatomic molecules such as lithium fluoride.

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So, lithium fluoride case is also very similar, we have  $1s^2, 2s^2$  electron and this electron combines with  $1s^2, 2s^2, 2p^5$  atomic orbital to generate bonding let us see whether we have nonbonding also similar to HF.

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So, this is  $2s$  and here it is  $2s$  and then  $2p, 2p$  and now here since we do not have the corresponding  $2p$  orbital. So, this also remain as nonbonding and then we have sigma, sigma  $2p$  or simply sigma and then this is  $2s$ , sigma  $2s$  and then this one remain nonbonding and then we have sigma here.

So, that means, essentially very similar to what happened in case of fluorine, lithium, hydrogen fluoride. So, this is sigma star. So, here in this case if we consider atomic orbital of lithium, atomic orbitals of fluorine and lithium fluoride. So, lithium fluoride you can explain. So, since 2 s do not have the corresponding low energy so it remains as nonbonding. So, both of these are essentially nonbonding mos.

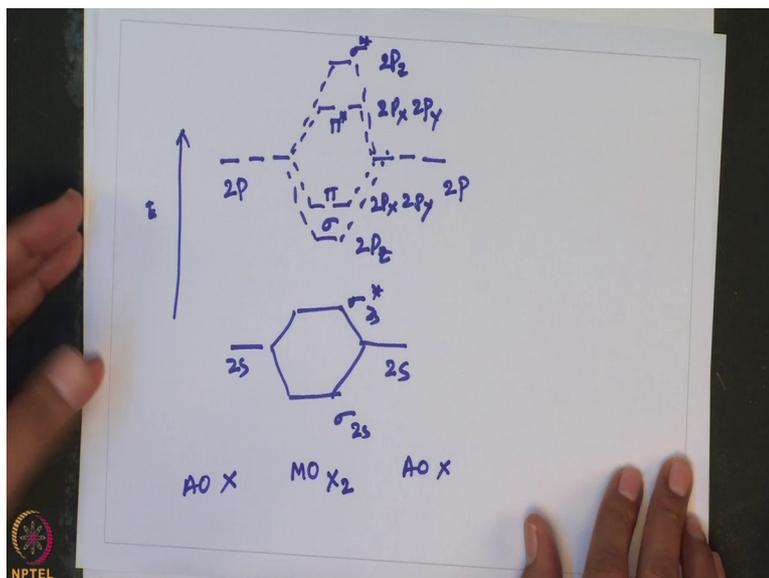
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So, here whereas, this one here essentially one of the 2p orbital that is preferably 2 p<sub>z</sub> combines with 2 s to generate sigma where these 2 electrons are, these 2 electrons are responsible for making lithium fluoride. For example, these 3 p<sub>x</sub> remains nonbonding and of course, one can go to this Lewis dot structure you can see here. So, these 3 pairs whatever is there that represented here 6.

So, one is this pair another these 2 pairs; that means, 3 pairs can be seen here and this whatever is there the sigma 2p that is responsible for making this bond so; that means, we can take some hint from lithium fluoride, Lewis dot structure and from there we can see we have 3 pairs of electrons are there. It has s 2p 6, now these 3 pairs are essentially non not at all interacting with lithium and they are here they remain as nonbonding; that means, some clue can be taken from valence bond theory as well as Lewis dot structure when we are writing MO diagram and they can be verified.

So, once if you are familiar with writing MO diagram for heteronuclear diatomic molecules you should be able to write for any complicated molecule by considering ligand group orbitals. So, this is a, let me write a general MO diagram here before I conclude this talk.

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So, this is about 2 s of course, here it is sigma and sigma star 2 s then we considered p p and here it can interchange. So, here it is essentially 2p z and here it is 2p x and 2p y same thing here and here it is pi and sigma and pi star and sigma star and here it is 2p z and here 2p x 2p y of course, I have just considered 2p situation one can also write 3 p and all those things ok.

So, if it is x atomic orbital and atomic orbital of another x here it is MO of X<sub>2</sub>. So, this how one can write of course, this will change depending upon electro negativity of the combining atoms. So, in my next lecture I would try to make you familiar with little more complicated molecules. So, have a pleasant reading.

Thank you very much.