Concepts of Chemistry for Engineering
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Lecture No. 16
Molecular orbital theory 4: Homonuclear diatomic molecules-II

We are discussing homonuclear diatomic molecules. We have already talked about things like H_2^+, H_2, He_2^+ and even He_2, which is not really a molecule, but shows some energy minimum.

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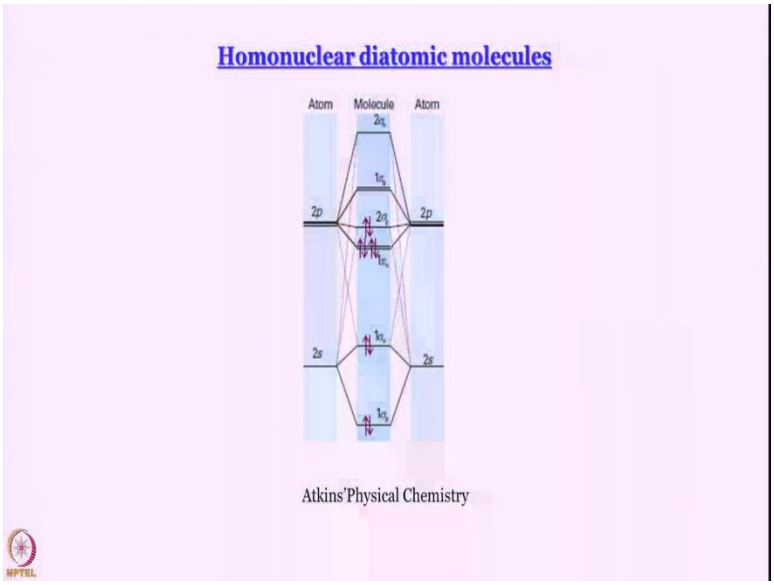

Now, we are going to talk about a little bigger homonuclear diatomic molecules things like F_2, N_2 and so on and so forth.

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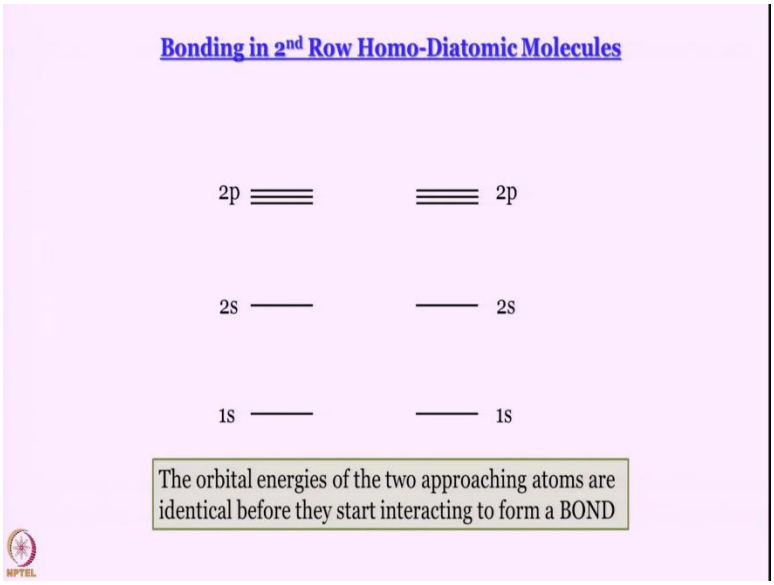

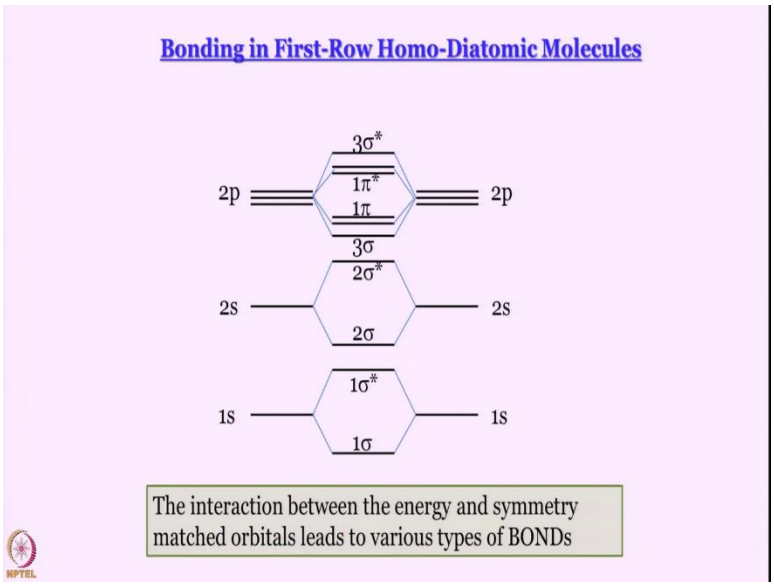

Now, the moment we discuss second row homo-diatomic molecules a problem creeps in. The problem is this. If you think of hydrogen atom, in hydrogen atom, actually, the energies of 2s and 2p are the same. However, for multi-electron atoms, the energies of 2s and 2p are not the same that is because of things like shielding and screening, which you are going to learn in a different part of this course. So, 2s and 2p are no longer degenerate.

The question is when the molecules form from these atoms, do we consider them to have different energy or same energy, because one very important rule of thumb for molecular orbital theory is that atomic orbitals participate in linear combinations only when they have compatible geometry

and comparable energies. So, if I draw this picture, where 2s and 2p are very different in energy, then the MOs that I expect to get at these. The two 1s orbitals participate in a linear combination to give me 1σ and $1\sigma^*$.

Now, here 1, 2, 3, these are just sort of roll numbers. 1σ means the first σ orbital that we have obtained going from bottom-up in energy ladder. $1\sigma^*$ means the first anti-bonding σ orbital that we have obtained, so on and so forth. So, 2σ would form from the two 2s orbitals. And if you go to 2p orbitals, generally, it is conventional to define the internuclear axis as the z axis. There, we will consider the 2p orbitals to combine to give us the σ combination that is 3σ and the corresponding anti-bonding orbital is $3\sigma^*$ and px and py. So, x, y, z, this is the bond.

Now, the two px orbitals can give you a π overlap. So, they will form one linear combination to give you one π orbital. The two py orbitals give you another kind of π overlap and that gives you the another kind of π bond. But this along x and this along y they have the same energies. So, what you get is you get degenerate π orbital, degenerate π^* orbitals and the degeneracy is 2.

Double degenerate π orbital, double degenerate π^* orbital arising out of linear combination of px and linear combination of py. See one σ bond is formed the axis are defined. Now px and py cannot combine. This px and this py cannot combine. It has to be px px π interaction, py py π interaction. That is what it is. So, question is, what should we do? Should we do it like this? Should we do something else?

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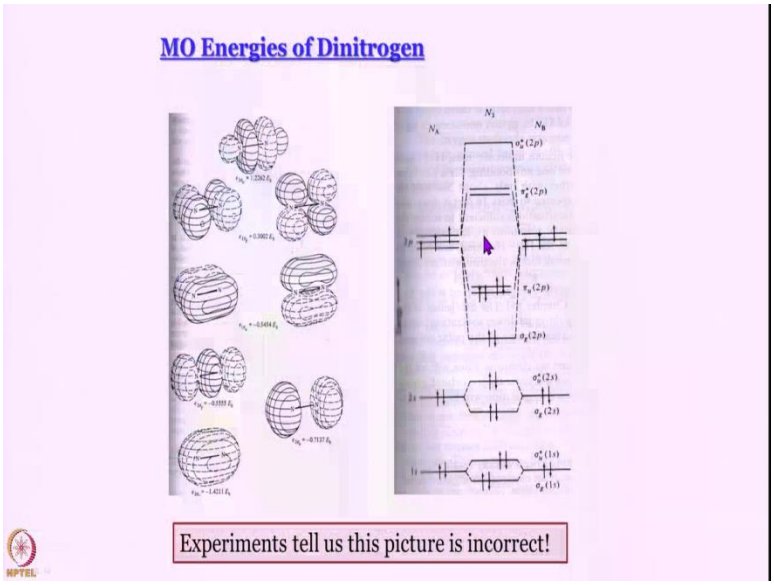

Well, if we go with the model, where there is separation in energies of s and p orbitals and you get molecular orbitals like this as expected, then this is what you expect for dinitrogen. For dinitrogen how many electrons are there? In the valence shell, you have 5 electrons. So, if we neglect, we do not even have to neglect, you can fill in the electrons here, but the point is the highest occupied molecular orbital in the case of hydrogen then would be a π MO.

What is the implication of having homo as a π MO? The implication is that this dinitrogen molecule should then be susceptible to addition reactions. So, in the organic chemistry that we learned, we know that we do a bromine water test for say, an alkene. Why, because you add bromine, one bromine atom goes to this carbon, one bromine atom goes to that carbon, this π bond breaks, and instead of a C-C π bond, now you have two C-Br sigma bonds. The same thing should have happened with nitrogen.

Nitrogen is a gas. You bubble it through bromine water. Bromine water should get decolorized then and you should get something like Br-N, N-Br, never happens. In fact, nitrogen is very inert. That is its role in the atmosphere. If we did not have nitrogen in the atmosphere, perhaps everything would get oxidized or catch fire or something. So, it dilutes things. It is a very inert gas.

And because of its inertness, have you heard the name of Prof. Acharya Prafulla Chandra Ray. Well, the English spelling is Ray, but actually, it is Ray. So, Acharya Prafulla Chandra Ray had made a compound in which this dinitrogen was made to react. I encourage you to find out what

that compound is called. The compound between mercury and dinitrogen, what is it called? What is the structure? Some skepticism had been expressed later on saying that there is not really that molecule, but then it has been no conclusive proof that proves that Ray was correct.

He was one of the founding fathers of modern-day chemistry in India. And the reason why that was such a big deal is that dinitrogen is so inert. Why is it inert? From this diagram, we expect it to be very highly reactive, very highly susceptible to addition reaction.

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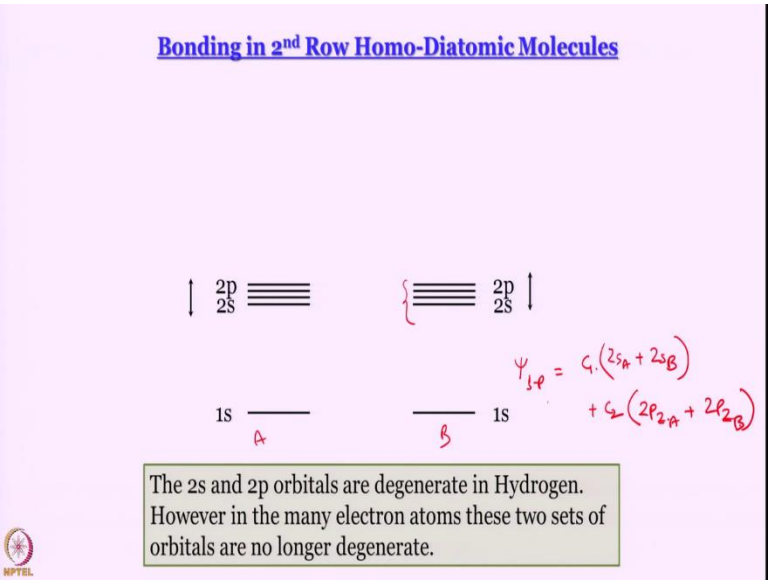

It is inert, because, see, if you go back to the situation of your hydrogen, then 2s and 2p have the same energies. So, in a situation that is close to hydrogen, where 2s and 2p orbitals are degenerate or very close in energy, then you have to write an MO like ψ_{sp} is equal to some c_1 multiplied by, we will call this A and I will call this B,

$\psi_{sp} = c1(2sA + 2sB) + c2(2pzA + 2pzB)$

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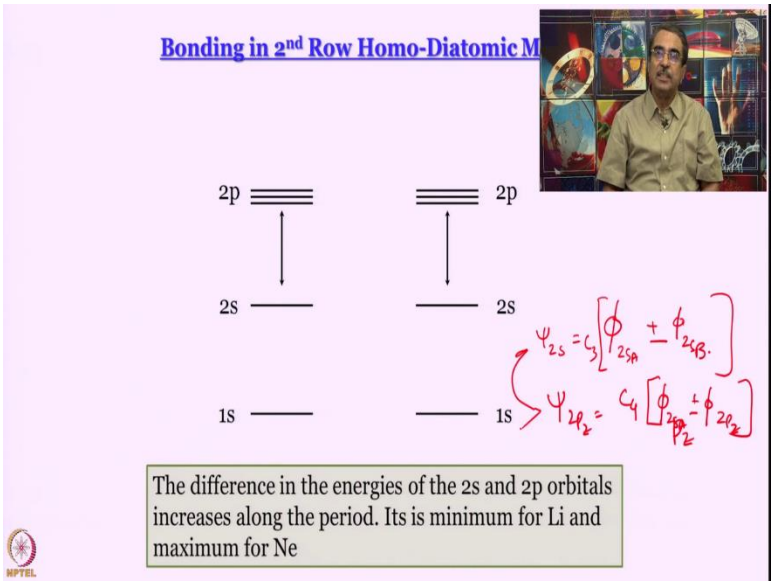

Whereas, the situation is like this, where there is a separation between, the energy between 2s and 2p orbitals then you have to write two different linear combinations. So, you can write like this ψ_{2s} is equal to, I wrote ψ_{2s} here, so I will write ϕ then. Φ's are atomic orbitals. $\phi_{2sA} + \phi_{2sB}$ and I have to write ψ_{2pz} equal to, I can write ± here and I can write some c_3 here. Writing c_3 because I have forgotten whether I wrote only one c_1 or whether I wrote c_1 and c_2. So, c_4 multiplied by ϕ_{2sA}-, well, $\phi_{2pz} \pm \phi_{2pz}$. These two will not mix. You have two situations

$$\psi_{2s} = c_3(\phi_{2SA} \pm \phi_{2SB}),$$
$$\psi_{2pz} = c_4(\phi_{2pz} \pm \phi_{2pz}).$$

So, there are other cases. If you use the energy diagram I showed you, then the magnetic property of fluorine is not explained. The magnetic property of F_2 is not explained rather. So, there are many such discrepancies.

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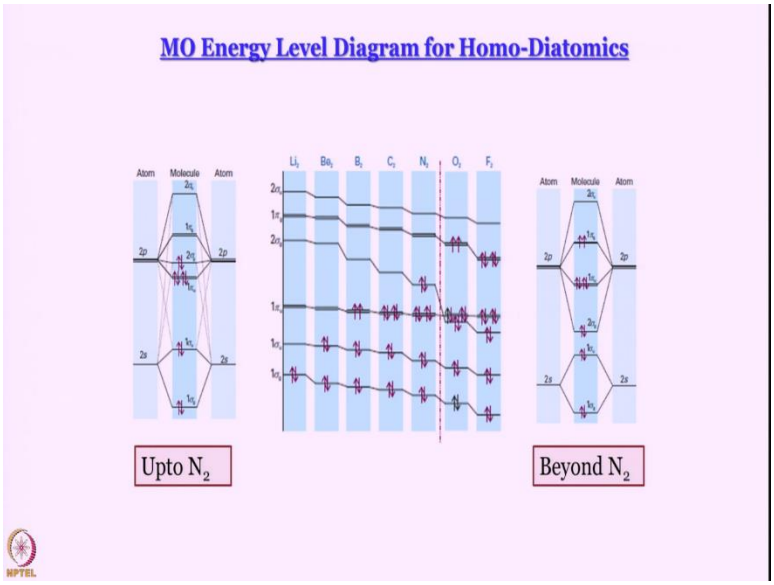

So, the current understanding is that, when the atoms are smaller when they are closer to hydrogen, that is when they are going to have this kind of a situation, where there will be sp mixing you can think or rather s and p are close in energy. In fact, I do not even like to draw like this. These are from Atkins. But what they are saying is that some mixing will be there. So, you are going to get this sequence of molecular orbitals.

When there is no mixing in a situation where the atom is large and energies of 2s and 2p are very different from each other, then you get the energy diagram that you expect. So, somewhere there is a switch in sequence. Look at this π and look at this σ, when you consider mixing, the sigma orbital is at higher energy than π. If you do not consider mixing, then the σ orbital is at lower energy compared to π.

And looking at experimental trait, what we see is that, what we say is that for dinitrogen, definitely, the HOMO has to be sigma that is where it is nonreactive and it fits in nicely if we use the model where sp mixing has taken place. However, for oxygen, that is not the case. So, we say, we find that there is a switchover in sp mixing traits when you go from nitrogen to oxygen.

Why is it between nitrogen to oxygen, nobody knows. It is just an experimental result. There is no way from basic theory that we can say that this is how it should happen and this should not happen. It is like that. That is the experimental observation. So, this is something that I believe you have

studied in 11^{th} and 12^{th} also. That is what we learn about homonuclear diatomics. And now we are going to go over and discuss hetero-nuclear diatomic molecules.