Introductory Quantum Chemistry

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Lecture - 46
MO theory of diatomics

So, we have seen the molecular orbited theory of hydrogen molecule; we have also seen the valence bond approach, but of the two theories actually even though valence bond theory gives better answers, simple valance bond theory gives better answers for hydrogen molecule; molecular orbital theory actually turns out to be easier to you, and it is the one that is mostly widely used. Even though valance bond theory also is being used by some people molecular orbited theory is by far the most successful theory, and therefore we will confine ourselves to the molecular orbited theory, and we will look at some diatomic molecule just to give you a flavor for the wave molecular orbital theory works.

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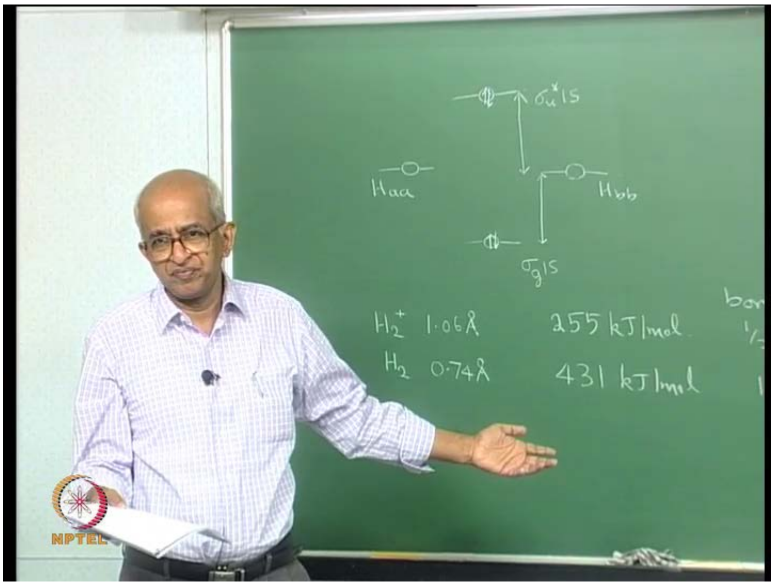

So, what molecular orbital theory would say is I mean let me just recapitulate. You have let us say two hydrogen atoms. These circles indicate that they have one orbital each and when you bring the two together they interact and give you a bonding orbital and an antibonding molecular orbital, and this was our H aa, this was H bb. In the case of hydrogen molecule ion and as well as in the case of hydrogen molecule they both have the same energy, and this is actually the energy of sigma g 1s and that is the energy of sigma u star 1s, and in the case of H 2 plus, what happens is that you have just one electron sitting here, just one electron sitting there.

And you can actually calculate the bond energy or energy that is needed to disassociate the molecule. In the case I have established actually I am giving you experimental values; in the case of H 2 plus you find that the bond length is 1.06 Angstroms, and the energy needed to disassociate or I mean we can call it bond energy; bond energy in the case of H 2 plus is 2 55 kilojoules per mol. Now, if you add one more electron you have H 2 molecule; that means you have two electrons sitting there both are going into the bonding orbital. As a result of which you would expect that the bond will get stronger, and if the bond gets stronger naturally you would also expect that the atoms are brought closer, and that is actually verified from experiment, in the case which this is H 2 plus; in the case of H 2 the bond length is 0.74, so you see that it has decreased the bond length, and the bond energy has increased to 431 kilojoules per mol.

And as you would know a chemist will say that there is a single bond between the two hydrogen atoms in the case of H 2 molecule. If that is the way it is you see in this case how many bonds would you say? The answer is that you see there are two electrons forming the bond in the case of hydrogen molecule. So, in the case of H 2 plus there are only 1 electron, so you would expect that it is something like half a bond, and in this connection it is useful to define something which we will refer to as the bond order. Now how should it be defined? Well, in the case of it should be defined in such a fashion that in the case of hydrogen molecule you get a bond order equal to 1 saying that there is one bond, and naturally you would expect there in the case of H 2 plus it should be half.

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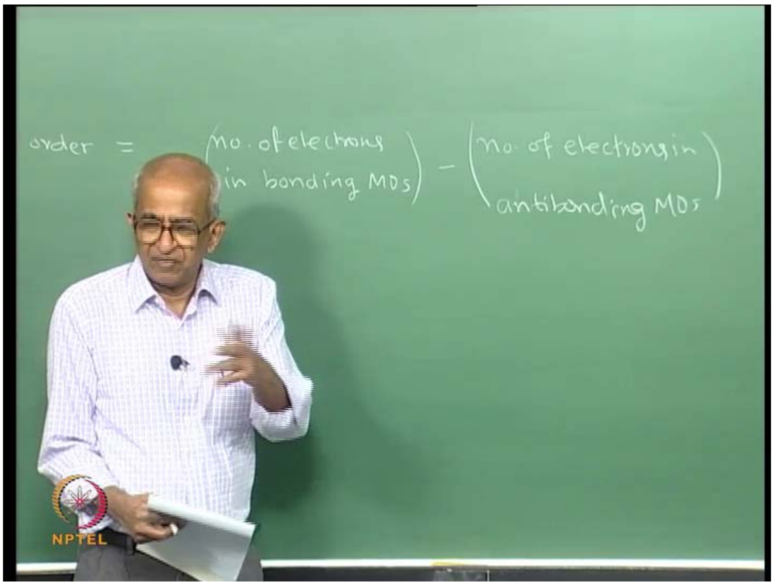

Now, the definitions that I am going to give you is little bit general because this will cover all the molecules that we are going to discuss. So, therefore, what I am going to say is ok, number of electrons in bonding MOs bonding molecular orbitals minus number of electrons in antibonding molecular orbitals. This is only natural you see. See, if you add electrons to bonding molecular orbitals that will stabilize a system while if you add electrons to antibonding molecular orbitals it will destabilize a system. So, these cause stability, this cause instability and so therefore, the net stableness will be obtained if you take the difference between these two and then of course, you have to say that ok, if I added two electrons to a bonding molecular orbital that will give me one bond.

Every two electron gives me one bond and therefore, what I will do is I will take this difference and divide it by 2, and that is the definition of bond order, and if you use that definition for H 2 plus there is one electron in a bonding molecular orbital; there are no electrons in antibonding molecular orbitals. So, you will directly get a bond order of half. So, same definitions if you apply to H 2 you are going to get a bond order of unity, ok. Now suppose you had a spacious like He 2 plus, right, He 2 plus have how many electrons? It has three electrons. So, two of them will go to this bonding orbital, and one will go to the antibonding orbital, and therefore, if you calculated the bond order what will happen? You will get an answer of half; bond order is going to be half because this will be 2 and that is going to be 1.

So, you get a bond order of half. This actually says that He 2 plus can excess; it has a bond which is not a full bond. Roughly speaking bond order is I mean not roughly speaking the bond order is half. So, the system you expect is stable, and it is possible to make the system in the lab. H 2 plus can be made of course, I mean you have to have sophisticated equipment to make the system; you have to make it in the gaseous space, but it is possible, and it has been made. It has a bond order of half, but now suppose I added one more electrons so that I would have He 2. So, you would have the second electrons sitting here, and what happens? You have two electrons in the bonding orbital; you have two electrons in the antibonding orbital, ok, and the way things are see the bonding orbital is stable; it is stable by that much amount, correct, because this is the energy of an atomic orbital.

So, compared to the atomic orbital the bonding orbital is stable, and the antibonding orbital is unstable by that much, but it is an interesting result of a molecular orbital theory which when we have seen the expressions, and if you analyze those expressions we can actually find that his height is actually larger than that height. So, therefore, what I am saying is that the antibonding orbital is more unstable than the stability of the bonding orbital, and therefore, if you added two electrons here and the two electrons there the system as a whole will be definitely unstable, and the bond order if you calculate it will be turn out to be equal to 0, right, and therefore you predict from molecular orbital theory you predict that the system has to be unstable, and helium w actually there is no covalent bond in the case of He 2 molecule, ok. So, now we will look at this definition we will use later. Now we are going at look at more complex systems; I will look at the systems like Li 2 Be 2 the first rod atomics, ok.

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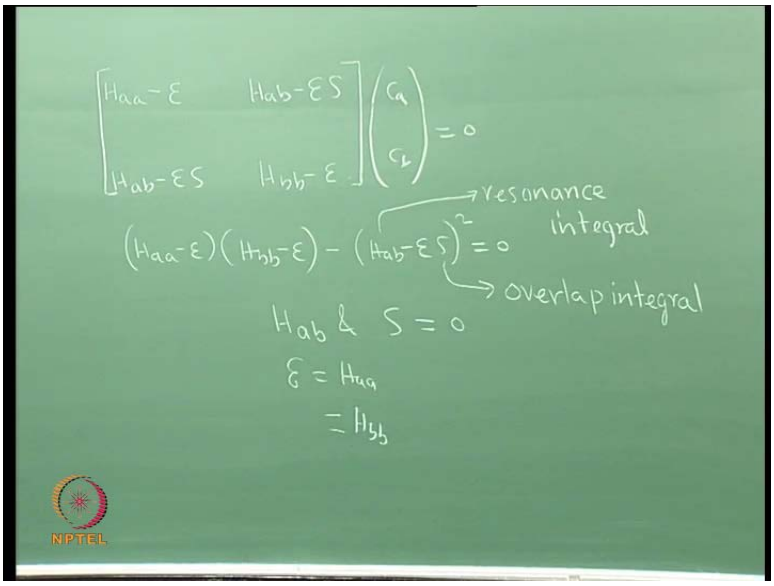

$$\begin{bmatrix} H_{aa}-\mathcal{E} & H_{ab}-\mathcal{E}S \\ H_{ab}-\mathcal{E}S & H_{bb}-\mathcal{E} \end{bmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

$$(H_{aa}-\mathcal{E})(H_{bb}-\mathcal{E}) - (\overset{\rightarrow\text{resonance integral}}{H_{ab}}-\mathcal{E}\underset{\hookrightarrow\text{overlap integral}}{S})^2 = 0$$

H_{ab} & $S = 0$

$\mathcal{E} = H_{aa}$

$= H_{bb}$

But before I do that I want to tell you some general things; remember our expressions according to molecular orbital theory was H aa minus E H ab minus ES H ab minus ES H bb minus E. You had a square matrix multiplying C a C b, and you said that this has to be equal to 0. This was our general expression, and then you said that you have to take the determinant of this matrix, and put it equal to 0. That actually means H aa minus script E in to H bb minus script E minus H ab minus ES the whole square is equal to 0, fine. Now this is a simple quadratic equation. Now remember I am not confining myself to H 2 plus or H 2. So, I would like to think of may be the bond between lithium and hydrogen or some such thing.

So, therefore, it is not really necessary that the two orbitals a and b are equivalent, and therefore, H aa need not be equal to H bb; energy of the orbital on n need not be equal to the energy of the orbital on a. That is the situation that I would like to consider. Now if we want we can actually solve this equation and find out the values of script e; whenever two orbital interacts you can use this equation and find out the energies of the resultant molecular orbitals, because I have two atomic orbitals. They will combine to give me molecular orbital’s, but suppose you had a situation where H ab and S both are equal to 0 both of them for some reasons suppose they happen to be equal to 0. Then what will happen? This term will actually be equal to 0, and then you will have this product equal to 0 which means that script E will be equal to H aa and the other possibility is it is equal to H bb; these are the two roots of my equation.

So, what does it tell you? It tells you that if I had a situation where the overlap indictor is as well as the indictor H ab which usually is referred to the resonance integral. That is the term which is usually used. So, if this is called the overlap integral, if it so happens that the overlap integral and the resonance integral are both equal to 0, then what happens? You get the allowed energy levels to be those of the two atomic orbitals, and this actually means that these two atomic orbitals will not combine. They will not mix together; if you try to add them up you see they refuse to mix together and to give you molecular orbitals. So, if two atomic orbitals interact what should happen is that the overlap integral and the resonance integral both must be nonzero, ok, right.

So, at least I mean H ab has to be nonzero. If H ab is nonzero then obviously, the orbitals will interact and form molecular orbitals. Now actually by looking at the roots of this quadratic equation you can arrive at other interesting conclusions. For example, imagine that this is H aa; this is H aa and that is H bb. So, I am saying that the two orbitals have somewhat different energies, fine. Then what you will find? You can actually analyze these equations, and you can also determine the values of C a and C b, and then you will find that in a such a situation what happens is that the new molecular orbitals that result the molecular orbital that result they will have one orbital of energy that much, and another orbital of energy that much. Well, this figure has not come out as correctly as I would like it to. So, let me just modify this; maybe I will rub of this.

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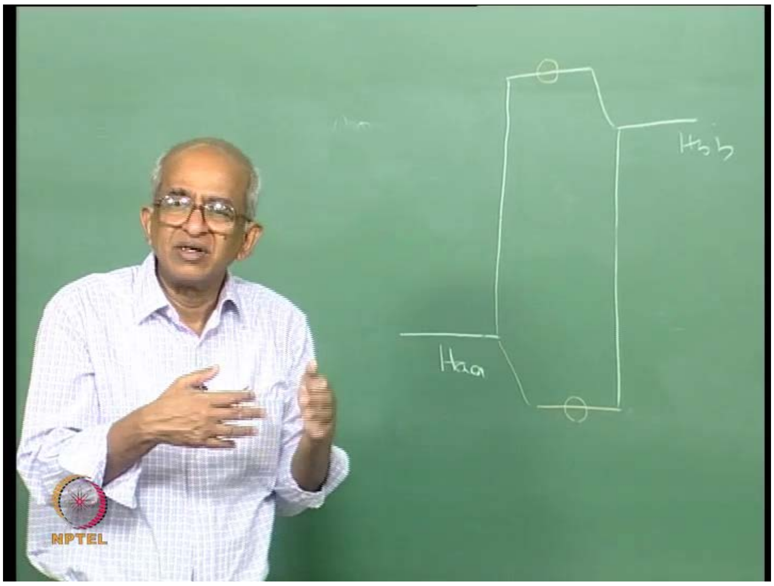

So, this is H bb, and that is H k a, and what happens is that I have a molecular orbital which may be having that much energy, and I have another molecular orbital having an energy of that much. So, what has happened is that these two atomic orbitals have interacted and they have given me molecular orbital's which I usually draw by representing these lines. These lines simply indicate that these atomic orbitals are contributing to the molecular orbitals, and what is the result that you find? You find that there is a bonding molecular orbital which I will represent like this and another antibonding molecular orbital, but the bonding molecular orbital what you should notice from the figure is that it is closer to the lower energy H aa while antibonding is actually closer to the higher energy, right.

This is what you will find, and further you will also find that if you looked at this molecular orbital it will have its major contribution from the atomic orbital located on a; the major contribution will be coming from the atomic orbital located on a with a small amount of contribution from the atomic orbital on b. And similarly this antibonding orbital will have major contribution from the atomic orbital on b with a lesser amount of contribution from a. That is what happens, ok, and further as you separate the two energy levels suppose we separate them and you make them large then what will happen is that the two orbitals have lesser and lesser interaction.

In order to have best interaction what should happen is that the energies of the two orbitals should match. If the two orbitals have energies which match then what will happens is that the splitting or the separation between the bonding and the antibonding molecular orbitals will be large. So, all these conclusions can be arrived from analyzing this simple equation, right. What are the conclusions? If s and H a b are 0 then there is no interaction, and if the orbital's are far apart in energy if the atomic orbital are far apart in energy then the interaction is weak, but if they are having almost the same energy then the interaction is the strongest, and you will get a strongly bonding molecular orbital as well as a strongly antibonding molecular orbital. So, with this information let us look at Li 2 the molecule Li 2.

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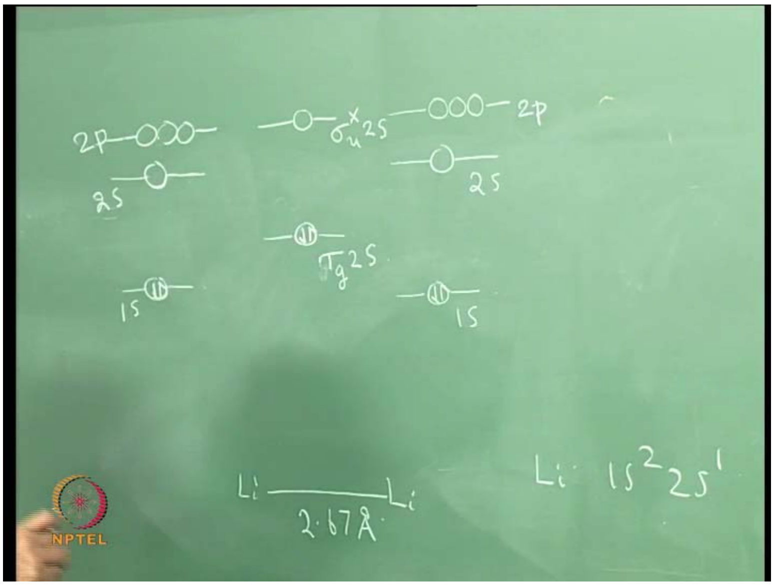

So, in the case of Li2 you have a 1s orbital on one of the lithium atoms, and you have 2s; this is 1s, that is 2s, and you also have 2p quanta lithium. On the other lithium also you have the same quant of thing; that is the 1s. You have the 2s, and you also have the 2p. Now notice the way I have drawn this picture. I have not put a large separation between 2s and 2p; remember that in the case of hydrogen atom the separation between 2s and 2p is actually zero; they are degeneration, right. And in the case of more complex atoms there is the separation due to electron-electron repulsion, right, and in the case of lithium we still do not have that many electrons. So, that the separation between these two is very large; that is why 2s and 2p I have drawn them to be close, ok.

And now what will happen? What I would expect to happen is that this 1s can interact with that 1s. They can interact with each other, but it so happens I mean we are interested in the equilibrium geometry of of molecule at the equilibrium geometry of the molecule which actually is at a distance of 2.67 Angstroms. So, this is one lithium; this is the other lithium. At the equilibrium geometry the bond length actually is quiet large; it is 2.67 Angstroms. In comparison with the bond length in H 2 plus or H 2 see they have bond lengths which are 1 and 0.74; in comparison with them this bond length is rather large. So, what will happen is that at that large separation the overlap of the 1s orbital on the first atom with the 1s on this second atom is actually very, very small.

They do not interact and therefore, what will happen? The 1s and the other 1s we can say ok, they do not interact at all. So, in the case of Li 2 you see these two you can say they do not combine if you want, right; they remain as they are. So, they are of not much. The electron configuration of lithium atom of course, is 1s 2, 2s 1. So, what is going to happen is this is going to be occupied with two electrons; that also are going to be occupied with two electrons, but then you have 2s of this atom interacting with the 2s of that atom, right. So, what will they do? They will combine to give you a bonding orbital, and they will also give you an antibonding orbital, ok.

Let me call this sigma g 2 s, and let me call this sigma u star 2 s, but then you may say immediately that ok, what will happen is that there are in total there are 6 electrons in the molecule, right; two of them are sitting in one of the 1s and the other two are sitting in the other 2s. So, therefore, there are two electrons left, and what will they do? They will actually go and sit in this bonding molecular arbitrary leaving all the other orbitals empty, correct, and actually that is what you can say happens, fine, but then of course, you have other interesting questions. You see for example, this 2s can it interact with 2p on this atom? Let may draw this pictorially. So, you have the first atom.

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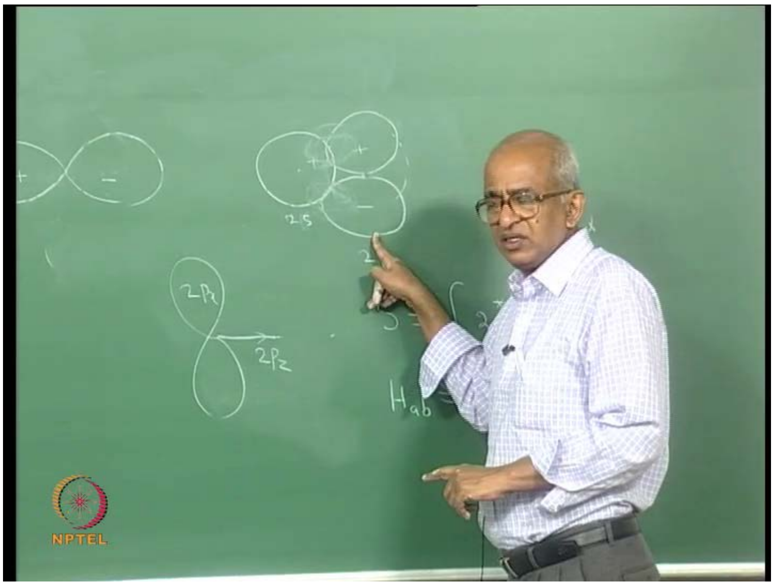

This is the first atom, it has a 2s. Here is the second atom. This is the 2s orbital on the first atom. Here is the second atom that has a 2s and then of course, this two will interact; there is no doubt about that. But now if suppose you think of a situation where I am taking of a 2p orbital and the 2p orbital on the second atom is like that. So, this is 2s, and this is 2p orbital; 2p orbitals there are three of them. So, therefore, I have to say which orbital I am taking of and the tradition as well as the diatomic molecule is concerned is to say that the intermolecular access, the line joining the two nuclei, right, that is taken to be the z axis. So, therefore, an orbital which point right in this direction will be called along the molecular access will be called on z orbital and the orbitals which are perpendicular to it like this orbital which is in the plain of the board or the next orbital which is perpendicular to the plain of the board. These will be referred to as 2 p x or 2 p y.

So, this is let me say 2 p x; this one is 2 p y, and an orbital pointing in this direction will be called 2 p z. So, what I am drawing here is actually interaction between the 2s on the first atom and 2 p x on the second atom. Now if you think of 2 p x on the second atom remember 2 p x has 2 lobes; one lope is positive and the other lope is negative while 2s is positive everywhere. So, if we think of this object that we refer to as the overlap integral s what would it be? It is going to be if you take the 2s multiplied by it 2 p x, strictly speaking I should put a star which is actually unnecessary because 2s atomic orbital is real everywhere, and 2 p x also is real everywhere. So, the star is not really necessary, and you will take 2s star multiply it by 2 p x, the volume element d 2 and integrate over the entire space; what would you expect? Well, in this case what happens is that you are integrating over all regions of space.

So, when you multiplied these two orbitals together you see here the wave function therefore, 2 p x is positive; the wave function for 2 s is positive. So, therefore, in this region the product is going to be positive. Now you have an equivalent region down somewhere here where the product you expect is negative and these two regions would be the same kind of regions except that the product has positive sign in one region while the product has negative sign in the other region, and integration as you know is a process of summation. So, when you have to perform the integration, what will happen? There will be regions from which the integral will have a positive contribution. There will be lots of regions from which the integral will have a negative contribution, and they will exactly cancel each other as a result of which this overlap integral will become 0.

And in this exactly the same fashion if you think of H ab the H ab would also have these regions where the H ab has positive contributions and the regions where H ab has the negative contribution, and they will exactly cancel each other, and therefore, this also will turn out to be equal to 0 and therefore, this is the situation where both the overlap integral and the resonance integral are 0, and if that happens so what is the conclusion? The two orbitals are not going to mix together. So, because of our analyses we find that the 2s atomic orbital cannot interact with 2 p x, right, 2 s on the first atom cannot interact with 2 p x on the second atom, and further you can also say that 2s cannot interact with 2 p y, right.

That also is not possible, 2 p y remember an orbital perpendicular to the plain of the board, but then if you think of 2 p z, let me say I have the 2 s the one atom and 2 p z on the second atom may be 2 p z will be something like this. See 2 p z is actually pointing towards the 2s. Let me say that I will take this lobe to be positive and that lobe to be negative; towards is positive everywhere, and then you would realize that see when you multiply things out you will have significant positive value here, because there the two orbitals actually overlap, right, and if you think of contribution from this region you see from that region the product actually is negative because 2 p x has a negative value; 2s will have a positive value, but the value of 2s in this region because it is far away from this nucleus. So, value is going to extremely small.

So, the contribution from the negative part, by that what I mean is the contribution from regions where the product is negative will be extremely small in comparison with the contribution from regions where the product is positive, and therefore, the net value of the integral will be positive, right, and not only the overlap integral the same conclusion is valid regarding H a b. So, therefore, in the case of a 2s interacting with 2 p z it is possible to have a definite interaction between the two, right. But then you should also notice that the 2s, here is the 2s and the 2p; over this 2 s and the 2 p z there they do not have the same energy, right; they have different energies.

So, suppose that energy separation is large then this interaction is not very important while in the case where the energy separation is small this interaction can be very important, ok. So, remember that in mind. Then the other thing is we have seen that this 2 p x cannot interact with the 2s. So, then which orbital on the other atom can it interact with? Answer is actually simple. You think of 2 p x on the other atom, its shape would be something like this, right. So, let me draw them.

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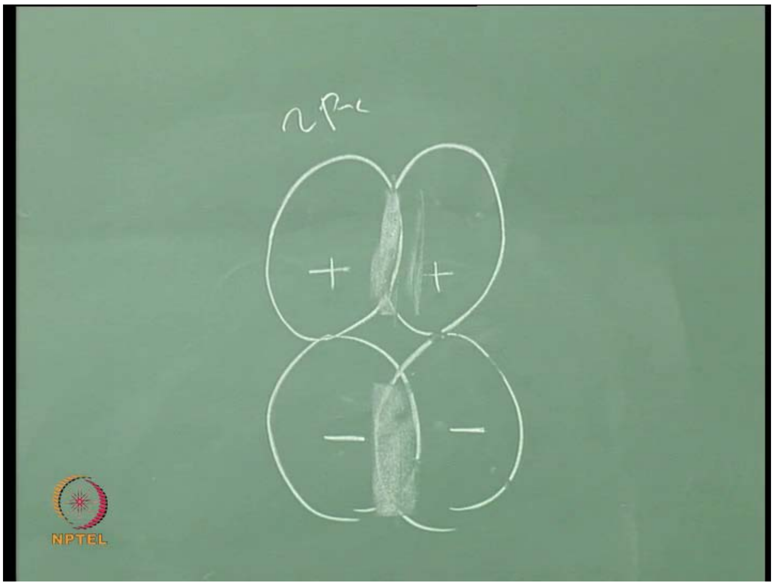

In a figure this is 2 p x on the first atom having plus and minus, and you can say ok, 2 p x on the second atom would be something like this, and in this case there is an interaction. Why is it that there is interaction? This lobe and this lobe of this p orbital and that lobe; they are actually both positive. So, if we try to calculate the overlap integral, what will happen? This two will multiply, and you will have a region here from which there will be a positive contribution, but similarly what will happen? You will have a similar region there where again the product, because you see both the functions are negative. So, the product is going to be positive.

So, the product is actually positive everywhere as a result of which the overlap integral will be nonzero, right, and therefore, the 2 p x on the first will definitely interact with the 2 p x on the second where the 2 p x around the first will not interact with 2 p y on the second, right, again because the overlap integral will turn out to be equal to 0. So, this 2 p x and the 2 p y on the second which is actually oriented like that they will not interact, neither will the 2 p x interact with the 2 p z on the other atom. So, with this information let me think of a general diatomic molecule; let us think of a general diatomic molecule and ask what are the results?

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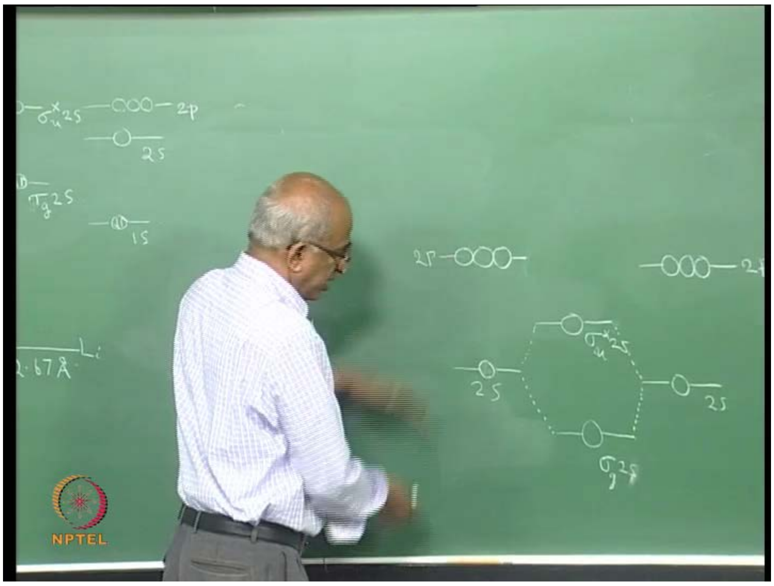

So, you have 2s here. In a general diatomic molecule you see 2p will not be very close to 2s, may be it is somewhere here. So, this is 2p, and you have 2s, and that is my 2p. When I say 2p actually you have three of them. So, you would have 2 p x, 2 p y and 2 p z. So, this 2s will interact with the other 2s, right, and you will get a bonding molecular orbital, and you will get an antibonding molecular orbital, ok, and that you usually indicate; I will put dotted lines here, and I will call this sigma g 2 p, sorry not 2p but 2s, and this is going to be called sigma u star 2p; sorry not 2p but 2s, right. Imagine that this separation is rather large, ok; the picture does not show that.

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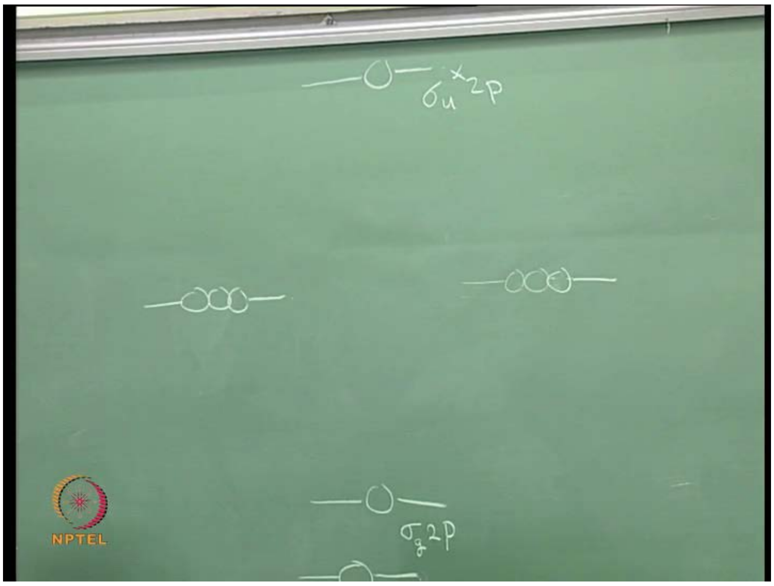

So, I will move this up. Okay, imagine that the separation is too large; why did I assume that? Because then what will happen is that this 2s and this 2 p z which can interact that interaction I can forget for the time being if this separation is large, correct, and then what will happen the 2p here will interact with the 2p there. I will get a bonding molecular orbital because of that and an antibonding molecular orbit because of that. How will you call it? It is going to be called a sigma g 2 p, right, and this is going to be called as sigma u star 2 p. I should probably draw pictures of these molecular orbitals how would they look like.

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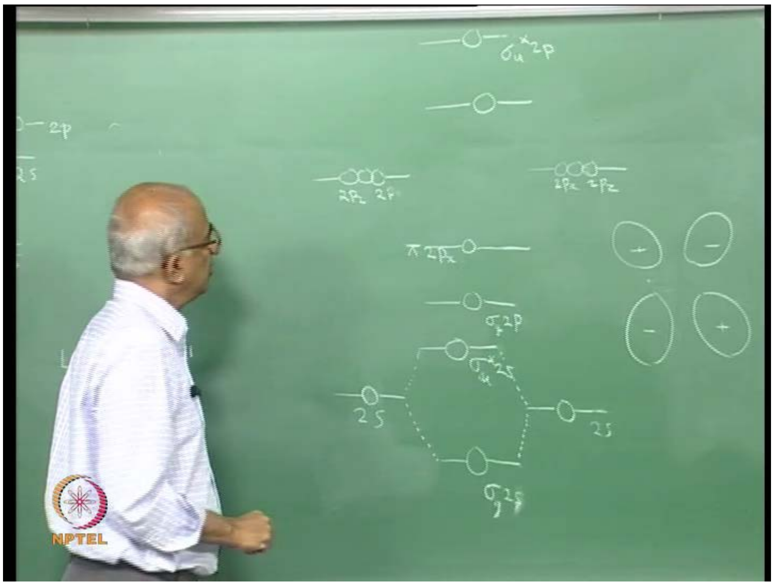

So, this is 2p on the first 2 p z and 2 p z on the second. Well, I will draw it in such a fashion that I will say it is positive lobe is on this side, and this is the negative lobe. This is the usual way people would draw it the first orbital; I mean if we draw them in such a fashion that they point towards each other. So, then what will happen? If you want to construct the bonding orbital you will have to just add them up, and if you wanted to construct the antibonding orbital you have to subtract the second from the first. So, if you added the two up, what is going to happen? You will have a positive lobe situated right in the middle, because you see this plus and that plus they will add up, and I will get this, and you will have a negative lobe on this side as well as a negative lobe on the other side.

So, these is actually sigma g 2 p, but instead of doing that I could take this, right; subtract it from the second which essentially means that I will change the sign. This plus will now become a minus and that will become a plus; after changing the sign I can just add them up. So, if I did that what will I get? I will get some orbital which looks like this. This is going to be minus, here it is going to be plus. Then you will have minus here and then you will have a plus here, correct. Now if you look at this you can ask how many nodes does it have the way it is drawn? Well, you see this will have a node somewhere here, because when separating the positive and the negative region there should be a surface, and it will have a another node there, both are nodule surfaces. So, this has 2 nodes.

What about this one? There will be one nodal surface somewhere like that; there will be a nodule plane like this, and then there will be another node like that. So, therefore, this has three nodes, and that essentially is the reason why this is not bonding while this one actually is bonding of course, you could also say that if you put electrons into this orbital the electron density goes into the internuclear region; while if you go to electrons into that orbital electron density does not go into the internuclear region and therefore, this is bonding while that is antibonding. So, this one we will call it sigma u star 2 p, and what does sigma mean? It is just the same as I have told you earlier. These are orbitals that have cylindrical symmetry about the z axis about the internuclear axis.

You can see that if you rotate it this orbital about the intermolecular axis the orbital remains unchanged; the appearance of orbital remains unchanged and that happens with this also. So, these are sigma g 2 p and sigma u star 2 p. So, those I have represented, and the orbitals actually these 2 p orbitals, what do they do? They will interact, and they are pointed towards each other and therefore, you would expect that they overlap and consequently the interaction is rather high. Now suppose you think of 2 p x here, and 2 p x on the other side that we have already accounted for the interaction of 2 p z on this side with 2 p z on the other side that we have accounted for, because that is how this bonding and that antibonding orbitals are found. But now suppose you think of 2 p x on the first again let me draw a pictorial representation of 2 p x.

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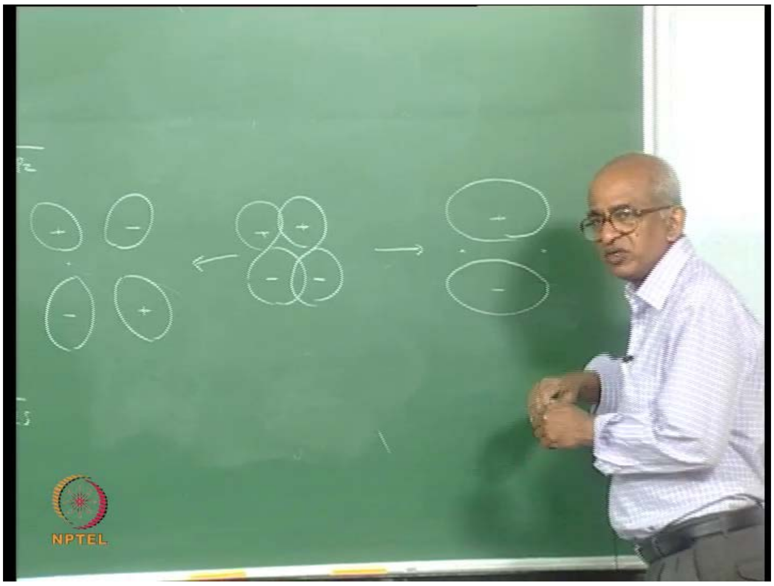

So, here is 2 p x on the first, and there is 2 p x on the second. Clearly the overlap integral is nonzero, but unlike the overlap between 2 p z's, 2 p z's were pointing towards each other, but these are not pointing towards each other. They are just overlapping sidewise and sidewise overlap is not as sufficient as overlap in the case where the two orbitals point towards each other, and therefore, you would expect that the value of the overlap integral s as well as the value of H ab, you would expect that it would be lower. So, therefore, these orbitals interact not as strongly as the 2 p z, and therefore, what will happen? When they combined to form bonds, right, when they combine to form bonding orbitals, not bonds; when they combine to form bonding orbitals, what will happen? The spitting of these orbitals will not be as high as in the case of 2 p z, because the value of H ab as well as the value of s is smaller, ok and further.

So, therefore, if you think of 2 p x interacting with 2 p x, can 2 p x interact with 2 p z on the other? No, definitely they cannot overlap integral is 0. It cannot interact with 2 p y on the other again the overlap integral and the resonance integral are both zeros. So, therefore, 2 p x on this can interact with only 2 p x on the other one, and what will you get? You will get a bonding orbital, ok, and you will get an antibonding orbital, and as if I told you this splitting is larger, because the overlap is larger while this splitting is smaller in comparison, ok, and what will happen if you just added the two orbitals together; if you just added these two orbitals together you are going to get the bonding orbital, how would it look like? You would have a positive region here.

The wave function would be positive there, and you have a negative region down here simply by adding that you can see, ok. So, here are the two nuclei; the other possibility is actually to subtract the second from the first; that means you are actually multiplying this with a minus 1. So, this lobe will become negative, and that lobe will become positive, and then you add. So, what will happen? You will have a negative lobe here; sorry, you will have a positive lobe there, then you will have a negative lobe here, a negative lobe here and a positive lobe here, correct; that is how it is. I mean all that you need to do is multiply the second orbital with minus 1 and then simply add it; that is what it is going to happen.

And you would realize that this has one node, where is that node? The 2 p x has both the 2 p x have nodes, where are they? They are in the y z plain, right. So, therefore, when you add the two up you are going to get that node. So, therefore, there is a nodal surface; it is actually a plain which is actually the y z plain. So, this has one node; what about this one? Well, the y z plane is a node for that, but in addition to that you have another node which is a one more plane like that. So, the energy of this is larger while the energy of this is lower. It is bonding and that is actually antibonding. Now these orbitals that I have described sigma g 2 s sigma u 2 s sigma g 2 p and the other one, they were all having cylindrical symmetry about the z axis about the internuclear axis, but this one if you look at this.

Suppose I rotated this orbital about the z axis; this is my z axis. If you rotated the orbital about z axis by a small angle you see the appearance will actually change. If you rotate it by 180 degrees, what will happen? This positive lobe will come here; the negative lobe will go there, right. So, therefore, that would be actually equivalent to multiplying the orbital by minus 1, right, and then if you rotate by 360 degrees of course, the orbitals appearance is unchanged. So, orbitals which have this kind of symmetry they are referred to as pi type molecular orbitals, right. So, therefore this orbital is actually a pi type molecular orbital, ok. It has come from 2 p x; its origin is from 2 p x, right, and further suppose you perform the operation of inversion if you inverted this orbital. Remember inversion, how do you do this? You invert it about the center of the molecule.

If you perform the operation of inversion it is obvious that the orbital will change sign, and therefore, this has to be classified as ungerade, and therefore, I will say that this is pi u 2 p x. On the other hand if you are thinking of the antibonding orbital which is shown here this is actually pi u 2 p x if we think of this ungerade orbital; sorry if you think of this orbital it is pi, because if I rotate it by 180 degrees about this axis about the molecular axis the orbital actually changes sign, and if you rotate by only a small angle it is actually the appearance itself will change.

So, this is actually classified as pi, but if we look at this it is actually having inversion symmetry, because if you inverted the orbital about the center of inversion of this molecule you will find that the appearance is unchanged. So, therefore, you will say it is pi g, and it has arisen from 2 p x, and in fact, it is antibonding. So, therefore, if you like you can put a star there to indicate that it is antibonding, right. So, these orbitals, the one is pi u 2 p x and the other one it should be called pi g star 2 p x. Now further whatever I have told you regarding 2 p x is actually valid for 2 p y; 2 p x and 2 p y are not very different. They are different only in the sense that the orientations in space are different, ok. If you say 2 p x is in the plane of the board, 2 p y is actually perpendicular to the plane of the board.

So, there is a 2 p y here; there is a 2 p y there. They are going to interact just the way this 2 p x interacts. So, what will you get? You will get a bonding orbital and an antibonding orbital. Their appearances are going to be exactly the same expect that they will be in a plane perpendicular to the plane of the board like that. So, therefore, and further they will have precisely the same energy as your these orbitals. So, therefore, from combining together of 2 p y here with the 2 p y there, you will get one more orbital having precisely the same energy as this. This is actually my pi u 2 p y, and here again you will get one more orbital, right, and that will be pi g star 2 p y, right. So, this is what happens if the energy separation between 2s and 2p is large, and this will be the order of the energies of the molecular orbitals; sigma g 2 s will be the lowest and starting from there it goes on increasing, right.

This is the way if this energy separation is large. This energy separation is large in atoms which have sufficiently large number of electrons. So, for example, if we think of oxygen atom or fluorine atom this is actually fine, this picture I have drawn, because the separation is large. But if we thought of something like carbon or if we think of b 2, right, this energy separation is not large, right, and if that energy separation is not large of a; obviously, what will happen this you will have to go closer, but then what will happen is that you see this 2 p z here will interact with the 2 s there. The interaction is not small, and similarly the 2 p z there will interact with the 2 s here as a result of which what will happen.

The result is that you see when they you have interactions the energy of this orbital will get lower, the energy of this will go up as a result of this interaction because of this contribution. So, therefore, what happens is that this energy level goes higher, and these energy levels actually what will happen in any interactions whatever is higher will go further higher, and whatever is lower will go further lower down. So, you can say ok, these two orbitals actually in a sense they push down while the two higher lying orbitals this one and that one, these are the orbitals that involve 2 p z. So, they will get pushed up, right, and therefore, for a molecule like carbon or b 2 the orbital order is little bit different. So, the orbital order is actually going to be, quickly let me try to draw this.

I hope I can be quick; I have to be there full in checking. This is actually 2 s that is 2 p; this is again 2 s that is 2 p. This will be sigma g 2 s; this will be sigma u star 2 s. What happens is that you see these two orbitals their order gets interchanged. So, this will get lower. So, therefore, this is actually going to be I u 2 p. I will not put this subscript x or y; it could be x or y. They are both having the same energy, then I would have the next one this goes above. So, I would have sigma g 2 p; what is the next one? The next one is actually pi g star 2 p, and the last one is sigma u star 2 p. So, this will be the order in which the orbitals are in the case of diatomic like b 2 or c 2, ok. So, we will use this in the next lecture. So, you have to draw these lines; I will draw them clearly in the next lecture.

Thank you for listening.