Quantum Chemistry of Atoms and Molecules
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Lecture-60
Non-Equivalent Hybrid Orbitals

In our discussion of polyatomic molecules so far we have talked about hybridization we have discussed sp sp2 and sp3 hybridization. These orbitals are involved in linear trigonal planar and tetrahedral geometries respectively. A very important point about these orbitals is that these are examples of equivalent hybrid orbitals but if you remember our very first discussion where we talked about Pauling's theory we had said that hybrid orbitals are formed by mixing of orbitals using mixing coefficients there is no guarantee that these coefficients have to be the same for our all orbitals energy has to be conserved of course.

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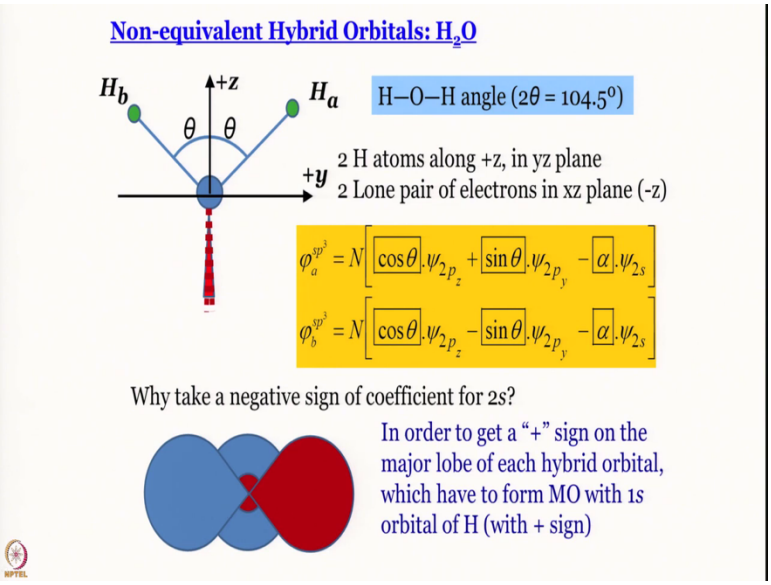

So today in our concluding discussion of hybridization we are going to talk about non equivalent hybrid orbitals and a good system where one has to use non equivalent hybrid orbitals is our good old water. In water molecule the bond angle is not 109.5 degrees as you would expect for this tetrahedral geometry. It is not very difficult to see that you expect water in water you expect oxygen atom to be sp3 hybridized.

Because you it needs 4 hybrid orbitals 2 for the lone pair sorry 2 for the bond pair and 2 for the lone pair but the bond angle experimentally observed for water is 104.5 degrees. So of course the hybridization is not exactly sp 3 it is something different it has to be something between sp 3 and well it has to be something beyond sp 3 because sp 2 bond angle is 120 degrees sp is 180 degrees. So, as you go from sp to sp 2 to sp 3 bond angle keeps on decreasing 180 to 120 to 109.5.

What we see is that for water bond angle is even lesser than 109.5 degrees so p contribution in these orbitals must be a little more than 75%. p contribution in the orbitals used to accommodate lone pairs that has to be a little less. So, this is something that we understand now we will work out how much p contribution what is the expression. Again as we can hold the molecule in whatever way we want in order to make our life simpler we hold it like this,

We hold the molecule in y z plane and we hold it in such a way that this H O H bond angle is exactly bisected by the z axis. So I have written this theta and theta which means bisection. So, 2 theta is 104.5 degrees theta would be 51.25 degree sorry 52.25 degrees. Where are the lone pairs lone pairs are in the z x plane. The good thing about doing this is that if something is in the y z plane some hybrid orbital.

Then there is no contribution from p x is not it so one parameter less. Similarly for the lone pairs the hybrid orbitals are in zx plane that means there is no contribution from the p orbital so one parameter less so that is how we are going to proceed. So let us write like this you might remember how we had written the expression in the very first the very first expression we had written for hybrid orbitals involved cos theta and sin theta.

Here also we write like that we say that the 2 hydrogen atoms are named H a and H b so the sp 3 hybrid orbital used to form bond with a well this is not really sp 3 notionally sp 3 I am writing like that but I might as well just have written phi a. So phi a is given by what will be the contribution of p z the angle between z axis and this hybrid orbital is theta. So contribution of p z has to be proportional to cos theta.

Then similarly the angle between y axis and this orbital is 90 degrees minus theta so this coefficient has to be proportional to sin theta and for psi 2s I do not know what the coefficient is I just write minus alpha and then the whole thing is multiplied by N because you have to normalize the orbital also. Similarly we can write an expression for phi b as well. The only difference between phi a and phi b is that this orbital this hybrid orbital used for bonding with H b is towards the negative side of the y axis.

So here will have a negative sign so we write that negative sign explicitly and write minus sin theta psi to p y but then why have I written a minus sign in front of alpha we do not have to, it might as well as might as well be plus it does not matter. But the good thing about writing minus sign for psi is this for psi 2 s is this. If you remember for 2s orbital there is a radial node is not it. So the sign of wave function near the nucleus is let us say positive.

Then it goes down to 0 at some point goes further down becomes negative here and then becomes 0 asymptotically after going through minimum. So if I just write psi 2s then it is likely to imply that this red portion is plus and this blue portion is minus. The problem is this now I am going to mix it with a p orbital and if you remember our discussion of why that nucleus is in the minor lobe of hybrid orbitals you can understand that the sign of the inner lobe is actually the sign of the minor lobe.

The sign the sign of 2s wave function inside between the nucleus and the radial node is the sign of the minor lobe of the hybrid orbital. So conventionally we like to keep the sign of the major lobe plus that is why we use a negative sign for the coefficient of 2s but it is not compulsory you might as well keep it positive it does not make any difference.

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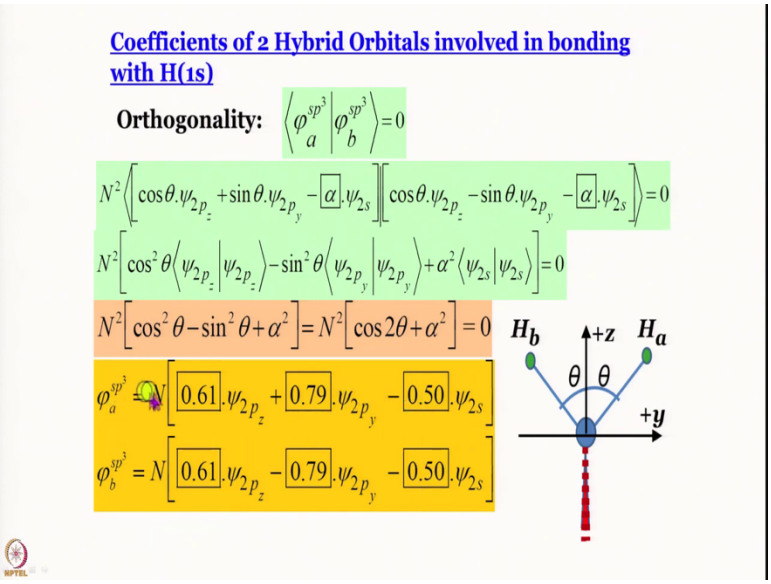

So, now to determine the coefficient first relation that we will use is orthogonality between these 2 hybrid orbitals. So this is the orthogonality relation as we know so we can write n square then in bra vector we write phi a sp 3 in ket vector we write this and when we expand this what we going to get? We are going to get sum of terms. In principle you have 3 and you are multiplying by 3 you should get that many terms but it is not required because we know that when we open the bracket we are going to get terms like.

So suppose I take this and this what will I get cos square theta integral psi 2p z psi 2p z over all space. Now this is normalized so this is actually going to be one. Similarly when you take sin theta psi 2 p y and minus sin theta psi 2 p y you are going to get minus sin square theta integral I will not even write it psi 2 p y in bra psi to b y in ket that is equal to 1 and then you get plus alpha square psi 2s in bra and psi 2s in ket vector.

However if you want to take this and this what will you get you get minus sin theta cos theta multiplied by integral psi 2p z psi 2p y overall space and we know that they are orthogonal so this is going to be equal to 0. So we do not bother about cross terms like those we simply open the bracket and obtain this expression and this further simplifies to this. So you get N square multiplied by cos square theta minus sin square theta plus alpha square is equal to N square cos 2 theta minus alpha square that is equal to 0 cos square theta minus sin square theta is cos 2 theta as we know.

Now do we know cos 2 theta? We do, do we know N? We do not but it does not matter because N cannot be 0 so you forget about that we equate cos 2 theta plus alpha square equal to 0 and we know that cos 2 theta is equal to 104.5 degrees so we might as well substitute the value of cos 2 theta here and find out the value of alpha is that clear. You are going to get alpha square equal to minus cos 2 theta.

So when you substitute that this is what you will get alpha turns out to be 0.5 and we take the plus root because we have written the minus sign already and when you use the values of this sine theta and cos theta cos theta and sine remember what theta is? 2 theta is 104.5 degrees so theta is equal to simply 52.25 degrees. So, cosine and sine of 52.25 degrees are 0.61 and 0.79 respectively we have got this.

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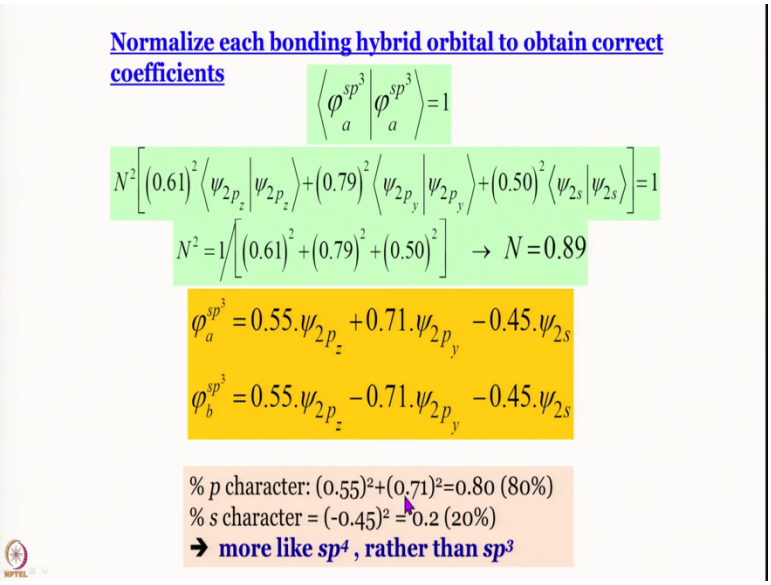

What is left to be done we have to find N how will I do it by using normalization we are going to normalize the orbital equate to 1, so you get an equation like this once again we do not have to bother about anything that involves a product of 2 different orbitals and we know that these orbitals are normalized. So these all become equal to 1 and finally you get N to be equal to 0.89 I am going quickly here because it is very easy we have done so many things already we are running out of time.

So in case there is a problem please do not hesitate to contact us. So, N equal to 0.89. Now it is done you just multiply whatever you had earlier sin theta cos theta 0.5 by 0.89 you get the final expression for these hybrid orbitals a and b and these are the final expressions. What can we find from here? We can find out the s coefficient and p coefficient sorry s contribution and p contribution. So we can find out the s contribution and p contribution from the coefficients and that gives us percentage p character is 0.55 square plus 0.711 square this square plus this square that turns out to be 0.8% s character is equal to 0.2.

So 20% s character 8% p character so this hybridization is actually sp 4 hybridization not really sp 3 hybridization. Now if I just say it casually you might think where did that 4th p orbital will come from? The 4th p orbital did not come from anywhere this exponents here simply are proportional to the s character and p character that is all. There are only 3 in fact the way I have written it here only 2 of the p orbitals have contributed but it does not matter.

The percentage p character percentage s character these are things that are reflected in what kind of hybridization it is. So we have this interesting observation for that the hybrid orbitals used in the bond bonding pair to used for the bonding pair in water are actually sp4 hybridized. What about the hybrid orbitals that are used for lone pair. Of course their hybridization has to be something like sp n where n is less than 3 yeah because average has to be sp 3.

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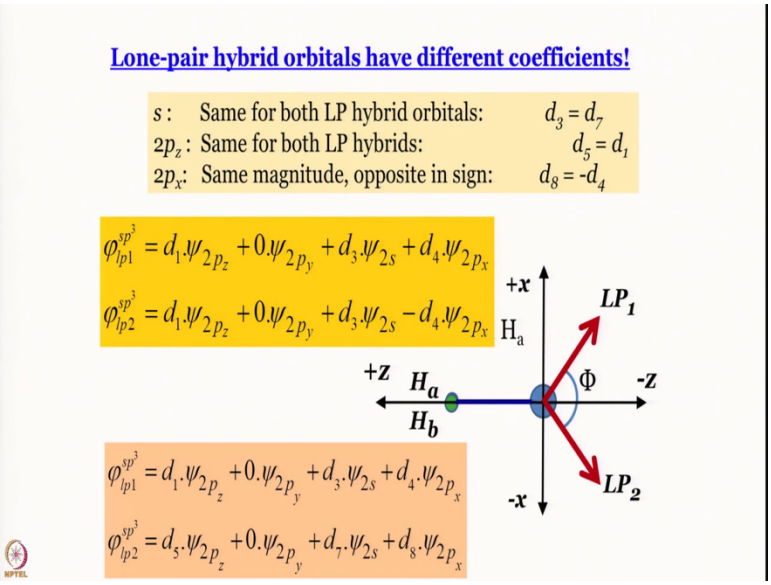

There are 3 p orbitals after all. So for the lone pairs we can write the expressions once again like this d one d 2 d 3 d 4 d 5 d 6 d 7 d 8 these are the coefficients we start with that. Then we remember that the lone the hybrid orbitals used for lone pairs they are actually in your x z plane; x z planes means contribution well coefficient of this psi 2 p i is equal to 0. So d2 dx of course has to be equal to 0 this is a different perspective of showing the same thing.

What do we not know? We do not know this capital phi we do not know the angle. So as we are saying d 2 equal to d 6 equal to 0 fine that is very simple. What more can we do first of all let us write the expressions with d 2 and d 6 set to 0 this is what you get. Now you have d 1 d 3 d 4 d 5 d 7 d 8. Now see it is not very difficult to understand that contribution of s has to be same for both these hybrid orbitals is not it. Remember the case of hybrid orbitals used for bonding pair contribution of s was same in both sp4 contribution of p was also the same.

In this case what will happen is contribution of s has to be same contribution of p z has to be same contribution p x has to be same that is what happened earlier also. Here the thing is that each of the p orbitals involved makes equal contribution to the both to both the orbitals because the symmetric look at this z axis look at the hybrid orbitals. The contribution of p z here will be same as contribution of p z here.

Look at the p x orbitals the only difference is that contribution of p x will be positive for LP 1 contribution of p x will be negative for LP 1 but magnitude has to be same so we can write d 8 equal to minus d 4 d 5 equal to d 1 d 3 equal to d 7 so this is what this pair of equation becomes.

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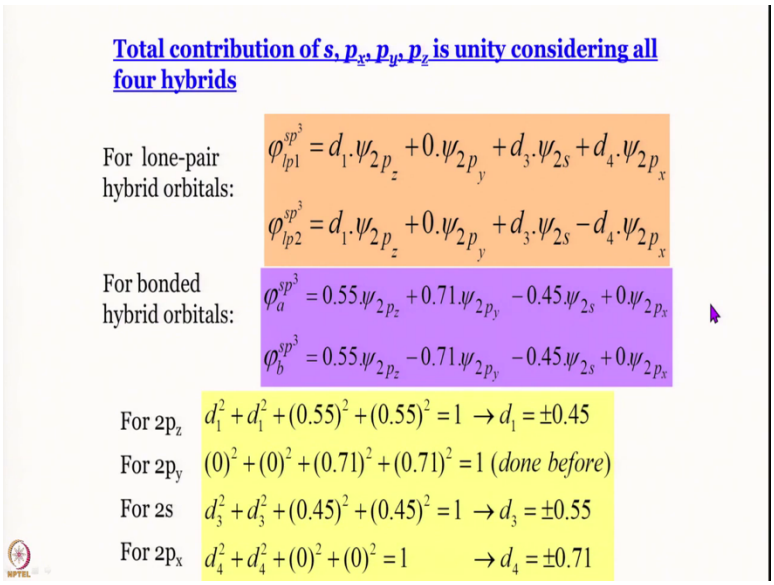

Now the matter is not very difficult we have to find 1 2 3 coefficients and we have 2 equations how do you do it? 3 coefficients 2 equations we can actually do it because we do not have 2 equations, we have 4 equations. Remember we have already worked out the equations for the other hybrid orbitals that turned out to be sp 4. Now we have 3 unknowns and 4 equations no problem actually to start with we have 4 unknowns and 4 equations.

It is just that we have worked out one of them already. Now what will I get then total contribution of 2 p z has to be one so d 1 square plus d 1 square plus 0.55 square + 0.55 square that is equal to one for 2s d 3 square + d 3 square equal to 0.5 square + 0.245 0.45 square + 0.45 square equal to 1 for 2p x 2d 4 square + 0 is equal to 1 that is very simple and from there you work out these d coefficients also.

I went very quickly here because I think this is very simple algebra which you can handle by yourself please let us know in case of any difficulty.

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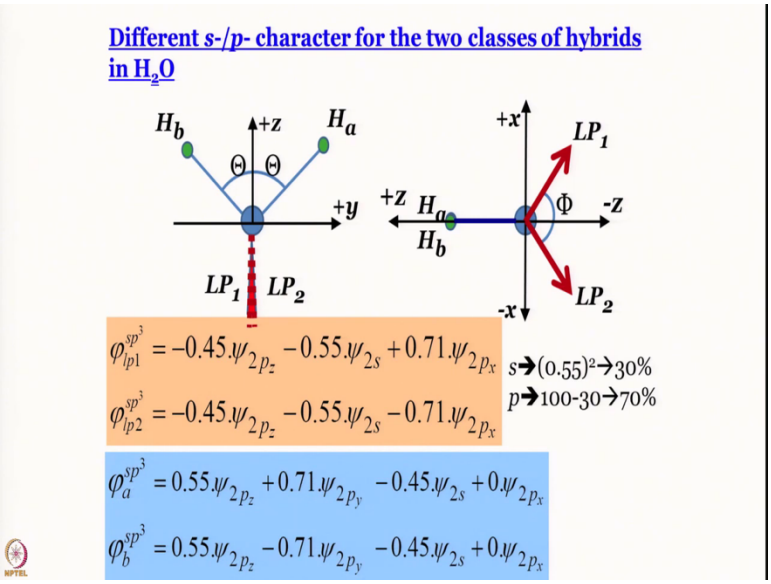

But to end this discussion what we observe is that in these hybrid orbitals used to accommodate the lone pair your percentage s character is 30% percentage p character is 70% or rather I am saying percentage twice that sounds little silly so s character is 30% p character is 70% so again this is not sp 3 this is not sp 4 this is s 2 point something. If I normalize with respect to z what is 7 with respect to 3, 7 by 3 so I can say sp 7 by 3, so p 7 by 3 will be 2.3 or something like that sp 2.3 something between sp 2 and sp 3.

So what will the angle be please work it out yourself I will not work out but you can work out yourself what is the angle between the hybrid orbitals that accommodate the lone pair. And this is a very bad question that we have. So this is what it is if you now compare all the 4 orbitals together you will see that it makes perfect sense total contribution of psi p 2 z is equal to total contribution of psi 2 s is equal to total contribution of psi 2 p x is equal to total contribution of psi 2 p y everything individually is equal to 1 there is absolutely no problem.

What we have done is that we have used different contributions of these wave functions to construct hybrid orbitals that are suitable for accommodating the bond pair and lone pair that is all we have done. We have synthesized the hybrid orbitals according to the experimental result. Please do not put the card before the horse and think it is the other way round.

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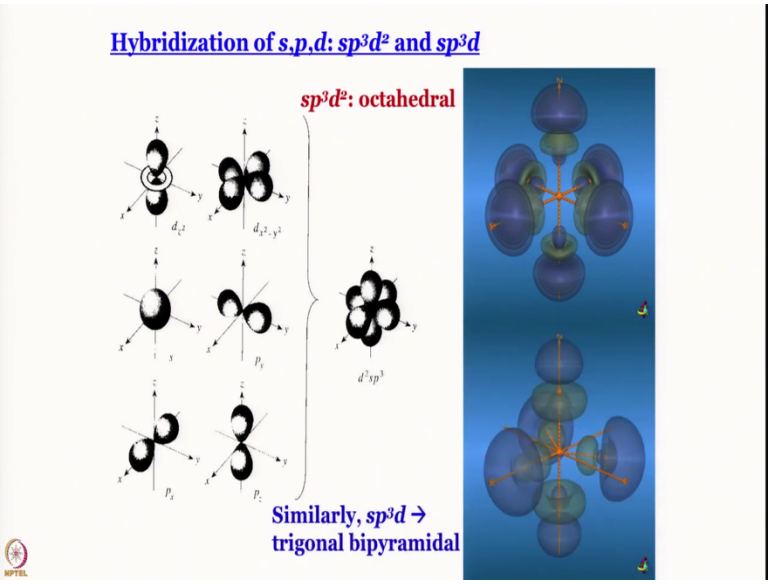

Last point just to mention in the passing is that sp 3 is not the only well s the sp orbitals are the not on not the only orbitals that participate in hybridization you can have for example if you want octahedral if you want to explain octahedral geometry the hybridization used is sp 3 d 2. You can have sp 3 d and so on and so forth. You can have trigonal bipyramid sp 3 d and you can work out the coefficients exactly in the similar way as you have as we have done in our sp sp2 sp3 sp4 and sp sp 2.3 hybrid orbitals.