Quantum Chemistry of Atoms and Molecules
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Lecture-59
SP3 hybridization

By now we have learnt how to generate expressions for hybrid orbitals by using linear combinations of atomic orbitals that we get by direct solution of Schrodinger equation. So as we said earlier why is it that hybridization is taking place so that the electron density is optimized to form the bonds. So see electron cloud is what we have we do not have like rigid particles and that is the beauty of the system.

The electron cloud can deform and adapt to the requirement that it faces. Right now the requirement we are discussing is formation of bond so if say for example boron it forms a trigonal complex a trigonal compound with fluorine BF3 so it has to react with 3 fluorine atoms it has to form bonds with 3 chlorine atoms in order to satisfy its valency you can actually go back to this very fundamental concept of valence.

So 3 bonds will be there and these 3 bonds according to Gillespie and Nihom VSEPR have to be at 120 degrees to each other that is why the electron cloud sort of deforms itself because the situation demands and forms these new orbitals you can think like that. Of course this orbital is used to the hybrid orbital is used to explain the situation. It is not as if they are the cause they had the effect of the cause really is minimization of the repulsion between among electron clouds.

Let us not forget that so you can think of these electron clouds as shape shifters remember I I can only remember movies from long ago so terminator where this bad element from future could sort of take the form of anything or remember species or many such movies are there. So electrons are like shape shifters and they can modify themselves according to the demand of the situation. And the demand we have discussed so far is formation of 2 bonds or 3 bonds.

We had said that we will work back calculate the angle between the bonds but I had a second thought about that. We are going to do a calculation but we will do it with sp3 hybrid orbitals, let us get ahead.

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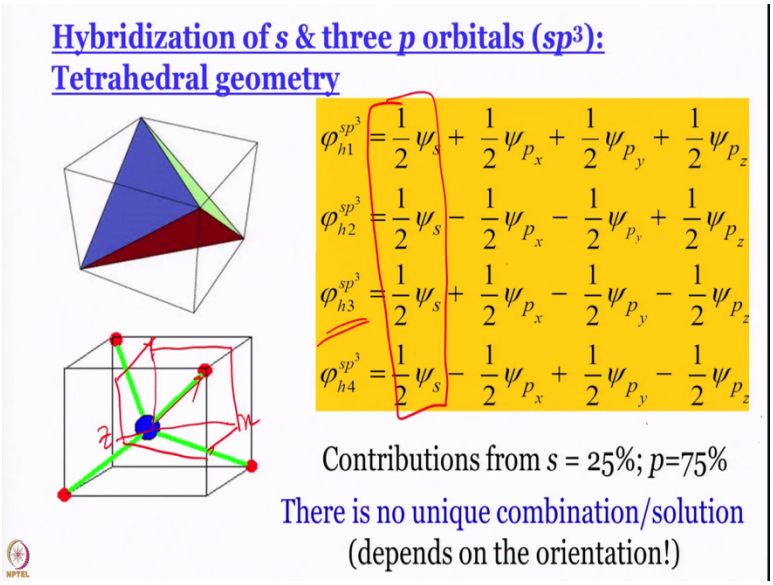

So now I want to talk about sp3 hybrid orbitals. So sp3 hybrid orbitals means 4 orbitals are there 4 hybrid orbitals that means they are required in formation of ab 4 kind of molecules where a is a central atom and they should form tetrahedral. Before doing anything else I can say that the angle has to be 109 degrees because this this is how this is a 1 good way of drawing a tetrahedron put a dot well first of all draw a box and unfortunately this has got distorted this is a all the sides are square actually this is a cube.

Perfect cube not cuboid, so put dots on alternate vertices and then join those dots to the center you have your tetrahedron. So this is what we want since we want 4 hybrid orbitals all the 3p orbitals have to participate and let us say to start with we have a situation in which all the 3p orbitals make equal contribution to each of the each of the hybrid orbitals. So what should the coefficients be? So before showing you the results let me just work it out.

So our expression will be something like this psi hybrid is equal to C 1 psi 2s and I want equal contribution from each of the orbit or p orbitals so I can write + C 2 psi 2p x + C 2psi 2p y + C 2 psi 2p z if you cannot read my handwriting please do not worry I will show you the final result in

in a nice form anyway. So, how many such hybrids are there I can write 1, 4. So, here everything will be C 1 is not it and total contribution of 2s is 1 anyway.

So what we get is 4 C 1 square is equal to 1 so C 1 is equal to half simple + half or minus half whatever does not matter but we can take either + half or minus half all that will change is your p orbital will look either like this or like this nothing else will change. In fact you will see a situation for coming very soon in which we are going to use a negative coefficient for psi 2s knowingly C 1 equal to half that is done what about this C 2's. um

Let me say something else what will the C 2's be for 1 thing I can write away this hybrid orbitals have to be normalized. So I can write C 1 square + 3 C 2 square is equal to 1 and I know very well that C 1 square is equals is equal to 1 4th because C 1 equal to half so I have 1 4th + 3 C 2 square is equal to 1. So C 2 square is equal to 3 4ths well 3 C 2 square equal to 3 4th C 2 is equal to plus minus half. So one solution is plus half I can write plus half for everything it is fine.

So let us start with that the totally symmetric answer in which every coefficient for the p orbital is plus half so the first wave function that we can write is and now before I say what the first wave function we can write let me just clear all this. And let us go back to the presentation mode that is where things are written much more neatly so hopefully it will be easier for you to understand. Just give me a second please.

All set this is the first one that we have already got what will the second one be? See your hybrid orbitals have to be orthogonal to each other and again I will start writing of course I will erase also later on. Suppose I write something like this phi h 2 sp 3 equal to this will be half not much doubt about that psi s. Now I will just write the orbitals for psi 2p x psi 2p y psi 2p I have not written to be there but anyway psi to pz.

Sorry for being a little inconsistent, now if I just multiply them and integrate over space I am going to get 0 in any case I know that mod of this coefficient first of all I can write like this + C 3 + C 3 + now C 3 + not a good idea to write C 3 again if I write + C 4 + C 5 and we know that

mod C 3 equal to mod C 4 equal to mod C 5 is equal to half because every p orbital that is what we are considering every p orbital makes an equal contribution to the wave function.

So the squares must be the squares must add up to 1 and they are equal to each other. So that is all fine. So now the mod's are same and what the other thing that I can do is I can take this integral phi h 1 phi h 2 is equal to 0 which means 1 4th + C 3 by 2 + C 4 by 2 + C 5 by 2 equal to 0 how did I get this? Because when I do the multiplication remember integral of say psi 2s psi 2p x over all space is equal to 0 they are orthogonal to each other so that is how we have got it.

And then they are normalized also and then remembering that actually these are all plus half well plus or minus half what it means is that I have to put in 2 minus signs for this quantity to be equal to 0. Let us say what I mean C 3 by 2 C 4 by 2 C 5 by 2 all mod of this mod of C 3 by 2 I can write like this mod of C 3 by 2 is equal to mod C 4 by 2 equal to mod C 5 by 2 is equal to half. So what are the absolute values sorry is equal to 1 by 2 into 2 therefore that 2 so is equal to 1 by 4.

So what I have here is that this is 1 4th this can be plus or minus 1 4th this can be plus or minus 1 4th this can be plus or minus 1 4th so the only way in which this will be 0 is suppose I put in a minus sign here and a minus sign here then I will get 0, 1 4th from here plus 1 4th from here 1 4th from here 1 4th from here minus minus that will be 0. And what I can do is in the next combination I can move this plus sign here take the minus sign there.

So I can move the plus sign around what it means is that the for the coefficients of the p orbitals 2 of the coefficients must be equal to minus half and 1 of the coefficients has to be equal to plus half that is the only way in which the condition of orthogonality of the hybrid orbitals can be satisfied there is no other way. So what we have done is remember we have actually constructed this wave functions under a lot of constraints.

We have made sure that contribution from each p orbital is exactly the same and then we have required that they are normalized and now we are required that they are mutually orthogonal also. So, that gives us that leads us to the conclusion that 2 of the p orbitals must have

coefficients of minus half the third will have coefficient of plus half so I first of all I can write like this and then all I do is I just move this plus sign first.

Could I have written plus sign here to start with yes of course how does it matter which one is h 1 which one is h 2 is in our hand. We will name accordingly so this is the complete set orthonormal set of hybrid wave functions. Now let us see whether the picture we have drawn is valid equal contributions from x y and z. Can you see where x y and z are here maybe I will try again this is the center this is a face center.

So join the face center with this the face center join with this x y and let us say this is the face center this is the easiest the most difficult to draw, draw the join the face center like this. So, this is your x axis this is y axis this is z axis let us say. Now you can think of these hybrid orbitals as vectors and you do not have to worry about psi s because it is non directional anyway. So, what we are saying is that every each of the axis x y and z contributes equally to the length of the vector.

We taking square so plus or minus will not matter we only talk about length not direction. So where will this resultant vector lie? Actually you can think of this smaller cube within cube this is a cube not a cuboid smaller cube within cube the body diagonal of that smaller cube that is your hybrid orbital and equal contribution of x y z ensures that it is there. So similarly you can see that the all the hybrid orbitals are actually along the body diagonals of the cube and it is not very difficult from your solid state geometry to work out.

That the angle between body diagonals of a cube is indeed 109 point whatever degrees. So, we have 25% contribution from s 75 contribution from p more importantly we have 25% contribution from each of the participating orbitals might be s might be p we are going to discuss another situation shortly. So remember there is no unique combination of solution if you change the orientation the coefficients will change.

What will not change is the relative contribution what will not change is the fact that they have to form an orthonormal set.

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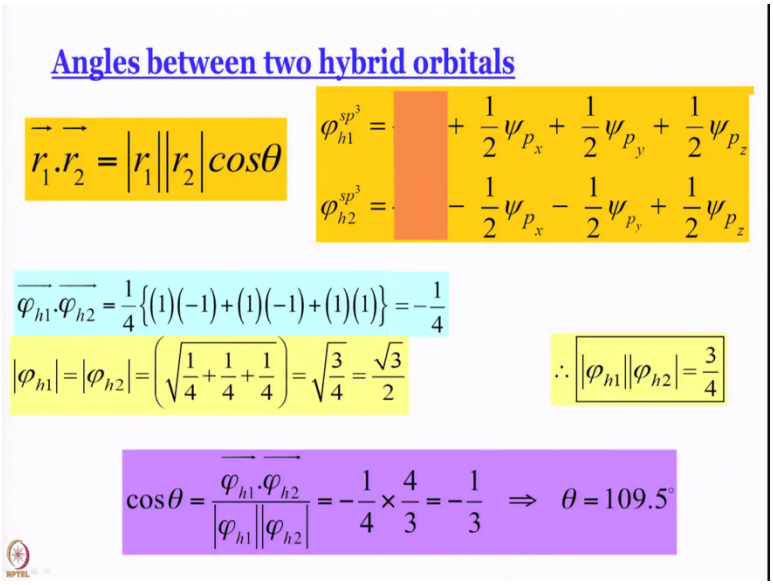

Complete orthonormal set now that being said we have worked out the angle anyway now let us work out the angle in a little more formal manner. And to do that we will work with h 1 and h 2 orbitals. If you remember the formula the working formula for dot product of 2 vectors this is what it is. You take a dot product r 1 dot r 2 that gives you mod r 1 mod r 2 magnitude of r 1 magnitude of r 2 multiplied by cos theta.

So what we can try to do is what is the unknown here the unknown is theta what is the angle between h 1 and h 2 that we do not know but knowing the vectors we can find out the dot product and we can also work out the magnitudes the length mod r 1 mod r 2 and we can find the product so we can try to find cos theta by from the by dividing the dot product of r 1 and r 2 by the product of the magnitudes.

To do that first of all we royally ignore the s orbital, we have washed it out with a different color we do not care about s anymore well for some time. Because s is not directional it does not count as a vector it does not contribute in this discussion. So the vectors that we want to work with are x y and z, p x p y p z all equal magnitudes. So the dot product here would be what now remember this cos theta business so cos theta of x and y is 0 this is well known in vector algebra but I am saying this in case some of us forgotten.

Dot product of x and y, y and z, z and x all that is equal to 0 dot product of x and x is 1, so what will I get? Half into half is 1 4th I can take 1 4th common so I will be left with 1 - 1 all that so the first term comes from p x dot p x 1 into -1. Second term comes from p y dot p y + 1 into -1 third term comes from p z dot p z that is + 1 into + 1 so what do I get the dot product turns out to be remember dot product is a scalar quantity not a vector quantity.

1 4th multiplied by -1 -1 + 1 that is minus 1 4th we have worked out the dot product. What about the magnitudes magnitudes? Will be well these are at 90 degrees to each other p x b y p z so magnitude will simply be well square root of half square plus half square plus half square yeah so so that will be root over 3 by 2 that is the length of the vector magnitude. So if I take product of magnitudes then I get 3 by 4.

So I have got the dot product to be minus 1 4th I have got the product of the magnitudes to be 3 by 4 what is cos theta? Cos theta is just the dot product divided by product of magnitudes turns out to be minus 1 third take cos inverse of that theta turns out to be 109.5 degrees. So we are convinced that this is an actual tetrahedron and everything falls together beautifully it is a tetrahedron.

In order to minimize repulsion between bond pairs but when we do that and we construct these hybrid orbitals it turns out that we get the correct value of the angle. And this is going to be very useful this kind of calculation in when in the next class we talk about non equivalent hybrid orbitals. We talk about water wait for it but let us finish this discussion what happens if I hold it in a different orientation I will not work out all of it I will work out a part of it and I will ask you to work it out work out the rest of it.

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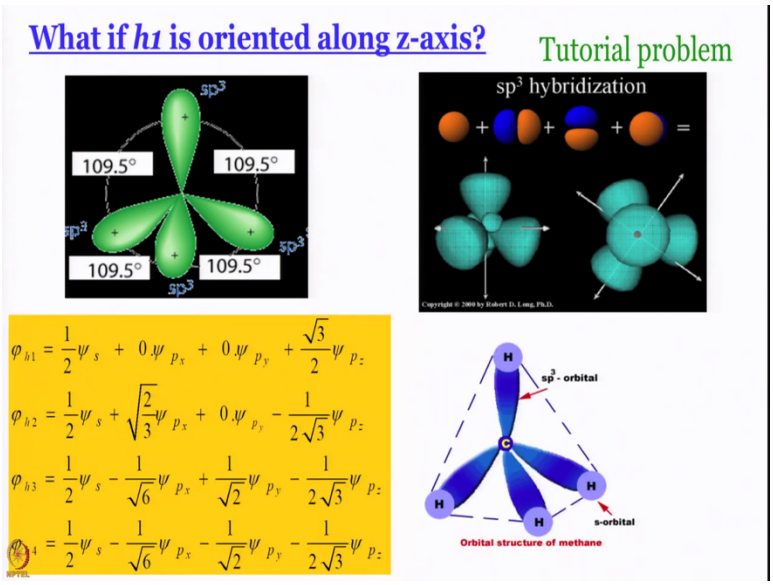

What happens if h 1 is oriented along z axis and let us say I hold the other 1 in the zx plane. So, I do not know whether this figure is very clear to you, this is what I mean, why can I not draw a straight line; so I am drawing on a screen, so unfortunately I cannot oh maybe I can use a ruler I do not have one that is all whether that is straight enough this is z axis this is x axis y axis is pointing towards us let us see.

Now I will since I can change color I will change color. What I am saying is I will put h 1 along your z axis this is h 1 and I will keep h 2 in this zx plane. Well this is x this is z sorry I should have written that so it will be something like this h 2 you know this is 109.5 degrees 90 degrees so 109.5 - 90. Now so where will h 3 and h 4 be 1 will be above the plane towards us let us see there is h 3 the other will be below the plane away from us h 4 this is how we have held the molecule.

Now we want to see what kind of coefficients we get and we want to check whether it is compatible. Whether it gives similar results compared to the earlier case where the coefficients were all either plus half or minus half great so how do I get the first one? First one is very similar let me write a little bit. So first one psi h 1 let us say is equal to C 1 into psi s no I will not write C 1; can you tell me what I will write?

See it does not matter how I hold it contribution of s has to remain in the same we still want these sp 3 orbitals so contribution has to be same everywhere and the total contribution has to be 1. So without repeating the calculation that we have done already I will write it is going to be 1 4th is going to be 1 4th C 1 C 1 square + C 1 square + C 1 square + C 1 square equal to 1, so C 1 square will be 1 4th C 1 will be equal to half.

So the same coefficient that we got earlier will be there for the s orbital but what about the p orbitals? Now they will not be the same see for h 1 I have held it along the z axis so only p z will make a contribution p x and p y will have 0 contribution. So I can write like this 0 into p x psi p x sorry + 0 into psi p y plus what will I write let me write what would it have been C 1 C 2 C 3 C 4, C 4 into psi p z let me rewrite looks like I have written in in deliberating cannot help it.

So psi h 1 hydride 1 is equal to half into psi 2 s plus again I wrote 2 anyway it does not matter + 0 into psi 2p x + 0 into psi 2p y + something C 4 into psi 2p z rest is simple this is normalized so you will get 1 4th + C 4 square is equal to 1. So C 4 is equal to root over 3 divided by 2 so already worked out 1 orbital and what I see is that first of all the entire p contribution is from 1 orbital that is p z. However if you take the coefficient square of coefficient of psi 2s and square of coefficient of psi 2pz what do you get?

1 4th is to 3 4th that is 1 is to 3 so this is still an sp 3 hybrid orbital and that is what we are trying to emphasize here. If you hold the molecule in a different way the coefficients will be different but the overall picture does not change total s character total p character will not change. What will change is contribution of individual p orbitals does not matter as long as the total s character and the total p character are not compromised we are absolutely fine.

Because we do not even know which is x n which is y and which is z we are; I thought this is indelibling now it is gone anyway. So we are just writing things in a way to simplify problems. So we are justified in simplifying the problem that is what I am trying to say its if you hold the molecule in an orientation that makes our problem little simple as long as the overall picture does not get distorted.

Now let us go ahead so this is what we had written and in fact we have gone further than what is written here we already know the values of C 1 and C 4 half and root 3 by 2. If you go to phi h 2 then again C 5 is going to be half this quite mundane now what will C 8 be a very easy way of proceeding is by using the orthogonality of psi h 1 mutual orthogonality of phi h 1 and phi h 2. So what you get is 1 4th + root 3 by 2 C 8 is equal to 0.

So C 8 hey we divided 1 4th sorry no what am I doing I multiplying phi h 1 by phi h 2 so this is 1 4 this is also 1 4th so 1 4th is actually correct but it is root 3 by 2 into C here the; everything is correct unnecessarily I had a panic attack. So C 8 is equal to minus 1 4th into 2 by root 3 is equal to -1 by actually root 6 is a minus sign actually it is because it is on the other side. So, I mean it is towards minus z so it is fine.

What is the contribution of this pz orbital now 1 6th ok as whereas contribution is 1 4th. So 1 6, 1 4 that is not sp 3 that is because this C 6 is nonzero, how do you find C 6 now simple 1 4th + C 6 square + 1 6th is equal to 1 from normalization condition and now since I have done so many and I have made a couple of mistakes also I will not do all this arithmetic anymore you do it yourself. I release and now just show you the final result and then I will go home.

So you know how to carry it how to get the coefficients this is how you get it and the coefficient for p x here turns out to be root over 2 by 3 now the thing is simple the other 2. Once again the easiest way of starting the problem is to start with the mutual orthogonality with the orbital that has a maximum number of 0 coefficients and then proceed then you have fewer terms to handle to start with at least.

But before going there just have a look here s contribution is half 1 4th p contribution what is it square of this 2 third + 1 4th of 3, so just work it out you will see that it comes to the same thing you still have s p 3 here it is just that contribution from p x and p z are no longer the same because orientation is not symmetric anymore. So symmetry actually is a very important role to play in handling quantum mechanical problems we have this NPTEL courses that we floated on chemist on symmetry some time ago.

Lectures are all available whoever is interested you are more more than welcome to have a look at the lectures. If there are questions I will be happy to answer them. So now the reason why tutorial problem is written here is that it is for you to do please work out the expressions for the third and the 4th hybrid orbitals and I am showing you the result here.

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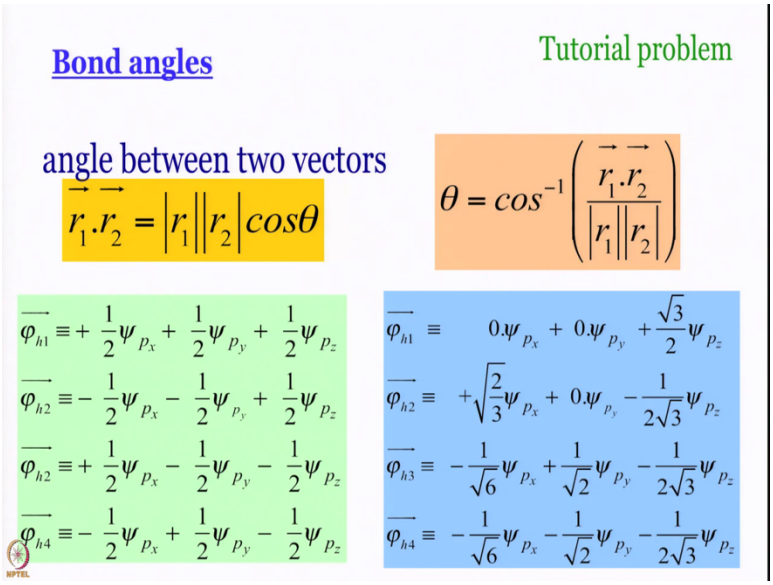

What I also want you to do is I want you to work out the bond angles using the formula that we have discussed this is something that I have done earlier.

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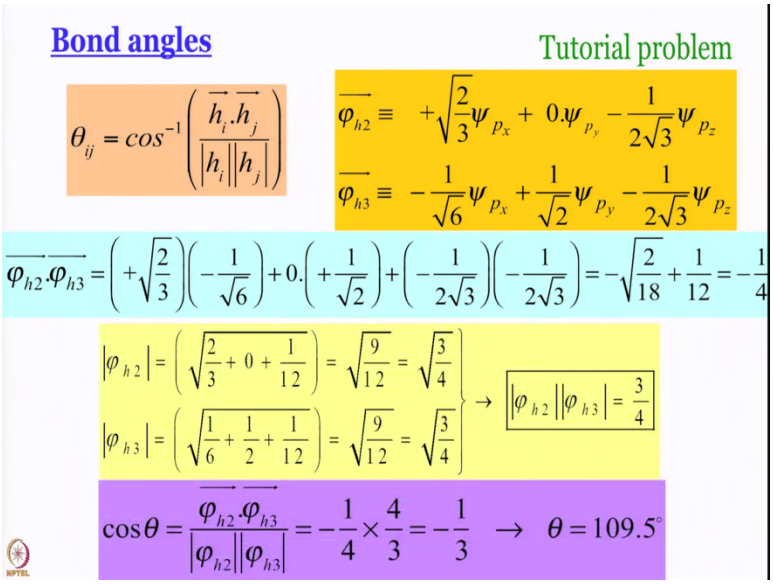

I do not know why you are written in bigger and smaller fonts but the point is work out the bond angles and you will see that the bond angle once again comes out to be 109.5 degrees. So once

again we have a scenario where you have a regular tetrahedron we have worked with hybrid orbitals that are all equivalent to each other same as character same p character and now I hope we have a little more quantitative idea of hybridization.

There is only 1 thing left on the agenda as far as hybridization is concerned and that is to discuss non equivalent hybrid orbitals that is what we will do in the next class.