Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-58
SP2 hybridization

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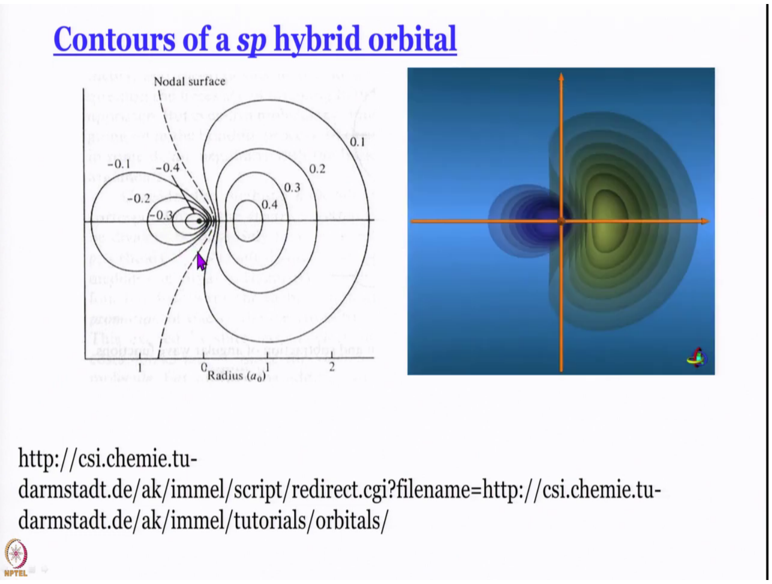

Contours of a *sp* hybrid orbital

http://csi.chemie.tu-darmstadt.de/ak/immel/script/redirect.cgi?filename=http://csi.chemie.tu-darmstadt.de/ak/immel/tutorials/orbitals/

We are learning about hybridization and we have shown you the contours of sp hybrid orbital. Well contours of other hybrid orbitals also look qualitatively the same right quantitatively of course that different sp hybrid means as you know we have taken linear combination of a 2s orbital and a 2p orbital notionally we always take 2pz orbital because generally if there is 1 bond we like to do it along z axis.

But have a closer look at the contour diagram so what I did not discuss in the previous module is just have a look at these numbers here of course it is 0 right this is the nodal surface. Then if you let us start with the major loop this 1 is 0.1 these are all relative numbers 0.2 0.3 0.4 and so here is the peak this should not be difficult for you to understand because we have actually plotted in real time. Those hydrogen atom orbitals earlier and you have seen how these 3d shapes come and what contour lines are and in the minor lobe.

Here I have shown the minor loop to have a negative sign of a function here also so it is -0.4 outside then slowly it comes in -0.1, -0.3 so sorry what am I saying -0.1 outside -0.2, -0.3, -0.4 is in the middle right so again it builds up on the other side and the nucleus is engulfed by the minor lobe.

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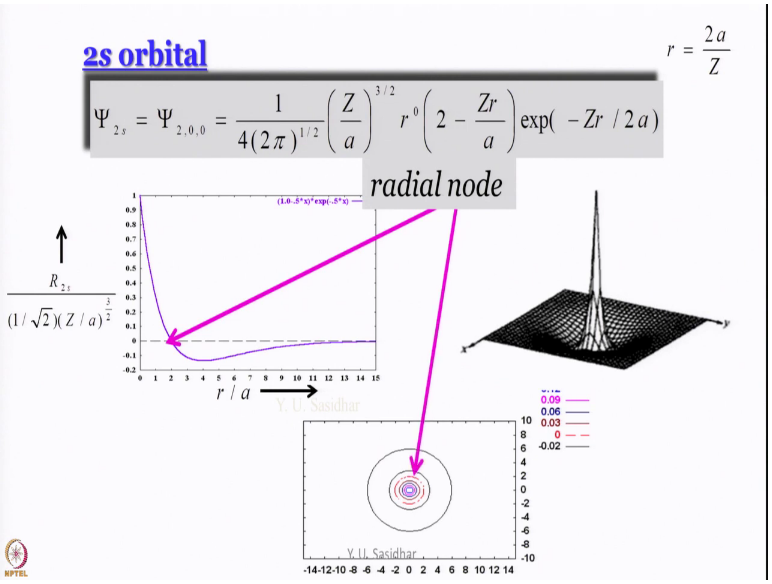

2s orbital

$r = \frac{2a}{Z}$

$$\Psi_{2s} = \Psi_{2,0,0} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2} r^0 \left(2 - \frac{Zr}{a}\right) \exp(-Zr/2a)$$

radial node

And we talked about this and then we said that if you look at the shape of 2s orbital 3d shape.

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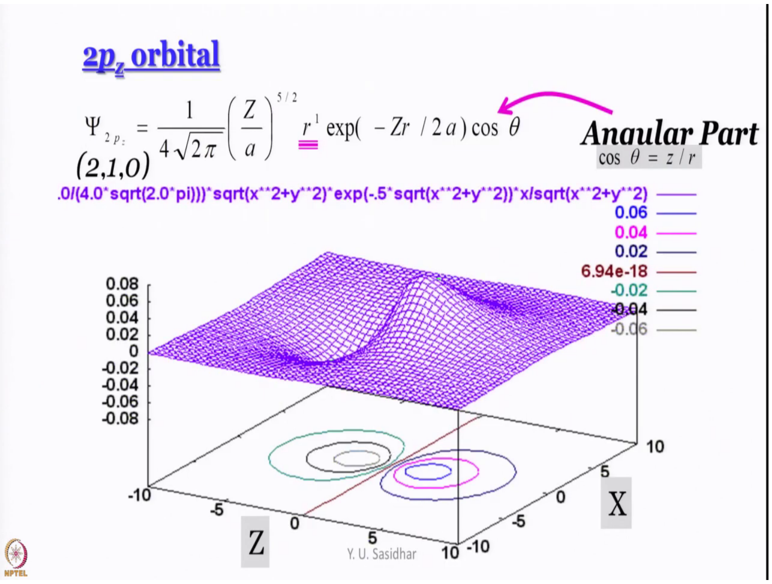

$2p_z$ orbital

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} r^1 \exp(-Zr/2a)\cos\theta$$

(2,1,0)

Angular Part

$\cos\theta = z/r$

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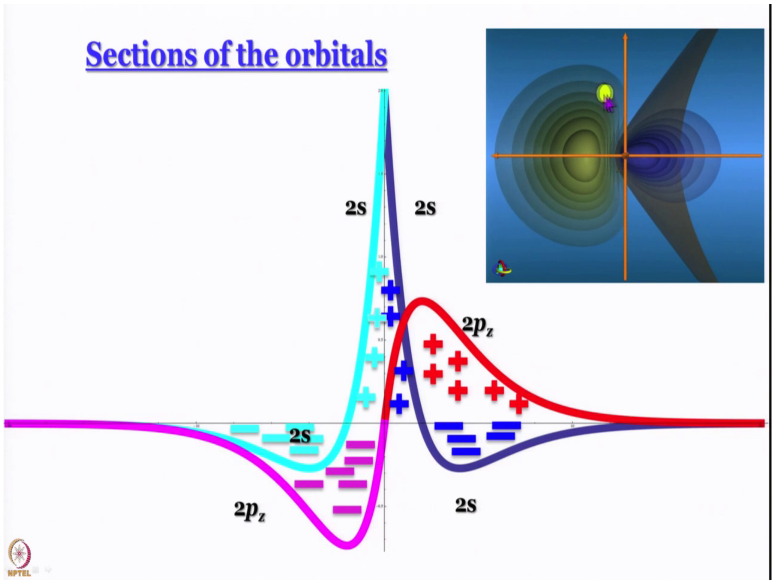
Sections of the orbitals

And 2p orbital 3d plot takes sections it becomes clear that in the immediate vicinity of the nucleus it is a sign of the 2s orbital that takes precedence and the interesting thing about 2s and 2p orbitals is that 2s orbital decays to 0 after a while with maximum at nucleus 2pz is the other way round it is 0 at nucleus rises to a maximum later on so well later on in terms of r at a longer values of r is more accurate.

So that is why in the immediate vicinity of the nucleus it is the sign of the 2s orbital that predominates and that sign does not predominate far away because it is more than offset by the 2pz orbital sign at long distances from the nucleus right. On 1 side you have constructive interference that is where you get the major lobe on the other side you get destructive interference that is why the loop becomes small.

So you can think that as a process of hybridization what happens is so what have we drawn this orbitals these are sort of this tell you where the probability is more right. If you think of a p orbital if you think of an s orbital it is it has no directionality. If you think of p orbital equal probability this side equal as that side right because this side is minus that side is plus in wave function psi psi square d r or well d tau let us say is the same right.

So same probability but we do not want that we want the electron density to be on 1 side so that the bond is highly directional then we will get a strong bond. So, by formation of this major lobe and minor lobe what we can effectively do is we effectively ensure that we have a situation where the majority the most of the electron cloud is on 1 side or rather we have prepared highly directional orbitals. Now when I talk like this of course I do not mean that we take acetylene and push the electron cloud we do not.

In acetylene the electron cloud gets rearranged because it has to form 1 each carbon has to form a bond with another carbon and a hydrogen atom right. So this is the driving force that ensures this rearrangement of new of electron cloud that in a very qualitative manner you can say is hybridization if you want to think of it without invoking even the little bit of math that we are doing. Everything if you remember the discussion we made of Pauling's introduction to this.

It is a field that determines what kind of hybridization there will be here the presence of other atoms that is the driving force how many bonds are to be formed that leads to a redistribution of electron clouds which in other words is formation of vibrate orbitals.

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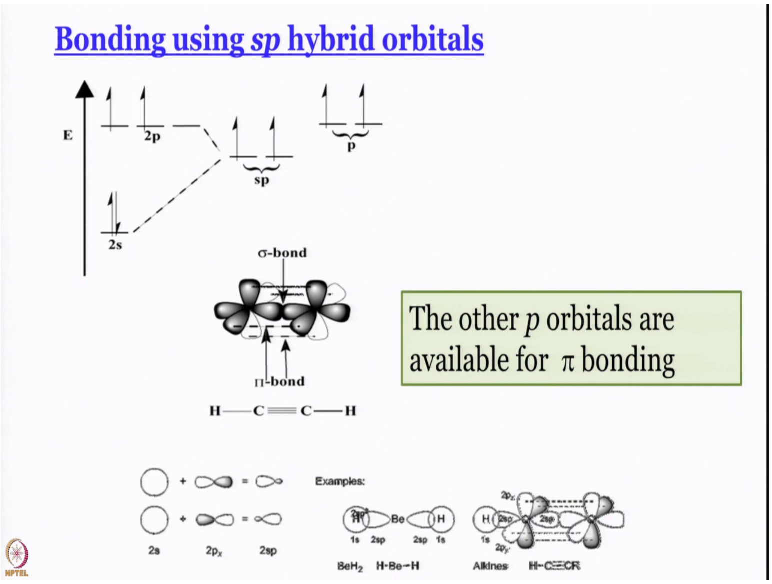

Bonding using *sp* hybrid orbitals

The other *p* orbitals are available for π bonding

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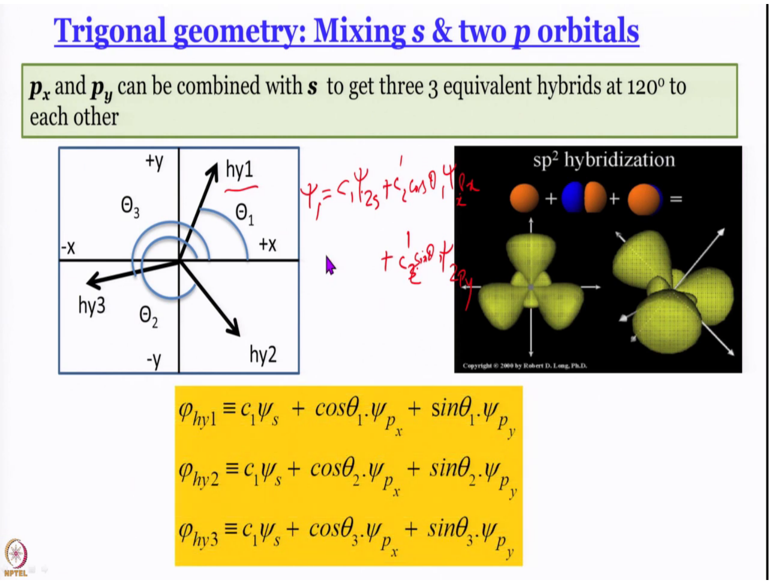

Trigonal geometry: Mixing *s* & two *p* orbitals

p_x and p_y can be combined with s to get three 3 equivalent hybrids at 120° to each other

$\psi_1 = c_1\psi_{2s} + c_2' \cos\theta_1 \psi_{2p_x}$

$+ c_2' \sin\theta_1 \psi_{2p_y}$

$$\varphi_{hy1} \equiv c_1\psi_s + \cos\theta_1.\psi_{p_x} + \sin\theta_1.\psi_{p_y}$$

$$\varphi_{hy2} \equiv c_1\psi_s + \cos\theta_2.\psi_{p_x} + \sin\theta_2.\psi_{p_y}$$

$$\varphi_{hy3} \equiv c_1\psi_s + \cos\theta_3.\psi_{p_x} + \sin\theta_3.\psi_{p_y}$$

So, we have talked about sp orbitals now it is time to talk about some other geometry sp orbitals are good for linear geometry now we want to talk about the next step. Linear geometry means ab 2 kind of molecules triatomic molecules of course acid acidity is not triatomic but let us keep things simple next I want to talk about ab 3 kind of molecules that is trigonal geometry. Since I need 3 hybrid orbitals like this and they have to be at 180, 120 degrees with each other I need 3 atomic orbitals to participate in the process of hybridization.

Now the orbitals that I use are s and p orbitals right 3 orbitals 1 has to be s always right you cannot really mix only 3p orbitals and get what you want. You mix 3p orbitals you will never get 3 orbitals in a plane hybridized that is why s is required so s and 2p orbital. So, let us work with for now P x and p y orbitals and let us say that this hybrid orbitals are in some orientation. So the angle with x of hybrid 1 is theta 1 the angle with x for hybrid 2 is theta 2 and for hybrid 3 the angle with x is theta 3.

Please remember I have only defined angles with x axis. So, now if I want to write an expression of these orbitals right what will the wave functions be? The wave functions will be something like so let us say I want to write I will write psi 1 for hybrid 1 I am writing psi 1 and please do not worry if you cannot read my handwriting in any case everything is written nicely down below that is equal to say some coefficient C 1 multiplied by psi 2s plus some coefficient multiplied by psi 2p x plus some coefficient let us say multiplied by psi 2p y I do not need psi

2pz right because I am working in the x y plane so p x and p y are the orbitals that I should use. So, I have held the molecule in the xy plane for my convenience. In ideal case scenario it should be held in any orientation in space right but I want to simplify the problem so I am putting it like this and will come back to this several times in our discussion.

So now see can I not write something like this C 1 is fine instead of C 2 I can write C 2 dashed multiplied by r in place of C 2 will you disagree if I write C 2 dash multiplied by cos theta 1 psi p x and this will be not C 3, C 3is going to be the same C 2 dash sin theta 1 psi p x that way we have a little bit of a control over the system right because what these cos and sine tell us is sort of the components we are working out components.

These are like vectors right these arrows that have drawn these are the hybrid orbitals you can think of this arrow as 1 hybrid orbital you can think of an arrow here as p x and arrow here as p y. So, like we resolve vectors into the components I can write like this then it becomes a little easier because you know what this has to be normalized also. So the C 1 dash can go out in the normalization constant what about C 1 will see.

So will write like this here I am not even trying to normalize yet actually there should be normalization constant multiplying this this C 1s see what we have written we have written same C 1 for psi s everywhere why because the contribution of s to all the orbitals has to be same we are working with the with equivalent orbitals. So s character is same, also there is only one 2s orbital in the atom. So there is I hope it is not very difficult for you if I write 3C 1 square is equal to 1.

Because see C 1 square is contribution of this s orbital in the first wave function C 2 square is a contribution of psi 2s in the second wave function second hybrid wave function. This well again this is C 1, C 1 square is the contribution of psi 2s in the third hybrid wave function. So the total contribution has to be 1 because there is 1 2s orbital so 3 C 1 square equal to 1 so C 1 is equal to one by root 3 this is something we are going to use later also.

So already without much hassle I have found out C 1 and what I can also do is if I know what theta is actually I do not have to do anything I just write the value of cos theta 1 I will write the value of sin theta 1 theta 2 sin theta 2 sin theta 3 cos theta 3 and I have got the hybrid wave functions then if required I can normalize. So, this is the most general strategy of writing expressions for your hybrid orbitals.

But what we will do is see we have simplified the problem here by holding it in xy plane so since we are willing to do that why not simplify it even further by holding 1 of the hybrid orbitals along 1 of the axis that will make life even simpler right.

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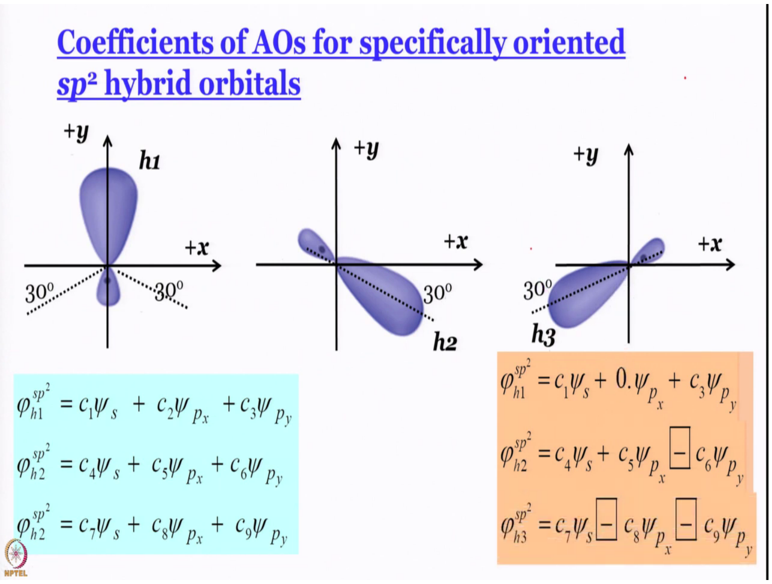

Coefficients of AOs for specifically oriented sp^2 hybrid orbitals

$$\varphi_{h1}^{sp^2} = c_1\psi_s + c_2\psi_{p_x} + c_3\psi_{p_y}$$

$$\varphi_{h2}^{sp^2} = c_4\psi_s + c_5\psi_{p_x} + c_6\psi_{p_y}$$

$$\varphi_{h2}^{sp^2} = c_7\psi_s + c_8\psi_{p_x} + c_9\psi_{p_y}$$

$$\varphi_{h1}^{sp^2} = c_1\psi_s + 0.\psi_{p_x} + c_3\psi_{p_y}$$

$$\varphi_{h2}^{sp^2} = c_4\psi_s + c_5\psi_{p_x} \boxed{-} c_6\psi_{p_y}$$

$$\varphi_{h3}^{sp^2} = c_7\psi_s \boxed{-} c_8\psi_{p_x} \boxed{-} c_9\psi_{p_y}$$

So this is how we are going to work it work out the actual coefficients for this problem. You might get a little baffled here and you might think what is going on who has told you that 1 of the hybrid orbitals is along y axis? Nobody has told me but nobody has told me where y axis is right it is in my hand. We are working in free space we are pretending as if we have this one molecule and nothing else.

So I can set my axis in whichever way I want if you have objections to me playing around with the molecule then I play around with the axis right. If Muhammad does not go to the mountain the mountain will go to Mohammed it is not so difficult this relative motion. So, let us say that we work in a situation where the first hybrid orbital is aligned with the y axis. The advantage of doing this is that your coefficient of this py is going to become 0 for the first hybrid orbiter.

So C 3 will be 0, first of all I have written a general expression for the hybrid orbital so what I am doing here is that I am writing phi for hybrid orbital wave functions I am writing sorry I am writing phi for hybrid wave functions I am writing psi for the pure atomic orbitals. So for h 1 I have written C 1 psi s plus C 2psi p x plus C 3 psi p y for the second hybrid I have written C 4 s I s plus C 5 psi p x plus C 6 psi p y for third 1 I have written C 7 psi s plus C 8 psi p x plus C 9 psi p y I just given numbers to coefficients.

You are free to use different notations you can I want to write C 11 C 12 C 13 or you want to write C 1s C 1p x C 1 p y different books use different notations please write whatever you want I have used a simple notation in which we give the simple tags to the coefficients. Now what more how more how can we simplify this but before that let us look at the picture once I have held the molecule in xy plane I have held h 1 along y axis.

So naturally the second hybrid is going to be like this let us say the second hybrid is towards the positive side of x and negative side of y the angle between y axis and h 2 is 120 degrees angle between y and x is 90 degrees so this angle between x and h 2 is 30 degrees. Similarly the angle between x and h 3 is 30 degrees and h 3 has to be on the other side. So minus x and minus y I hope that is not difficult to understand.

Now let me try try to write the coefficients 1 by 1. So, we have written psi h 1 sorry phi h 1 sp2 to be retained C 1 from here C 1 psi s plus as we said earlier there is no contribution from p x here because the orbital is aligned with h 1. Is there a contribution from psi s? Definitely otherwise the shape will not change right. So, no contribution from p x and a contribution from C 3 so 1s orbital and 1p orbital is con are contributing does that make it a sp orbital? No it does not it, is still sp2 orbital please hold on to this thought and will come back to it.

Now do we know what this C 1 is actually we do remember this C 1 must be equal to C 4 must be equal to C 7 remember because s orbital has to make equal contribution to the all the hybrid orbitals. So C 1 must be equal to C 4 equal to C 7 so 3 C 1 square must be equal to 1 as we have discussed earlier C 1 is actually 1 by root 3 so you already know 2 of the coefficients C 1 is 1 by root 3, C 2is 0. Can we figure out C 3?

Well I have done it in a particular way on the slides but let us just go by whatever we are discussing. So this is 1 by root 3 C 1 C 2 equal to 0 and we know that for normalization C 1 square plus C 2 square plus C 3 square must be equal to 0 so 1 by 3 plus C 3 square is equal to 0 what am I doing I am as usual making a mess, if it is 0 then that is the end of it is not it. Physical chemists are sometimes obsessed with 0s but they are also obsessed with 1.

We are talking about normalization condition remember right we are talking about normalization condition which means your integral phi h 1 sp2 phi h 1 sp2 that has to be equal to 1 which means I will write it here and then I release integral C 1 psi s put a bracket here plus I will not even write this because you are already convinced that this is 0 plus C 3 psi p y and the same thing C 1 psi s plus C 3 psi p y that is equal to 1.

If you expand this what do you get you get C 1 square integral psi s into psi s over all space what is this? This is equal to 1 because psi s is normalized. Similarly I can get C 3 square again I will get psi p y into psi p by integral whole square plus I write C 1 C 3 integral psi s psi p y that is going to be equal to 0 right because this s and p are orthogonal to each other. Similarly the last term will also be equal to 0.

So C 1 square plus C 3 square will be equal to 1 so 1 third plus C 3 square equal to 1 so C 3 is equal to 1 minus 1 third is 2 third root over 2 by 3 not very difficult to figure in fact it is very easy to figure out I do not even have to do the rest, you can I think figure out the rest by yourself. It is very, very simple fun like this is like solving sudoku or something and it gives you some very interesting insight.

Hold on to the thought the question that we had raised that in the first orbital we are mixing your 1s orbital and 1p orbital, so is that sp hybridization and we said no the hybridization is still sp2. How did that happen actually I have answered the question already but I have not told you that will come to the answer but by then see if you can figure it out yourself. See if you can convince yourself that it is really sp2 and not sp.

Meanwhile we will go ahead and will write the expression for psi h 2. So, psi h 2 I can write as will keep C 4 where no need I already know that its 1 by root 3plus C 5 here I will explicitly write minus C 6 because I know very well that psi 2 is on the negative side of y so the value of p y value of coefficient of p y has to be negative. So what I will do is I will keep the coefficients the C's not coefficients the C's C 1 C 2 C 3 I will keep them to be either 0 or positive so I will write this sign explicitly that will be minus.

And if I want to write an expression for psi h 3 will you agree with me that it has to be C 7 psi s with C 7 equal to C 1 equal to C 4 equal to 1 by root 3C7 psi s minus C h psi p x minus C 9 psi p y will you agree with me. Because this h 3 is towards minus x as well as minus y so both the coefficients should have explicit minus sign.

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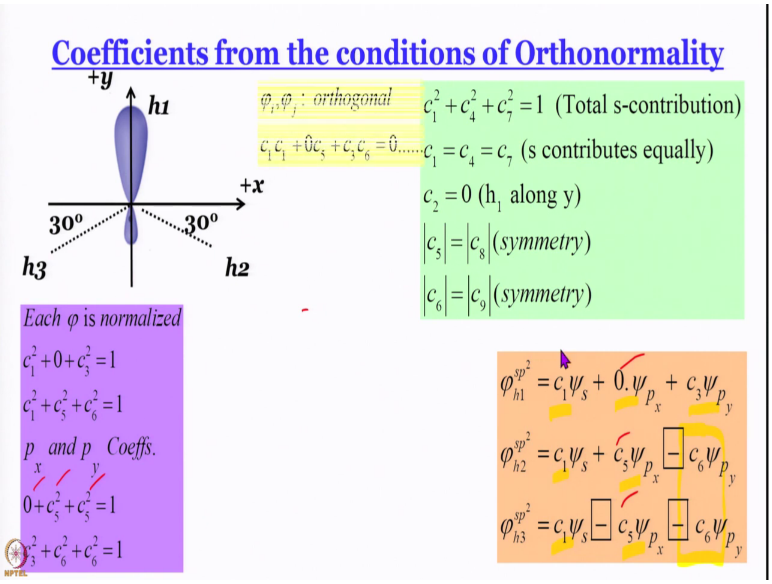

Coefficients from the conditions of Orthonormality

φ_i,φ_j : orthogonal

$c_1c_1 + 0c_5 + c_3c_6 = 0$......

$c_1^2 + c_4^2 + c_7^2 = 1$ (Total s-contribution)

$c_1 = c_4 = c_7$ (s contributes equally)

$c_2 = 0$ (h_1 along y)

$|c_5| = |c_8|$ (symmetry)

$|c_6| = |c_9|$ (symmetry)

Each φ is normalized

$c_1^2 + 0 + c_3^2 = 1$

$c_1^2 + c_5^2 + c_6^2 = 1$

p_x and p_y Coeffs.

$0 + c_5^2 + c_5^2 = 1$

$c_3^2 + c_6^2 + c_6^2 = 1$

$$\varphi_{h1}^{sp^2} = c_1\psi_s + 0.\psi_{p_x} + c_3\psi_{p_y}$$

$$\varphi_{h2}^{sp^2} = c_1\psi_s + c_5\psi_{p_x} \boxed{-} c_6\psi_{p_y}$$

$$\varphi_{h3}^{sp^2} = c_1\psi_s \boxed{-} c_5\psi_{p_x} \boxed{-} c_6\psi_{p_y}$$

Now how do we go about it how do we work this out now we remember the angle. The angle is 120 degrees so this angle between x and h 2 is 30 degrees this angle between minus x and h 3 is also 30 degrees this we have done already this is total x s contribution is 1. See what happens is when we prepare the slide we have some particular kind of chain of thought by the time I come and I speak here in front of you or in front of the camera the chain of thought sometimes evolves.

So I might not be saying things exactly the same sequence but everything is there. So we have already figured this out this is important this is something I have not said see mod C 5 is equal to mod C 8 do you agree mod C 6 equal to mod C 9 mod C 8 equal to mod C 9 do you agree here I have already written C 5 unfortunately. So what I am saying is modulus of the coefficient so well there is no need to write modulus also because I made the coefficients the C the C's I made them positive already.

So mod of coefficient of psi p x has to be the same for h 2 as well as h 3 because the angle is 30 degrees right. So what will this component be they should be the same in magnitude. So I will write this as C 5 I will write this as minus C 5. Similarly this will be minus 6 this will be minus C 6 what else can we write? We can write all these things C 1 square plus 0 plus C 3 square equals 0 we already did that.

C 1 square plus C 3 square C 5 square plus C 6 square equal to 1 that is again from normalization condition you will get the same equation from h 2 as well as h 3. So for p x and p y coefficient 0 plus C phi square plus C phi square equal to 1 this is C 5 this is C 5 this is 0. Now we are almost done right because once again how many p x orbitals are there this is 1 p x orbital right that is why we are saying that this C 5 what is where is it gone 0 plus C phi square plus C phi square equal to 1 0 C 5 C 5.

And when I take square this minus minus square of minus becomes plus also. So I do not remember where the white space is I will write here um so what do I get here 2 C 5 square equal to 1 so C 5 is equal to 1 by root 2 I hope you have your pen and paper with you please write these values down because I have everything written down in the next slide but if you write down you can check. So, 1 by root 2 that is what I have got; so how many coefficients are left now out of the 9 coefficients we have figured out all these.

Oh I need the pen we have figured out these we figured out this we have figured out C 5s also we figured out C 3 the only thing that we now want to find out would be C 6? How do I find C 6? Is it difficult? It is not difficult, it is very easy right because now you can use anything you can use normalization condition by taking C 1 square plus C 5 square plus C 6 square equal to 1 or you can use orthogonality also you can say this C 1 square plus 0 plus C 3 into C 6 equal to 0. So, you already know C 3 so only unknown will be C 6 and you can find it out right.

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So, when you do that this is what you get I hope the coefficients we worked out are all matching 1 by root 3 root over 2 by 3,1 by root 2 this we worked out these come out to be 1 by root 6. So very nicely we have been able to figure out the coefficients of the atomic orbitals in the hybrid orbitals hybrid sp2 orbitals when we hold the molecule in xy plane with 1 of the hybrid orbitals along the y axis. We found the coefficients and we have written the expressions.

And first thing we see is they are all orthogonal to each other they are normalized we have used the non normalization condition are they orthogonal it is easy to see h 1 and h 2 are h 1 and h 3 1 by root 3 into 1 by root 3 is 1 by 3 then root 2 by 3 into minus 1 by root 6 is equal to what root 2 by 3 by root 3 is equal to again 1 by 3. So plus 1 by 3and here we are multiplying plus by minus so is minus 1 by 3 that is equal to 0.

So you please satisfy yourself that how many pairs can you take 3C 2 right factorial 3 by factorial 23 pairs all the 3 pairs of these h orbitals hybrid orbitals they are orthogonal to each other please convince yourselves. Please work them out please also convince yourselves that they are normalized but it is not even required because we have used normalization condition to even construct them.

Now we come back to that question the first one is it sp2 or is it sp well to answer the question we need to remember that the mod square of any coefficient gives us the contribution. So in the first orbital contribution of psi s is one third or you can write 0.33 if you want I like 1 third better. Contribution of p y is square of root 2 by 3 well 2 third. What is the ratio of um how do I write it s character I write like this is to p character oh man such bad handwriting the ratio of s character to p character is 1 by 3 is to 2 by 3 is 1 by 2.

So sp2, sp2 means contribution of s in that orbital is 1 third total contribution of p is 2 third I should not have said that now because there is a little bit of spoiler for what I am going to say after this but it is ok. So contribution from p orbital has to be twice the contribution of s orbital that is the meaning of sp2 it does not mean that exactly 1 s orbital has to mix with exactly 2p orbital. We are dealing with wave functions here so scaling remember scaling the scaling and all can be done.

Let us look at h 2 what is the contribution of s orbital that is a foolish question now because contribution is same 1 third. What is the contribution of psi p x it is actually half what is the contribution of p y its actually 1 6th. So, what we see is that p x contributes to a lesser extent to h 2 than does p y and that is not so surprising right not so surprising also. Sorry what am I saying p x contributes to a greater extent than p y this is half and this is 1 by 6th that is not so surprising just look at this figure.

This angle is 30 degrees this angle is 60 degrees it is no wonder that the contribution of the of p x is going to be 3 times more than contribution of p y right look at the components you will get it but what is the total contribution of p orbitals? Half plus 1 6th is equal to since it is easy I will actually do it in detail is equal to 4 by 6 is equal to 2 by 3 total contribution of p orbitals is 2 by 3 same as what it was in h 1 right.

So total contribution is the same and it is not very difficult to see the total contribution of p once again here is 2 by 3 as compared to 1 by 3 for s so all are sp2 hybrid orbitals all are equivalent and meaning of sp2 then is what is the contribution that contribution of s is 1 3rd total contribution of p total p character is double of that 2 third 0.33 and 0.67 if you will right, so this is what we have worked out from square of coefficients we have established that contribution of s is 0.33 contribution of p I should write 0.67.

In all the orbitals they are all equivalent and using them you can now perform bonding in the familiar way for these molecules that are familiar to all of us. So much for your sp2 orbitals well we started in a way that the angle is 120 degrees but our time is turning out so we stop now but little bit of this discussion of sp2 orbitals is left for the next class. We will do back calculation like what we did earlier remember when we were testing our approximate methods.

We work with systems for which exact solution was known and we try to see whether we get the result we are going to calculate the angle and see whether we get 120 degrees that is going to be very useful for us when we talk about sp3 orbitals later on. But let us take that along with sp3 orbitals in the next class.