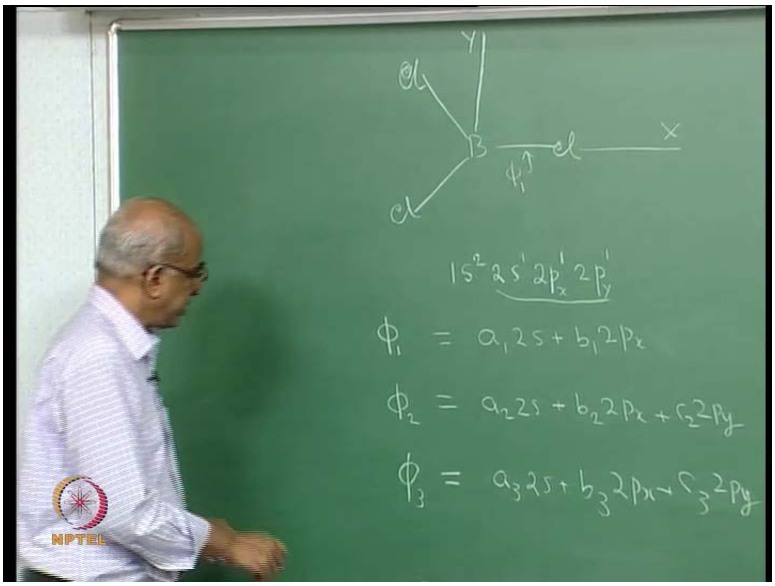
Introductory Quantum Chemistry
Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 48
Hybridization Huckel Theory

(Refer Slide Time: 00:24)



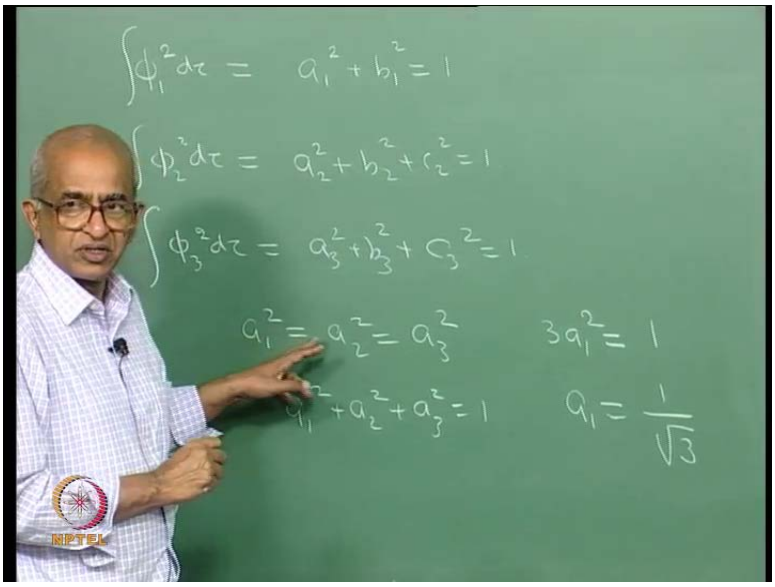
So, we will discuss the case of B C l 3; B C l 3 is a molecule which as nice shape the 3 chlorines are sitting at the 3 coordinates of an equilateral triangle. And the electron configuration of boron n is actually 1 s 2 2 s 2 2 p 1. And in order to explain of the formation of a triangular molecule with all the 3 bonds being equivalent; what we have to do is we have to imagine that 1 electron is from ordered from here and put into the next 2 p orbital. So, let me call this 2 p x this one; I will code 2 p y and that also as 1 electron and then these 3 orbital will mix together. That means they will hybridize together and will give me 3 new orbitals, 3 new hybrid orbitals. The first one I will call phi 1, the second 1 will be phi 2 and third 1 is phi 3.

So, because you see the orbital involved at 2 p x and 2 p y I will say that the x y plane is the plane of the molecule. So, this is my y axis and that is my x axis let us say this is convenient. And phi 1 is actually going to be written as a linear combination of these 3 orbitals; you do not worry about 1 s we worry only about these 3. So, I am going to have 2 s plus B 1 2 p x plus C 1 2 p y. Similarly, phi 2 will be a 2 2 s plus b 2 2 p x plus c 2 p

y and the third is going to be a 3 2 s plus b 3 2 p x plus c 3 2 p y. And of course what do we want to do we want all these orbit to be normalized not only should they normalized they should all be orthogonal to one another right.

And, so using these conditions and some physical arguments we will determine all this coefficients a 1, a 2, a 3, b 1, b 2, b 3 and so on; straight away I can make a simplification here. Because the way I have chosen the geometry right this B C l bond is along the x axis. Let me say that phi 1 is the hybrid orbital which is use to form that bond; then what will happen it would have contribution only from 2 p x this is only simplifying things; so that we can easily calculate. So, this bond will involved a hybrid orbital involving only the 2 s and to the 2 p x it will not involved the hybrid; it will not involved 2 p y. So, therefore immediately I can say that c 1 must be 0. So, it is convenient because I am get rid of one of the unknown by this simple physical argument.

(Refer Slide Time: 04:03)



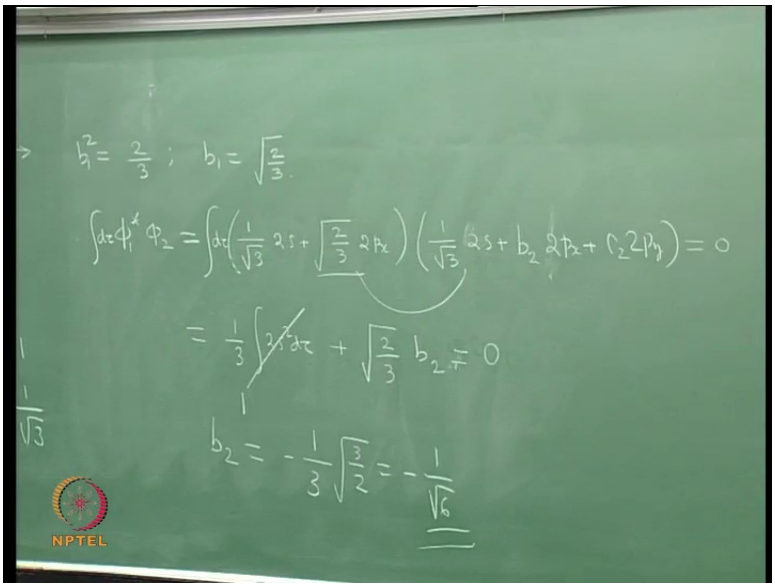
And, then if that is the way it is phi 1 is normalized which implies that integral of phi 1 square d 2 over the entire phase; we have calculated this kind of integral in the previous lecture you will take this square of this integrate and put it equal to 1. If you did that you remember that 2 s is normalize, 2 p x is normalize they are orthogonal to one another. So, effectively you will get a 1 square plus b 1 square equal to 1. And as I told you earlier a 1 square is the contribution of 2 s; a 1 square determine the contribution of 2 s 2 this automatic orbital phi 1; b 1 square determines the contribution of 2 p x 2.

That hybrid orbital a 1 square determines the contribution of 2 s to the hybrid orbital phi 1 and b 1 square determines the contribution 2 p x to the hybrid orbital phi 1. Similarly, if you integrated phi 2 square d 2 you are going to get the similar equation; that is going to be a 2 square plus b 2 square plus c 2 square and this should be equal to 1; integral phi 3 square d 2 must be a 3 square plus b 3 square plus c 3 square right. Now, all the orbitals I want to that to be equivalent. So, if they are all to be equivalent what does that mean it means that a 1 square, a 2 square, a 3 square should have the same value otherwise the one orbital more contribution from the s orbital.

So, I have this condition that a 1 square must be equal to a 2 square plus which is equal to a 3 square. And further if I added all this things up see these is contribution that s orbit 2 s makes to first hybrid, second hybrid and third hybrid I have only 1 s orbital. So, if I added all of them up if I added a 1 square plus a 2 square a 3 square the answer must be 1 because it is only one s orbital. So, I arrive at conclusion that a 1 square plus a 2 square plus a 3 square must be equal to 1. And these two together immediately tells me that 3 a 1 square must be equal to 1; implying that a 1 can be taken to be 1 by square root of 3 correct. So, if you choose a 1 to be 1 square root of 3; I can put this 1 by square root of 3 here. And then of course I can choose a 2 say; a 2 square is actually equal to a 1 square. So, I can choose a 2 to also to be equal to 1 by square of 3; a 3 also to be equal to 1 by square of 3.

So, therefore I have determine all this 3 numbers; now what do I have? I have determine b 1 that will be my next aim but I know that in the I have this equation; in this equation a 1 is 1 by square root of 3 that implies this equation means b 1 square must be equal to how much? This is a 1 is 1 by square root of 3; that means b 1 square must be equal to 2 by 3 or b 1 must equal to square root of 2 by 3. So, I have determine that and I get this square root of 2 by 3 fine. And now I would like to determine b 2; how will I determine b 2? The answer is I impose the condition that phi 1 and phi 2 have to be orthogonal.

(Refer Slide Time: 08:17)

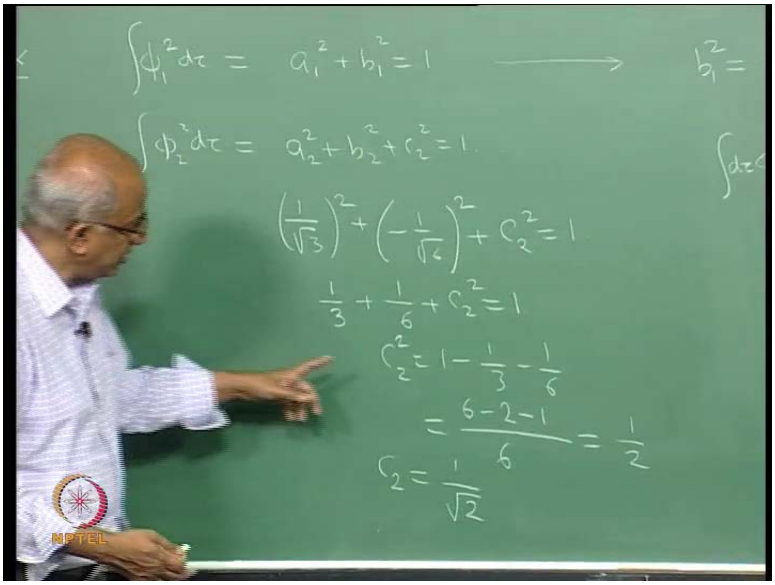


So, if you multiply phi 1 with phi 2 again strictly speaking phi star with phi 2. But star has no effect those everything is real what is if that you are going to get you have to multiply these 2; Just for the sake of illustration let me do this multiplication; these must equal to 0 and what does that mean? It means the following see if you multiplied by these 1 by square root of 3 2 s into that; you are going to get 1 by 3 integral of 2 s square d 2 that will be just one of terms and this I know is 1. Because 2 s is normalized then if you multiplied 2 s with 2 p x and integrate over the entire space you are going to get a 0. So, I am not going to write it down and if you multiplied this with that again it is going to be 0. So, therefore this term into any of terms what will happen only this term with 2 s will survive and the other terms vanished.

Similarly, this term if you multiplied with 2 s the answer is going to on and integrated over entire space answer will be 0 multiply these with that; what will be the answer? It is going to be root 2 by 3 into b 2 right because 2 p x and 2 p x. So, in square integrate over the entire space is 1; and this into that integrate over the entire space will be 0. So, therefore this is actually equal to 0 fine. And hence I can now find b 2 this is this object is 1, this is 1. So, what you would find for b 2; b 2 will be equal to minus 1 by 3 into square root of 3 by 2 which is actually equal to minus 1 by root 6 right. And hence I will now substitute for b 2 this is actually minus 1 by root 6; now this last orbital also should be orthogonal to this correct.

And, that implies that this b 3 also must be equal to the same number; you can proceed in exactly the same fashion you will find that this must be equal to minus 1 by root 6. So, we had left with the job of determining c 2 and c 3.

(Refer Slide Time: 12:06)

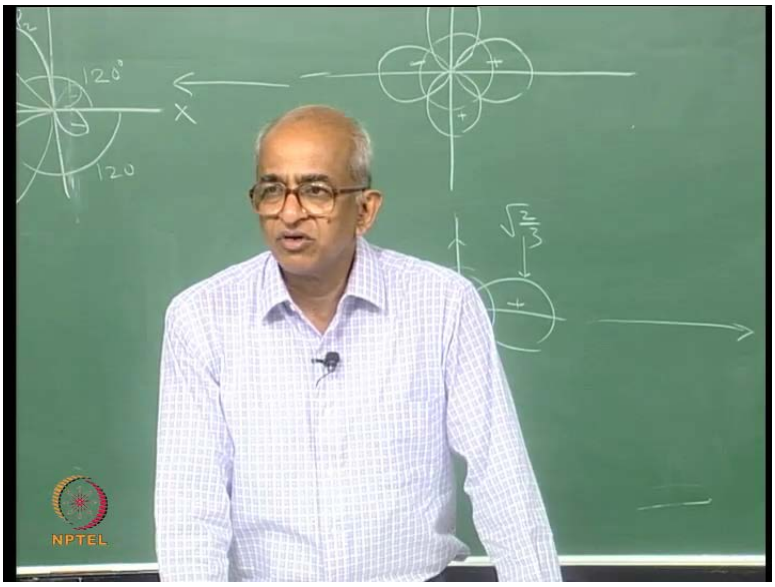


So, how will you determine that the answer is very simple you use this equation a 2 we know how much it is a 2 is 1 by root 3; b 2 is minus 1 by root 6 correct. So, what will happened you are going to get 1 by 3 plus 1 by 6 plus c 2 square is equal to 1; which means c 2 square is actually 1 minus 1 by 3 minus 1 by 6 if you calculated this; this is actually 6into sorry 6 minus 2 minus 1 divided by 6 and how much is that? It is half. So, c 2 square you find it is equal to half correct and therefore what I can use for c 2; c 2 you can say it is 1 by square root of 2 fine. So, this we have determine c 2 will be 1 by square root of 2; what about c 3? Well, it cannot be the same because then this 2 orbital will be identical, but then when you look at these what is what is that you find c 2 all that this equations says is that c 2 must be equal to 1 by 2. So, therefore this square equal to 1 by 2 I have another possible solution, and that will be minus 1 by root 2; and that is the one that I should choose.

And, therefore this is going to be equal to minus 1 by root 2 y, because you see otherwise the 2 orbital will be identical fine. And then you can actually verify this orbital into that orbital; you can calculate overlap and find that it is 0. Similarly, all this orbitals are

orthogonal to one another; each one of them is normalized right. So, having constructed these orbitals I want to look their shapes.

(Refer Slide Time: 14:36)



So, this is my 2 p x; that is my 2 p y and of course if you try to represent 2 s also in the same picture the picture become somewhat complex and these is how it appears. But you have the same the sorry to have the first hybrid orbital what should I do? I have to take 2 s multiplied by square of 2 by 3 same things wrong I take 2 as multiplied by 1 by square root of 3 had to it 2 p x multiplied by square root of 2 by 3. If you did that say what you are doing is you are taking 2 s this is 2 p x and you multiplied these by square root of 2 by 3 and that by 1 by square root of 3 added that 2 up what is the result?

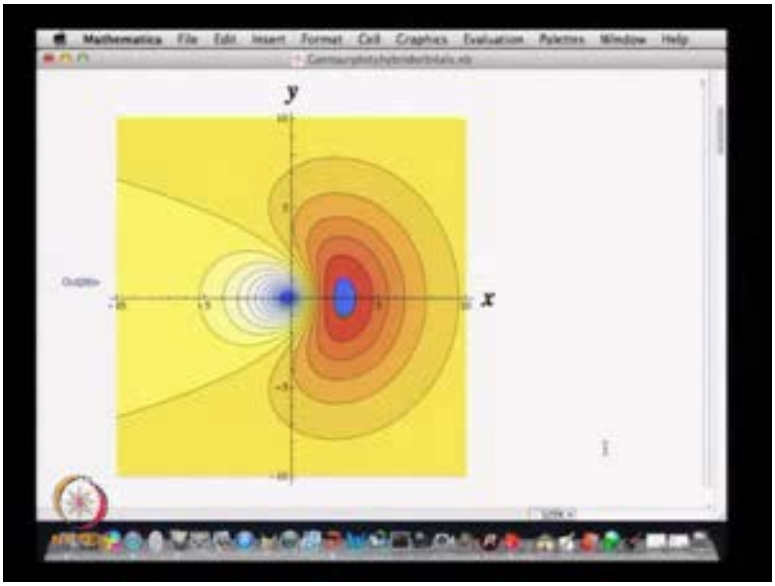
The result is simple you will get the hybrid orbital which actually points in the x direction; this slope will be positive that log will be negative. And if you took 2 s multiplied by 1 by square of 3; 2 p x if you multiplied by minus 1 by root 6. That means, you are actually multiplying 2 p x with a minus sign. So, therefore it is actually making it to point in the opposite direction it tells to point in the opposite direction but then you are also adding 2 p y. So, therefore the that contribution actually would like to make the orbital point in this direction in the y direction.

So, therefore what will happen? You have 2 contribution; one would like to pointed in the negative x direction the other will like to pointed in the y direction. So, the net direction in which the orbital point is neither in the x direction or in the y direction. But

somewhere in between it will point in such a direction such that this angle is 120 degrees. And last orbital will naturally point in a different direction; it will actually point in such a direction such that this angle is 120 degrees. So, this is phi 2 and that is phi 3 this slope is positive, that is negative, this one is positive, this negative; and I have drawn same kind of thing here. So, these are the 3 hybrid orbital what you find this that the very hybrid orbital are actually pointing towards the 3 coordinates of an equilateral triangle. And these hybrid orbital are then use to form bond with 3 chlorines.

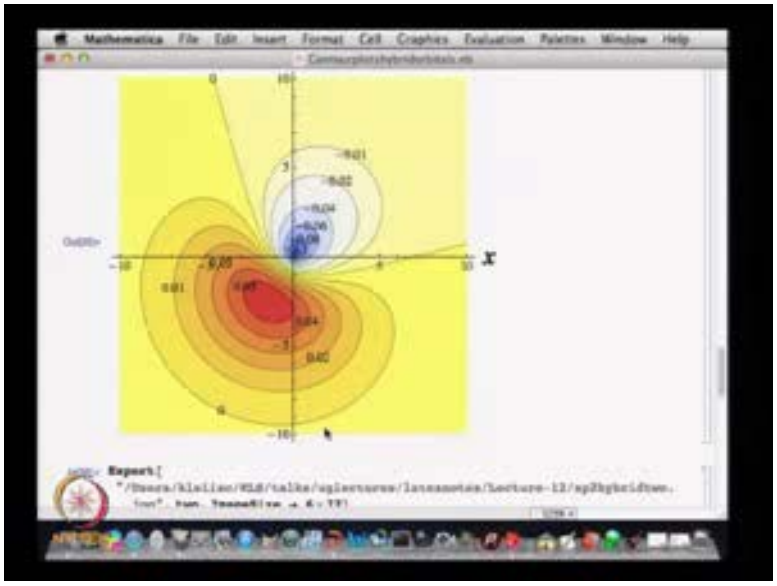
And, naturally what will happen the 3 chlorines will be locate at the coordinates of an equilateral triangle just explaining the geometry; and not only the geometry the hybrid orbital are all equivalent. And therefore the bonds all have the same strength I have a mathematical file showing this orbitals.

(Refer Slide Time: 18: 25)



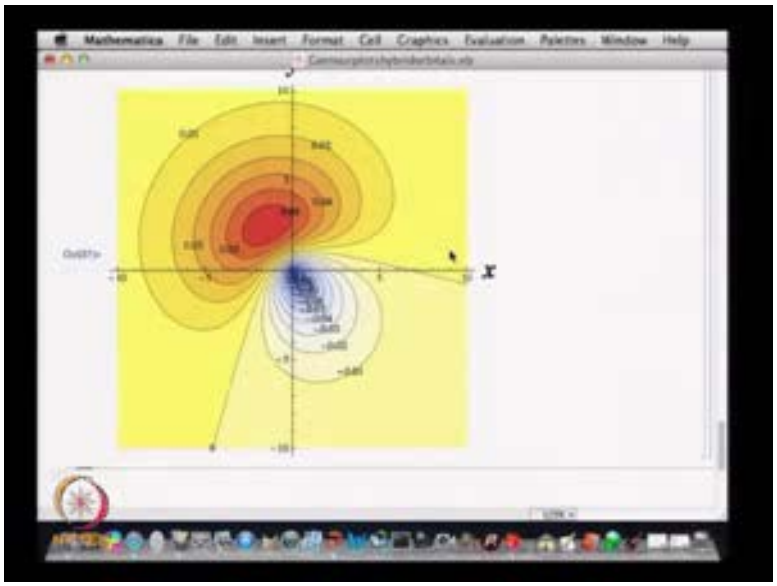
So, this is actually what I referred to as a contour plot of the first hybrid orbital phi 1. And notice that it is actually pointing in the x direction right in the x direction; x is marked correctly at least in this picture make it a little bit smaller; so that we can see the y axis also. So, that is your x and that your y axis; and you can see that it is pointing in the x direction this is your hybrid orbital phi 1, then if you look at the hybrid orbital phi 2.

(Refer Slide Time: 19:11)



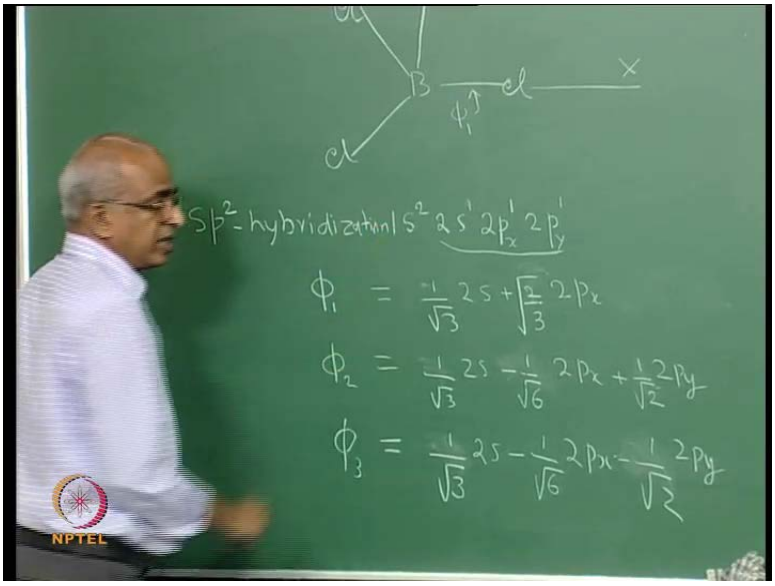
Well, this is not phi 2 but this is hybrid orbital phi 3 in our notation. So, in which direction is it pointing you can see that is actually pointing in a down ward direction; such that the angle with the positive direction x axis is how much 120 degrees; these are contour plots. What do contour plots main I can just remind you these lines are drawn in such a fashion that along this contour plots the value of the wave function is actually 0.02 for this one this line.

(Refer Slide Time: 20:11)



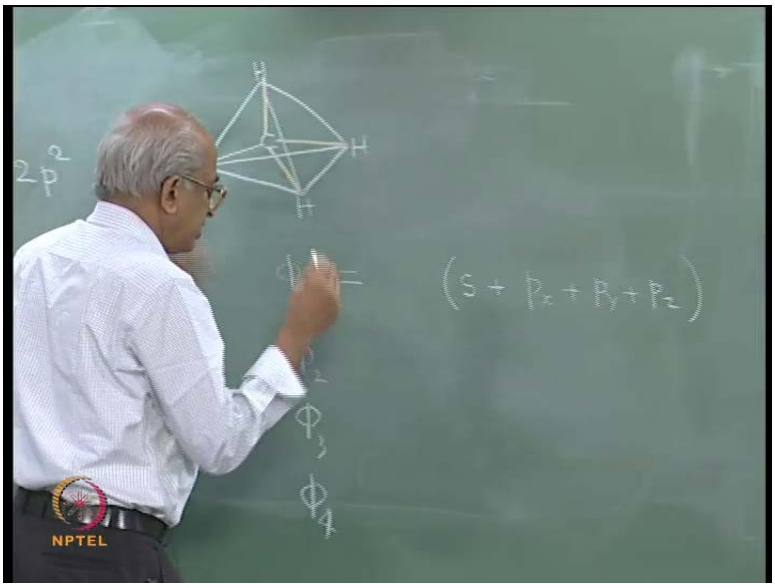
For example, as a value of the wave function 0.04 you can see that in these direction the function is actually positive or at this point the function is positive while l the in the along these contours the function as a negative value. And the obviously there is a contour this is that contour where the function has the value 0 so this is it has a node. And, these is this is the second hybrid orbital which we have qualified to and again you can see that it makes an angle of 120 with the x direction. So, you have 3 equal and hybrids pointing towards the coordinates of an equilateral triangle.

(Refer Slide Time: 20:51)



Now, the last case that we will discuss in the case of hybridization is p 3 hybridization; incidentally I forgot to mention this particular weight. Because you are actually mixing you 1 s orbital and 2 p orbital you referred this as is p 2 hybridization. And hybridization in which you makes only 1 s with a 1 p that is referred to as a s p hybridization. And now we will discuss the case of C H 4.

(Refer Slide Time: 21:11)

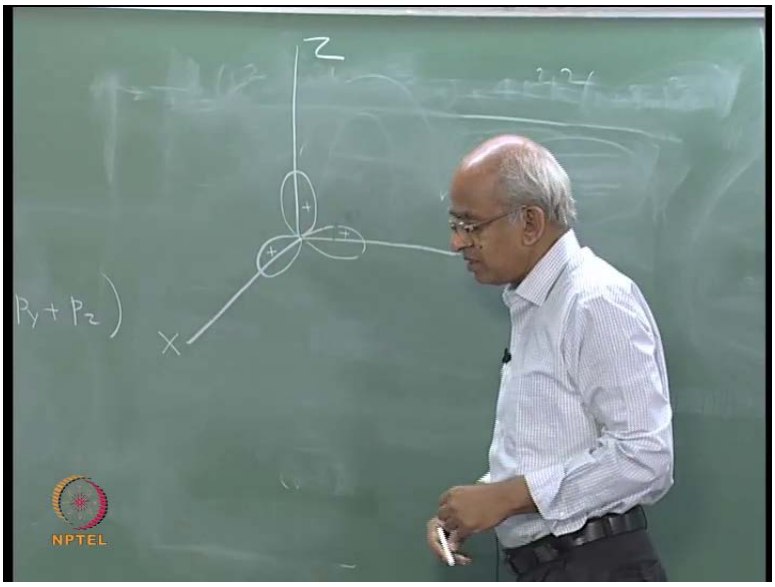


C H 4 actually is external contributed tetrahedral molecule. So, let me draw a tetrahedron and what the molecule has is actually hydrogen atoms; 4 of them sitting at the coordinates of a regular tetrahedron with carbon atom occupying the center of the tetrahedron. So, the carbon hydrogen bonds are represented by these lines. And, all the bonds are equivalent we have the same bond lengths; and how does one explain the structure of this molecule. Well, the electronic configuration of carbon is 1 s 2 2 s 2 2 p 2 and in order to explain the formation of this molecule what one imagine says that 1 electron is promoted from 2 s to 2 p. So, that you have an s and p x, p y and p z orbitals; this orbitals available for bond formation. And to the way you have to imagine is that these 4 orbitals hybridized together to you give 4 equivalent hybrid orbitals which we will denote by the symbols phi 1, phi 2, phi 3 and phi 4.

So, in this case it is fairly straight forward; you see the only conditions that the orbitals have to satisfies that they have to be normalized each one of them has to be normalized and each one has to be orthogonal to one another. And of course they all have to be equivalent to one another. So, actually in the case of phi 1 it is fairly easy with you write as expression for phi 1. And also for other I will not actually derivative it but this is one possible way in which you can construct hybrid orbitals. And that is to say that you will take s at with p x, p y and p z. And of course the result has to be normalized; you can easily calculate the normalization factor very simple actually very simple calculation; if

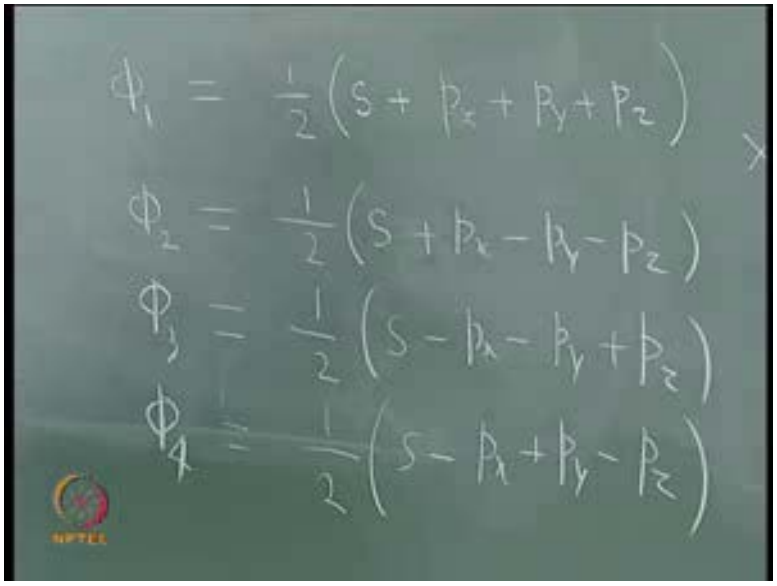
you calculated it you will find that the answer is 1 by 2. And again think of the way in these orbital is to be is going to be oriented in space.

(Refer Slide Time: 24:11)



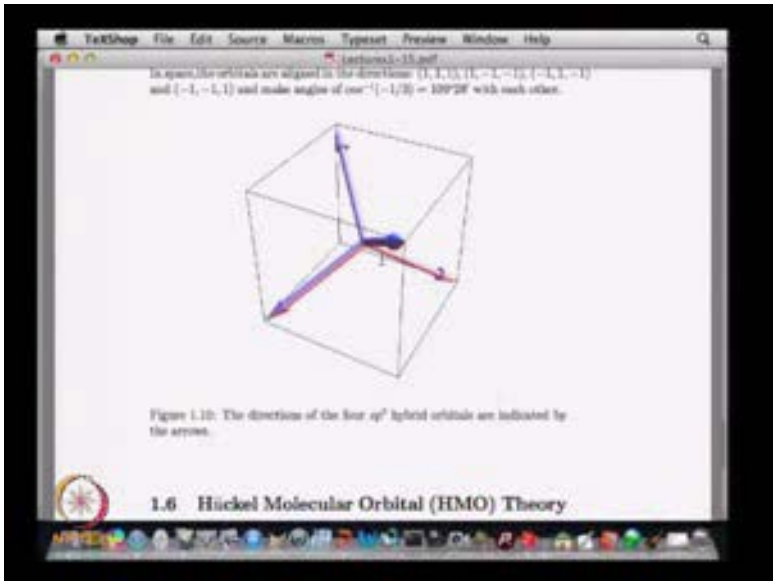
See, if this is my coordinate system the p is that as it positive lobe pointing in this direction the positive lobe; I am only showing the positive lobe that is for p is at for p x the positive lobe is in this direction. And for p y the positive lobe is in that direction this is x, y and z. So, if you added this things together you can imagine that the result will be an orbital in which the positive lobe of that orbital will make equal angles with x, y and z. So, therefore if I may put chock here it will be making some such angle which is the these angle will be the same as that angle which will be the same as that angle. And therefore you will get the hybrid orbital which is actually making the same angle with x, y and z.

(Refer Slide Time: 25:15)



You in a similar fashion I can also find out phi 2 what will it be? Well, I can write it as s it is actually very as I said if I put s plus p x minus p y minus p z normal I said factor is just it is 1 by 2. And, why do have 2 negative signs? Well, it is very clear why you should have 2 negative signs because these and that has to be these 2 have be orthogonal. So, if you multiplied by this with that and integrate over the entire space you see s into s you will get that that will be a s square. When you integrate over all space you will get unity these into that will also give me unity by while this into that will give you minus 1; these will also give you minus 1. So, you would have 2 minus 1 and 2 plus 1. So, and therefore the net result will be 0. And similar if you think of phi 3 you would have 1 by 2 very simple to construct it is it will be s minus p x minus p y plus p z and the last one will 1 by 2; s minus p x plus p y minus p z. And in fact it is actually possible to make a nice picture of these using mathematical. But we will not do that I shall simply show you the way this orbitals are oriented in the next slide.

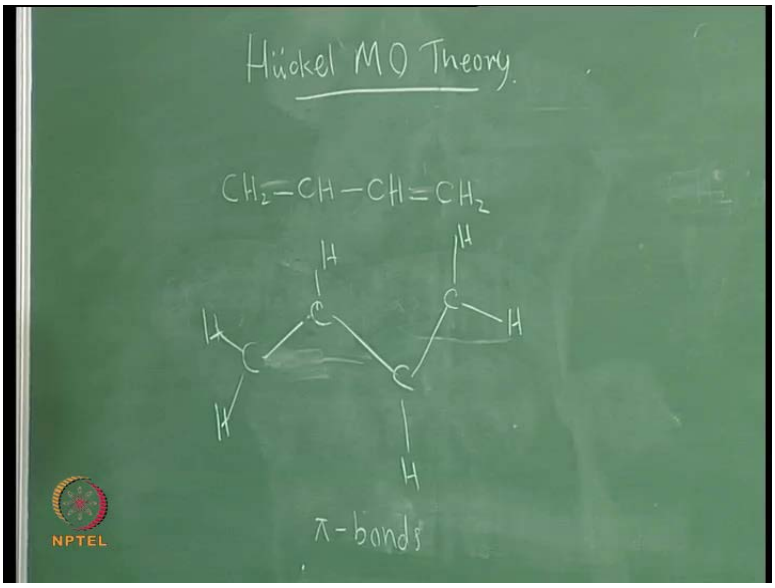
(Refer Slide Time: 27:02)



I told you that well this is this particular direction is the direction in which my hybrid orbital phi 1 points. And then these are the other direction right I will shown with these arrows are the other directions in which other orbitals are pointing. And it is also be as there from the figure that there are pointing towards the alternate coordinates of a regular cube right; what is shown here is a regular cube these is 1 corner or 1 vertex and this is the next one. So, if the first one is pointing in this direction; the second does not point in that direction. But to the other corner that is why it is a alternate corners. And using this information it is possible for you to calculate the angle between these hybrid orbitals; you will find that these is the tetrahedral angle 109 degrees 28 minutes perfect head tetrahedral angle.

And, therefore you see that these orbitals are equivalent there are actually pointing in equally good direction in space; and this completely explains the formation of tetrahedral C H 4 molecule fine. Now, this actually concludes my discussion of hybridization. And we will now discuss another very interesting topic which is subjected Huckel molecular orbital theory.

(Refer Slide Time: 29:03)



Huckel molecular orbital theory remember which discussed the particular in a box problem I said that these is a model for conjugated systems. So, particle confined to a box you can say that well this will form a molecule form a model for conjugated systems. So, here is a somewhat better model for conjugated systems. So, if you think of a conjugated system like 1, 3 butadiene the molecule will be C H 2. Well, at these point I will have to depend upon your previous knowledge I will remind you that each one of just carbon see a speed 2 hybridized. And this will leave a p orbital perpendicular to the plane of the molecule. So, each one of them is s p 2 hybridized and the s p 2 hybrid orbitals use to form 3 bonds.

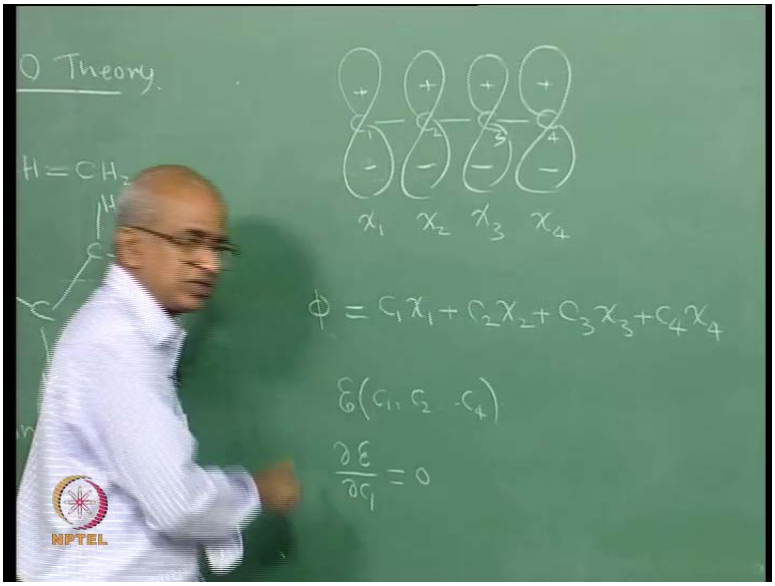
For example if you think of this carbon it is s p 2 hybridized; it forms a bond with these 2 hydrogens. So, that is 2 bonds and then it forms a bond with the carbon a sigma bond; you see that is the another the description. Similarly, this carbon it forms one sigma bond with this carbon; one sigma bond with the other carbon and one sigma with the other hydrogen. So, all of them are especially hybridized and they all the sigma hybrids; all the hybrid orbitals are use to form sigma bonds.

So, that actually leaves a p orbital let me remove the these double bonds; this is the what is referred to as a sigma frame work of the molecule I can even making it better by say that; I have a system like this that is correct geometry of the molecule roughly. So, these are actually the sigma bonds found by the hybrid orbitals. But this actually levels a un-

hybridized p orbital perpendicular here the assumption is that the molecule is in the plane of the bonds, so therefore the un-hybridized p orbital with perpendicular to the plane of the bond.

So, there is one here there is one that carbon sitting like that; one on this and the fourth on this. And these orbitals these p orbitals are parallel to one another. So, they will overlap and they will form bonds. So, the Huckel theory was formulated by Huckel along ago to describe only the un-hybridized p orbitals; how they combined together to form a right what are refer to as pi bonds or they form what is refer to as the pi system of the molecule. And this theory describes only the pi system of the molecule. And we will not to be draw picture like this.

(Refer Slide Time: 32:38)



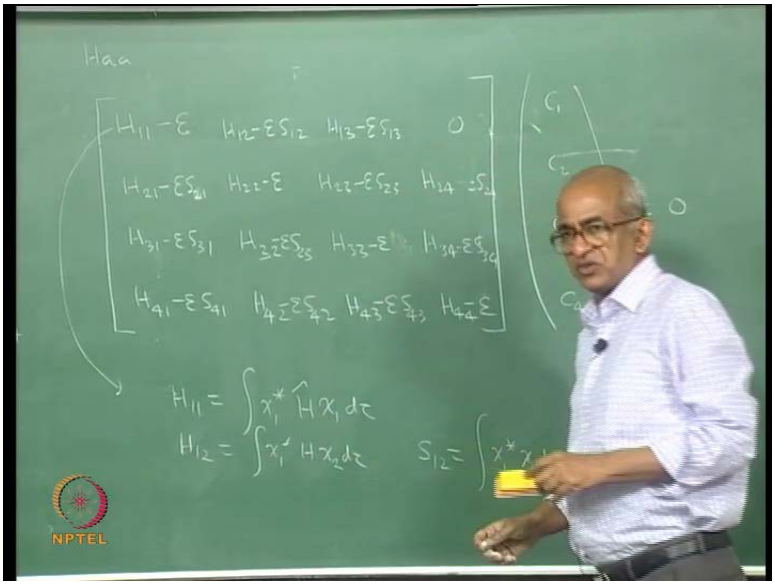
But what I will do is I will say I have 4 carbons you know you are chemist. So, you know that there are hydrogen and so on; all that mean I interest to may is this p orbitals which are perpendicular they are all parallel to one another; they are all perpendicular to the plane of the molecule. And this p orbitals I need a notation.

So, what I will do is I will call this chi 1 these is on the first carbon; this I will call chi 2 it is on the second carbon, this is chi 3 and chi 4. Now, it is usual to have this is a conjugated systems which can be quite long. And if you had 10 atoms what will happen? You will have chi 1, chi 2, chi 3, chi 4 etcetera until chi 10. And now you know where a molecule orbital description what we would do is we would have a combination like c 1

chi 1 plus c 2 chi 2 plus c 3 chi 3 plus c 4 chi 4. You will say that molecular orbital are obtained they have the form c 1 chi 1 plus c 2 chi 2 plus c 3 chi 3 plus c 4 chi 4.

And, then what I should do I will have to do a variational calculation how will I do the variational calculation? I would write on expression for script e I assume that my molecular orbitals are given by these; then use this in a variational calculation. In the variational calculations script e is now going to depend upon not 2 parameters but 4 parameters. So, therefore you would have e being a function of c 1, c 2 etcetera and until c 4. If you have 10 orbitals so it is being a function of 10 coefficients. The next will be you will put dou e by dou c 1 equal to 0. Similarly, you will put dou e by dou c 2 duo e by dou c 3 dou e by dou 4 c 4 equal to 0; what you will get? You will get 4 equations in this case.

(Refer Slide Time: 35:00)



If you had 10 coefficients then you will get 10 equations. And they can these equations can be written just as we did earlier they can be written in a matrix form; the wave we wrote this matrix equation I hope you still remember in that case we had only a 2 by 2 matrix that is because we had only 2 atomic orbitals combining. But now we have 4 atomic orbitals combining. So, naturally the equation the matrix equation that one has will have the c 1, c 2, c 3, c 4 these are contributions of these atomic orbitals to the molecular orbital pi.

And, what will be nature of this matrix when we can write by looking at the previous things that we have done it is the first element here is going to be H 1 1; earlier you had H a a that is because you are calling the orbitals 1 s a, 1 s b. But now you have H 1 1 what is H 1 1? Let me just remind you H 1 1 will be defined to be integral of chi 1 star H chi d 2 right. So, you would have H 1 1 minus script e then what will be the next element it is going to be H 1 2 minus script e s 1 2; what is H 1 2? It is quite simple integral chi 1 H chi 2 d 2 that will be H 1 2 and s 1 2 will be integral chi 1 star chi 2 d 2 this is.

So, by analogy with the case of s 2 plus we can write this. So, the next element will be H 1 3; I am running out space here also. So, maybe I should write smaller this will be my first row right; this first row into that should of course give me the answer 0; that is my first equation this is equation we obtained if you differentiated script e with respected c 1 and put the derivative equal to 0. Similarly, if you differentiated with respect c 2 and put the derivative equal to 0 the answer that you are going to get you H 2 1 minus e s 2 1; H 2 2 minus script e H 2 3 minus script e well this is T D S probably should have taken a smaller molecule as the example.

So, that I mean I do not have to write so many. But it is not difficult let me just continue to write right; this is all that is going to happen and the definition as for these numbers H 1 1, H 1 2, H 1 3, H and 4 and so on; they are all similar to what I have define here. So, this is what you Huckel he wrote this equation. And then you said let us make this equation as it stands is very difficult to handle. So, let us make some simplification and physically mutative simplifications; if you think of s 1 4 what is s 1 4; s 1 4 actually in words multiplying chi 1 with chi 4 right I should say chi star.

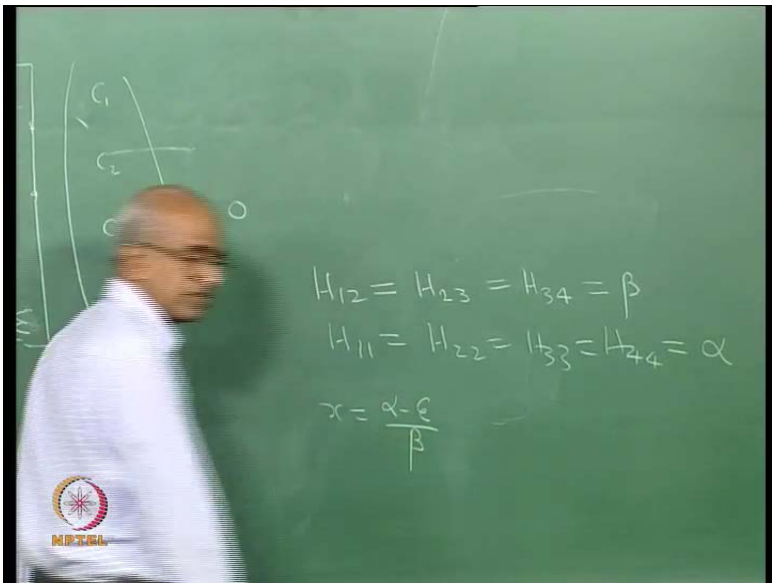
But it does not matter chi is real. So, you multiply with chi 1 with chi 4 now chi 1. So, it is actually overlap integral involving chi 1 and chi 4; and these atom are for away correct. So, therefore what would you expect s 1 4 I would expect it to be very close to 0 very, very small and not only s 1 4 even H 1 4 right. Because at the atom are for away because the atomic orbitals chi 1 and chi 4 are for away I would expect that this also will be 0. So, therefore what I will do definitely H 1 4 and s 1 4 both or 0, so therefore very close to 0. So, I will replaced with 0 this makes thinks easier H what about H 1 3 they also are for away; there are not very close. So, I will say that this is 0.

Now, H 1 2; H 1 2 is actually is on neighboring there are all neighboring atoms. And therefore what would I expect? I would expect that the value of H 1 2 is not small value of s 1 2 it is not that small actually if you evaluate; if you can evaluated roughly will find that just answer of 0.25. But Huckel did not want to consider even that because you want to away very simple theory. So, you said we will we will neglect this s 1 2 which means that all the overlap integrals that occur in this expression I am going to say they are all 0. And matrix cell the element of this matrix like H 1 2, because 1 and 2 are on neighboring carbon atoms I am not going to neglect it. So, if I did the same kind of think here s 2 4 there are not on neighbors. So, this is going to be 0 s 2 4 also 0 but H 2 3 definitely is not 0 s 2 3 I will approximately it has 0.

Because 2 and 3 are neighboring then coming to here H 2 1 you look at these H 2 1 it involves orbitals 2 and 1. So, this not 0 s 2 1 I will neglect; H 3 1 involving carbon atoms 1 and 3 this is 0 that also is 0; H 3 2 is not 0 this I will put it equal to 0 this is neglected. And this is 0, that is 0 this I will neglect right and to everywhere else I have everywhere that I have rubbed of things is put 0; this 0 better that it is written here.

So, that is the simplifying assumption. Now, you will make further simplifications see what is H 1 2? H 1 2 is actually interaction between chi 1 and chi 2 it represent interaction between the what is known as the resonance integral; H 1 2 is referred to as resonances integral. And it represents the interaction between chi 1 and chi 2. And similarly H 2 3 it represents the interaction between chi 2 and chi 3. Now, we I would expect that there are applicable they do not have it to be exactly equal because the carbon atom or not equal. But I will make the approximation that the interaction between these and that is same as same interaction between these and that.

(Refer Slide Time: 43:15)



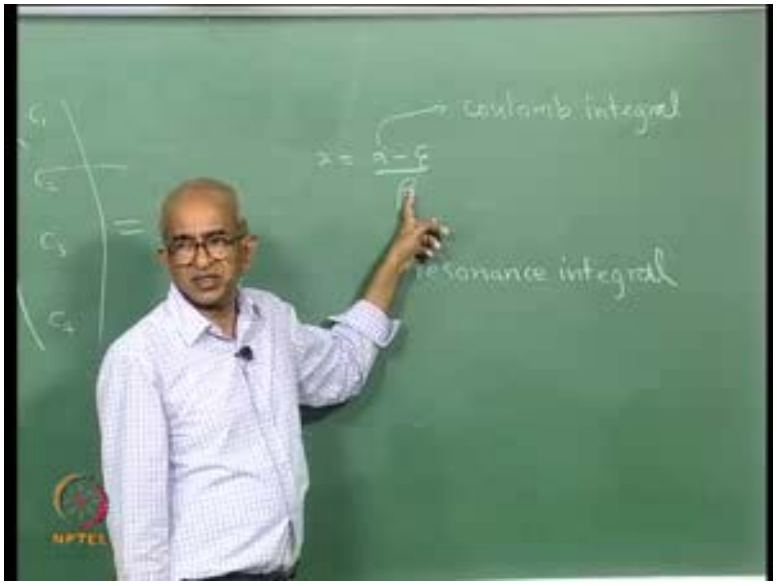
That actually means that H 1 2 is assume to be equal to H 2 3 which again I will assume is equal to H 3 4 and do. So, I am assuming that all this elements H 1 2, H 2 3, H 3 4 they are equal and their value I am going to denoted by the symbol beta; they all the same this is another approximation. Then H 2 1 is a 3 2 H4 3 in the same fashion they are equal to beta. Then H 1 1, H 2 2, H 3 3, H 4 4 these are actually energies of the atomic orbitals chi 1, chi 2, chi 3 these are energies remember these are energies of the atomic orbitals chi 1, chi 2, chi 3, chi 4 etcetera I will say that they are also equal, because there are all the atomic orbitals on the carbon atom. So, what was happened my theory has simplified a lot these is while I am making the assume that H 1 1 is equal to 2 2 it is equal to H 3 3 which is equal to H 4 4. And that I am going to say they all equal I shall denote them by the symbol alpha.

So, let us now say this is alpha strictly speaking this will not be equal to that it is only approximately true. But I do not know worry about that because my 3 d is very simple and crude this are all equal to alpha; and these numbers H they are all equal to beta fine. So, these is my new matrix equation after all this simplifications. And it looks much nicer than the previous expression that I had. And if you like you can even make it appears simpler I will multiply from the left hand side with a 1 by beta.

So, what do you mean by multiplying a matrix by 1 by beta? That means, you each element you are dividing by beta. So, naturally if you multiply beta this beta will

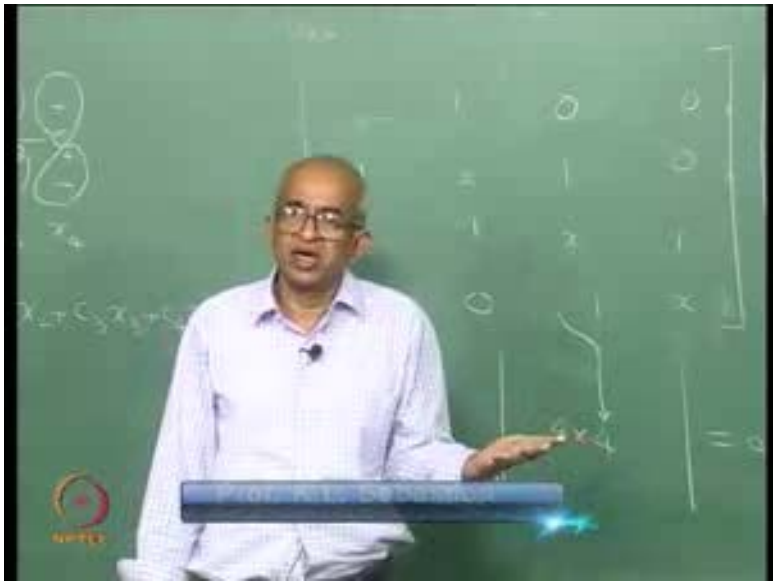
converged into a 1. So, all the betas that are there they will all be converged unity after this multiplication. So, you have 1 here, you have 1 here, 1, 1 and 1. And here you will have this divided by beta, here this divided by beta and that as well as that. And as you it is tedious as to write alpha minus script e divided by beta. So, what I will do is I will adopt a short hand notation I will say that I will use the simple x x is alpha minus script e divided by beta. And, therefore along the diagonals what do I have I just have this object x. So, therefore you see you see how simplified the theory and of course after all this simplification you have a very nice looking matrix equation.

(Refer Slide Time: 46:54)



Let me just remind you x is actually equal to minus script e divided by beta; beta is referred to as resonance integral. And alpha referred to usually refer to as the coulomb integral; these are the traditional words use to denote this integrals. Now, what is our aim? Our aim actually is to find script e correct; that is our aim essentially we want to find script e. And of course when you look at the definition of script e it is clear that sorry when you look at the definition of x it is clear that if able to determine the value of x; then naturally I will get the value of script e.

(Refer Slide Time: 47:52)



So, therefore this matrix equation you see I have to manipulate and determine the different possible values of script e definitely means I have determine the different possible values of x. Now, if this matrix equation is to have know trivial solutions what do I mean by that? Well, an obvious solution will be c 1, c 2, c 3, c 4 equal to 0 that is referred to as trivial solution. Now, if does matrix can be invented; if you can find it inverse then you can multiply from left hand side with the inverse. And you will find that c 1, c 2, c 3 c 4 will be equal to 0 which is not acceptable.

And, therefore what should happen the determinant of this matrix should be equal to 0. So, you will write these determinant I am not going to write to repeat it but this matrix if you it is going to occur there. And you will have to put it the equal to 0. And this is a 4 by 4 determinant right and x is occurring only along the diagonals. And if you expanded the determinant what is going to happened? You will get an equation which involves x to the power of 4 right. If you have this matrix equation and if you said that I am going to evaluate the determinant of matrix. And put it equal to 0 you will get a quadratic equation in x.

And, they quadratic equation in x how many solutions would you have? You will have 4 solutions and these 4 solutions are the energies of the molecular orbitals; they will determine right this 4 solutions will give me energies of 4 molecular orbitals. They will give me 4 different values of script e; these are the energies of the 4 molecular orbitals

that are found from these atom orbitals. We will continue our discussion in the next lecture.

Thank you for listening.