Mathematics for Chemistry
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Lecture - 38

So, today we are going to look at simple application of the projection operator. The projection operator method, in this context is something that is used to construct suitable basis functions. Now, we will take an example of this. The problem statement here is that construct the basis function for two dimensional representation of group D 3 starting with an arbitrary function x y plus y z plus x z using projection operator. So, our goal is to start with this arbitrary function, and assume for now that we do not know what a suitable basis for this two dimensional representation is.

So, you have no idea. Assume that you do not know what suitable basis is. So, then how do you use projection operators to construct the appropriate basis function? This is the application of project. This is an illustration of the projection operator method; and you can use this method to actually to decide later on, which are the suitable linear combinations to use. So, let us remind our self, what is this group D 3 is?

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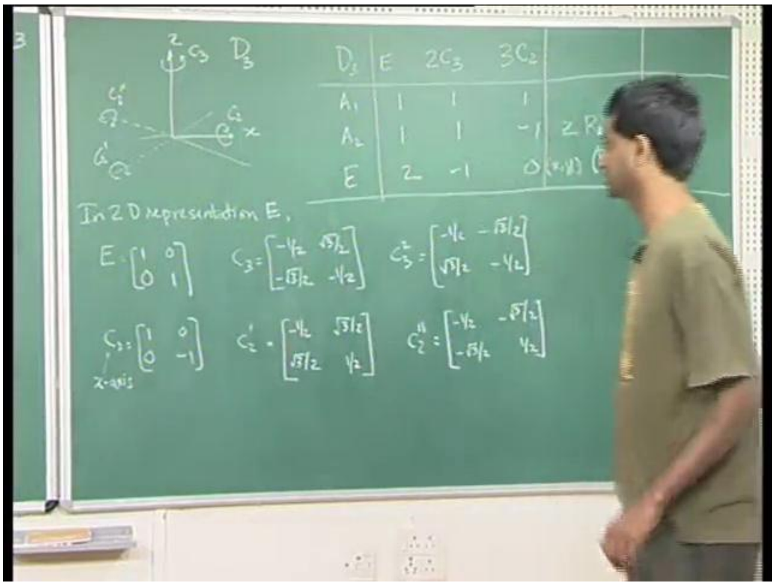

So, D 3 is a group of order 6. It has identity. It has C 3 and C 3 square and three C 2 axis. So, we align the C 3 axis along the z axis, one of the C 2 axis we align along the x axis, the other two are in the x y plane, the other two C 2 axis are in the x y plane and this angle between them as 120 degrees. So, these are the various elements of these groups. These are the various classes and you can easily work out using the great orthogonal theorem. You can you can work out.

There should be three irreducible representations, that is two one dimensional irreducible representations and one two dimensional irreducible representations. Then, you can also work out that these should be the characters. So, let us say we know this much about the group. Now, what we want to do is to find out what are suitable basis functions for two dimensional representation starting with this arbitrary function.

Now, we already know that x and y form of basis as does R x and R y. Now, what we are looking at, is suitable products from such basis. In order to do this, we need to write the appropriate projection operation and see what they give. So, we will use this technique and we will project out.

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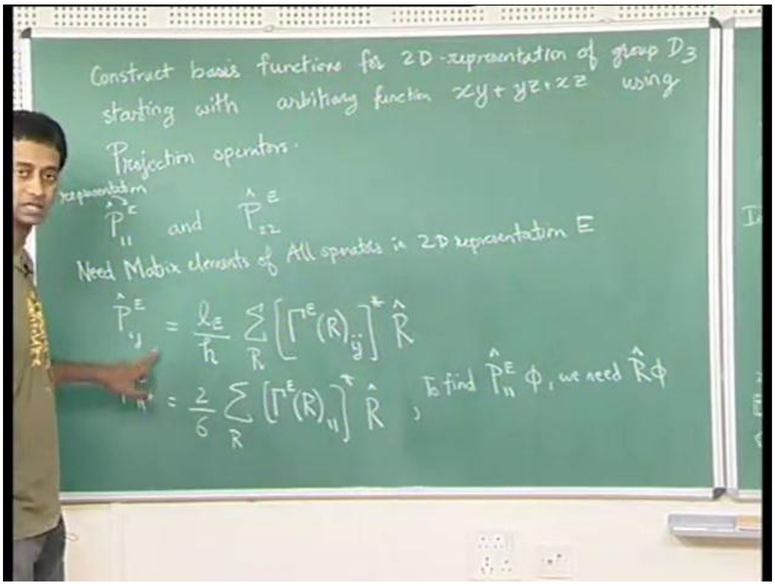

So, we want to project in the representation. So, this is the representation. So, you want to construct an operator that is characteristic to the representation and we always have two indices here. So, let us work out the diagonal elements. So, it will work out the P 11 and P 2 2 show that these two are sufficient to derive to get two basis functions. So, we are looking at the one projection. We are looking at the P 1 1 projection operation and P 2 2 projection operation.

So, now what we going to do is we are going to write these operators and operate them on this quantity x y plus y z plus x z and that will immediately give us two orthogonal two dimensional representation for this irreducible representations. So, it will give us two basis functions. So, let us start following the procedure now. In order to do this, we need the matrix elements we need the matrix of all operators in two dimensional representation E.

So, we need the matrix elements of all the operators in this two dimensional representation E. If you can work out that in this two dimensional representation E, this E should not be confused with this E. This is the representation E and this is the identity. The identity is always diagonal matrix. Since, it is a two dimensional representation it has 1 1 0 0. Then, you can work out C 3. C 3 will have this representation minus half minus half. So, you can work this out by actually calculating the matrix elements in the three dimensional representation.

Then breaking up the three dimensional representation into a two dimensional and one dimensional representation, so you can work out C 3, C 3 square, C 2 and C 2 prime. Since, it is along the x axis we can we can work this out. So, we find C 2, C 2 prime and C 2 double prime. So, these are the various matrix elements. We notice that the character of E is 1 .Character of C 3 is minus 1 and character of C 3 square is minus 1. Both these, character of C 2 is 0 and C 2 prime is 0. C 2 double prime is zero and that is here.

So, this is a valid two dimensional matrix representation of E. So, we need this matrix elements and then we need to construct the appropriate pos. So, this is the way to construct projection operation. Let us remind ourselves. So, if we want P E i j, then we calculate this by l l of E that is the dimensional of E divided by h. So, for any representation the dimensional of that representation divided by h is sum over all operations of the group.

Then, you look at the matrix element in this representation of R and you look at the i j th element, take a complex conjugate and you look at R and multiply by R. So, this our projection operation, this projects onto this, this l i j th element. Now, suppose you want to calculate P E 1 1, then what you need is l E is 2 h is 6 and then what you have is sum over R all the operation. You need gamma, you need the matrix element of the operation and you need the one matrix element. So, you need the one element of the matrix and take a complex conjugate and multiply it by R.

Now, each one element of these matrices are 1 minus half minus half. So, those are the one elements. So, we have this part. This part is something we have quite easily. Now the question is, what do we choose for R? So, for R we put each of the operations and when you operate on any function we need to know, how that R operates on the function. So, let us say, here to find P E 1 1 on any function we need R operator on any function.

So, if you want to know how P E acts on any function, you need to know how R acts on any function. So, this we have to say, how is E acting on the function is x y plus y z plus x z? So, E operates on these now. E is the identity elements and when it operates on it, you will just get the same thing. Now, how do you know what happens when C 3 operates on this function? In order to find out what happens when C 3 operators on this function, you need to know what happen when C 3 operators on x.

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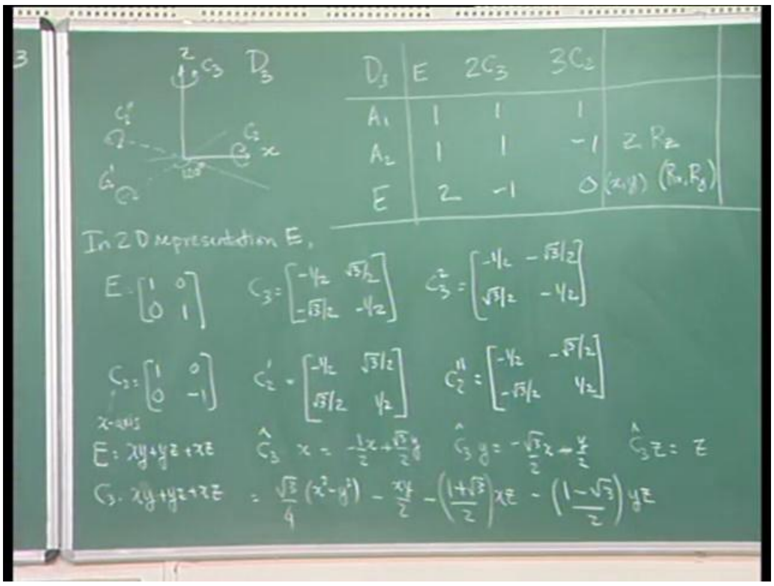

So, if you know what happens when C 3 operates on x, y and z independently, then you can calculate what happens when C 3 operates on this, on this and on these functions. Similarly, for C 3 square, for C 2, C 2 prime and C 2 double prime, so you just need to know how these functions act on the coordinates. Now, you can immediately see the when C 3 acts on x, it will give you minus half x plus root 3 by 2 pi, that is what i gives you.

When C 3 acts on y, you get minus root 3 by 2 x plus minus y by 2. When C 3 operates on z, you just get z. So, what you have seen is, you have seen what happens when C 3 operates on x, y and z independently. So, now you can calculate what happens when C 3 operates on x square or x y plus y z plus x z. So, when C 3 operates on this, what you get is x into y. So, it is product of these two. This y into z will be product of these two and x into z will be product of these two.

I will write the total expression. So, the total expression that you will get is root 3 by 4 into x square minus y square minus x y by 2 minus 1 plus root 3 by 2 x z minus 1 minus root 3 by 2 y z. So, you can take all these products and you can verify that this indeed is an expression. So, this was an illustration, but you can easily see that you can do the same thing for each of other operations.

So, you have to do this for all the other operations. You have to find out how C 3 square operates on this. So, similarly for C 3 square, C 2, C 2 prime and C 2 double prime , you have to find how all these operations acts on x y plus y z plus x z. So, each of them will give you some big function. What you have to do is, this is what your R of phi is. So, you have all the expressions of R of phi. Now, you can combine this to calculate your P E 1 1.

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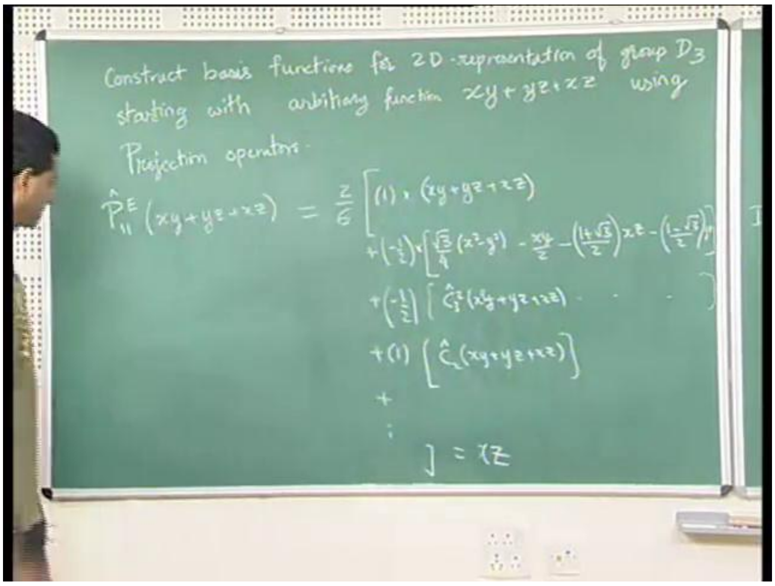

So, let us go ahead and do that. So, what we have is P E 1 1 is equal to this. So, you have 2 by 6 times. Now, now you have six terms corresponding to each of the six operations.

Now, the first what you see is that everything is pre multiplied by gamma 1 1 star. So, for identity you have 1 into the effect of identity on this operations. So, I should rewrite this as P E operates on x y plus y z plus x z. So, this is equal to this. So, you have 2 by 6 into you have some of areas terms and so the first term is just 1 into x y plus y z plus x z.

Because, the identity operates on x y plus y z plus x z, it just gives itself. Now, for C 3 the one matrix element is minus half. So, you have minus half. Now, when C 3 operates on this, you get this whole thing into root 3 by 4 x square minus y square minus x y by 2 minus 1 plus root 3 by 2 x z minus 1 minus root 3 by 2 y z, so all this is multiplied by minus half. Then, similarly you will have for C 3 square. So, you will have minus half into again sum of various terms. Then you will have for C 2 the one element is 1.

So, plus 1 into this is c 3 square operator done on on x y plus y z plus x z. This is C 2 operator on x y plus y plus x z and so on. So, you have these six terms and you have to collect all of them together. When you collect all of them together, what you will find is that you will get some function and that function is what will tell you what is the one one projection of this function. If you work out the whole thing, what you will get is that if you look at all the terms, you will have terms like x square minus y square terms like x y terms like x z, y z. You collect all the terms together and you will get a very simple looking expression. Everything else is cancelled. All you will be left with is x z. So, P E 1 1 will just give you x z. So, the projection of this onto the 1 1 matrix element is just x z.

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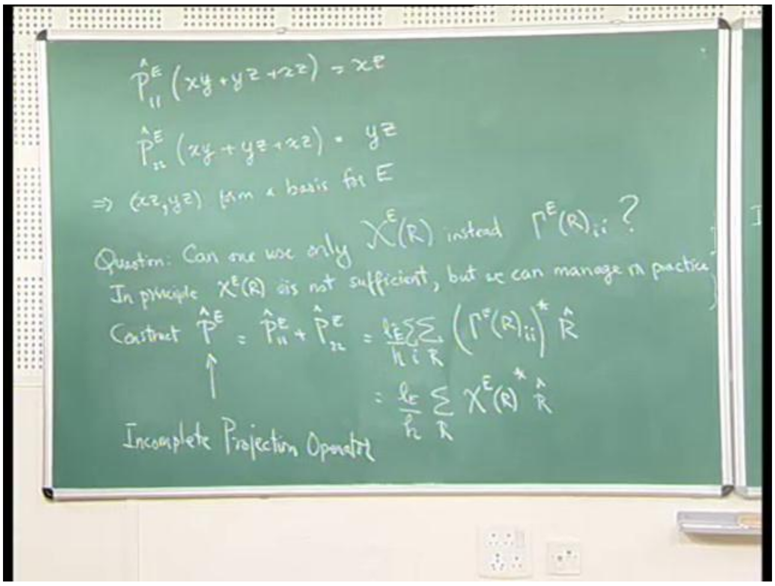

So, what we get is. P E 1 1 of x on x y plus y z plus x z is equal to x z. Now, the same thing can be repeated for P E 2 2. So, the two element and everything will look identical. Only thing, instead of using the one one matrix element you will use two matrix element. So, it will be 1 minus half minus half minus 1 half. So, these three will be the same. These three will change sign.

When you put all that together and calculate this you will get it equal to y z. So, just using P E 1 1 and P E 2 2, we constructed two basis functions x z and y z. So, P E 1 1 projects this onto this, collects a diagonal projection of this and that is x z. Similarly, this collects another diagonal projection that is y z, so this implies y z forms a basis for E. You can indeed show that this suitable basis is x z, y z. In fact there is another basis that can also be got from this projection, which is x square minus y square x y.

So, there were terms involving x square minus square and x y and they can be shown that they also form a basis. So, using this projection operation you can find suitable basis for the two dimensional representation. So, what we have seen is that x z and y z, you can you know from an starting arbitrary function. You found suitable basis for this two dimensional representation. You can actually work out lot more basis function using this projection operation method. I will not go to the details of that, but you are encouraged to try out and you know generate some of the other basis function.

So, what you will find is that if you start with x y, you will be taken to a mixture of x square minus y square and x y. So, that is how you generate the other two basic functions. Well, so the point is, you know this method can be used to actually get a suitable basis. Now, what I want to point out is that this method is extremely tedious because we have to construct the matrix element of each of these operations. Now, that itself is a tedious process for a two dimensional representation. You know construction of matrix elements is not that easy.

For one dimensional representation, the matrix element is just a scalar and that is just a characteristic. But for two dimensional representation, the character has characters. Then, you have to take the characters and you have to identify the suitable two dimensional representation. You can imagine that for a three dimensional representation it would be even more difficult. So, you have to calculate all these matrix element only then you can construct suitable projection.

So, the question is, can one use only chi of R instead of chi E of R instead of gamma E of R i i? So, instead of using all the elements, we just want to use a trace. The answer is that it is not sufficient, but you can get it in some cases. So, in principle chi E of R, this is for two dimensional. But for three dimensional representations that is not sufficient. But we can manage in practice. So, what I mean is that formally you think that trace contains much less information, then the actual values of the matrix element.

So, the trace of C 2 character of C 2 is 0. The character of C 2 prime is also 0. The character of C 2 double prime is also 0, but then that matrix elements are very different. So, it is important you see that for the projection operation we need to actually know the matrix element. Now, the question is, can we get this by using this trace? Let us see what happens. So, we construct P E is equal to P E 1 1 plus P E 2 2. So, I am just summing over all the diagonal elements. So, if you have a three dimensional representation, then you sum over all the three diagonal elements.

So, now this is equal to sum over R l i by h sum over R. What you have is gamma sum over R and l E gamma E of R I, that is the i th element. What you have is just sum over. I sum over all the diagonal element. What you can do is, you can interchange the order of the sum over i and the sum over R and you can show that this is nothing, but l E by h sum over R. What you have is chi R of R star R. So, now you only need the trace. You do not need the individual matrix element. You only need the trace. You do not need the individual matrix element.

Unfortunately, you still need to know how these matrix elements operates on the arbitrary function. So, how you still need to know R operates on this? But what you will see is that it turns out to be much easier to calculate. You can show that you still need to know all these in a sense, you still need to know all these for all the operations.

However, it will turn out to be a lot easier to calculate because in some cases you just need the sum of C 2, C 2 prime and C 2 double prime. So, you just need the sum of these three and that in general is easier to calculate. So, you can show this is called the incomplete projection operation. This quantity is called the incomplete projection operation. Also, using the incomplete projection operation, can we construct a suitable basis? The answer is yes.

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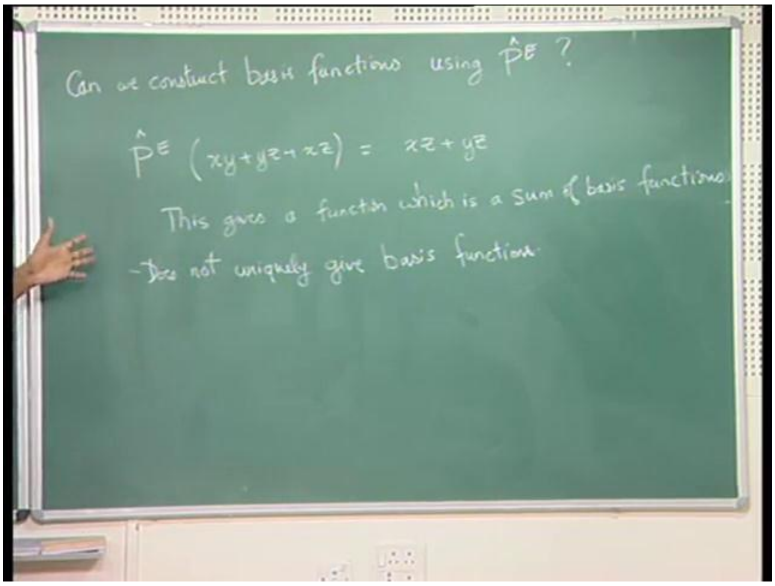

Can we construct basis function using P E? What you will show is that P E has operator on x y plus y z plus x z. This will turn out to be just x z plus y z. This is just x z plus y z, because it is just the sum of these two operations. So, what you get is a function and at this point y, you do not know that x z and y z they together form a basis. You just have this combination of x z and y z. It takes a little bit more work to actually show that the two the two function x z and y z are the function of form at basis.

So, basically this gives function which is a sum of basis functions. So, it gives something which is sum of basis functions and in principle you can break this into two functions in many different ways, but it does not uniquely give basis functions. Now, it does not uniquely give basis functions. So, can you take this and show that indeed this is composed of those two basis functions? The answer is usually you can do this, but you need to use some other techniques.

Let us now use the procedure of symmetry adapted linear combinations. So, how we can use the projection operation? How we can construct some symmetric linear combinations, some symmetry adapted linear combinations? The first example, I will do is fairly straight forward.

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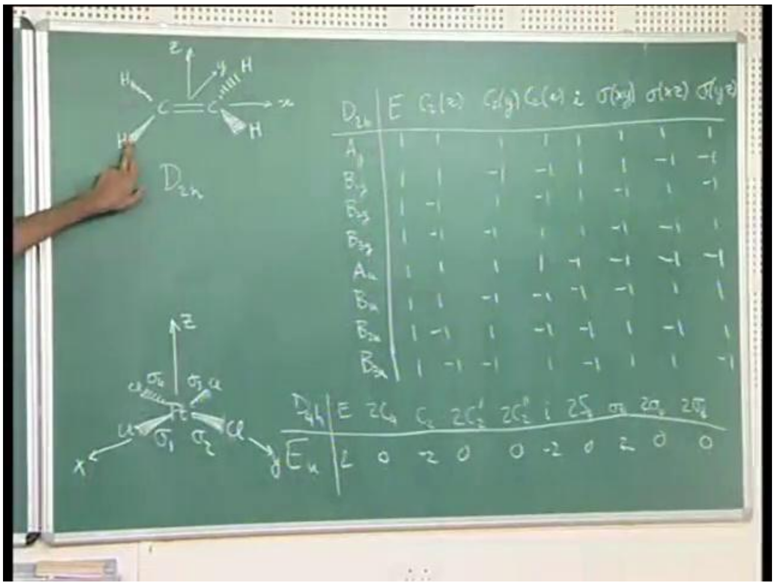

This is considered, the molecule ethylene. So, it is a planer molecule. One double bond, so C 2 H 4. So, in ethylene construct S A L C, using S orbital’s on H atoms. So, using the four S orbital’s on the four H atoms, that is on the four hydrogen atoms, let us construct some symmetry adapted linear combinations.

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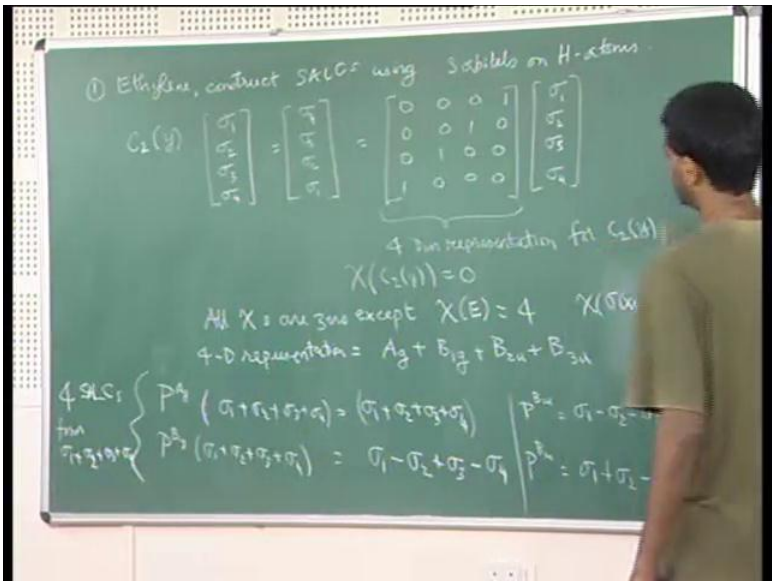

Now, a few things you should know. The first is, the S orbital is located on these four hydrogen atoms. So, the geometry of ethylene is the planer molecule. It is perpendicular to the plane of the board. We will choose our axis so that along the C C bond is the x direction and in plane of the molecule is though x y plane, okay? Now, this molecule belongs to point group D 2. Here, h D T h has eight operations. They are e there in C 2 axis. So, x axis is a C 2 axis, as is y axis and the z axis. So, there are three C 2 axis ok.

This is C 2 z y and x and there is a center of inversion. So, you can take this and you can get it inverted. So, we will get that it has a center of inversion. It has three sigma planes. So, each of the x y plane, the x z plane and the y z plane, they are all planes of symmetry. So, now if you work out the classes, it will turn out that there are eight classes. There are eight symmetry operations and 8 classes. Since, there are 8 classes, there have to be 8 irreducible representations and each of them have to be a one dimensional representation.

So, there are eight one dimensional irreducible representations denoted by G B 1, G B 2, G B 3 to G B 8 and then A union B 1 union B 2 union b 3. You and I have reproduced the character table. I have just a point. Note, if you notice an A G there is 1 1 1 1 1 1 1 1. In a U, it is 1 1 1 1 and minus 1 minus 1 minus 1 minus 1. So, if you take any of the G representations, it will be symmetric. The first four and the next four will be the same. So, for example, 1 minus 1 minus 1 1 1 minus 1 minus 1 1, whereas if you take the corresponding U representation you will have 1 minus 1 minus 1 1 as it was.

But then this one has changed signs. So, it is minus 1 1 1 minus 1. So, now let us contract S A L C using the S orbital on hydrogen atom. I am going to call this as follows. I will call this as orbital sigma 1, this sigma 2, sigma 3, sigma 4. I will just call this sigma 1 sigma 2 sigma 3 sigma 4. Now, you ask a question, if I take this sigma 1 and if I perform a C 2 operation, let us say C 2 y operation, what will happen to sigma 1?

So, if I perform a C 2 y operation, you can see that rotates about a y axis. So, sigma 1 will become sigma 4. So, you can do this for all the four orbital's. So, if you do C 2 about the y axis, let us write it as sigma 1 sigma 2 sigma 3 sigma 4. Then, what you get is the following. Then, sigma 1 goes to C 2. C 2 means this will go to sigma 4, sigma 1 will go to sigma 4, sigma 2 will go to sigma 3, sigma 3 will go to sigma 2 and sigma 4 will come to sigma 1. It is not hard to show.

Now, this I can write as 0 0 0 1 0 0 1 0 0 0 0 0 1 0 0 0 times sigma 1 sigma 2 sigma 3 sigma 4. So, I can write in this form and so, this becomes four dimensional representation for C 2 of y. So, this is the matrix correspond to a four dimensional representation of C 2 y and chi of C 2 y equal to 0. Now, you can see that you take chi of any other operations. So, for examples if you take chi of C 2 z C 2 x, you will get again 0.

So, the chi is for all these operations which will be exactly equal to 0. You will find that only 2 of the phi are non zero, only two of the chi are non zero and they correspond to E and i. So, all chi are 0, except chi of E. Since, it is a four dimensional representation, you have to have one along the diagonals, chi of E equal to 4 and chi of i. So, not chi of i and chi of sigma x y. So, the molecule is in the x y plane. So, chi of sigma x y is equal to 4. So, if you do a sigma operation and if you reflect about the x y plane, then sigma 1 stays sigma 1, sigma 2 stays sigma 2 and all these remains as they are.

These two have non zero characters and everything else has characters 0. So, this is what we can use easily. Now, starting with this we can easily construct various combinations. So, let us look at the projection. So, we can look at projection onto it, so before we do that, we can do one thing. So, in this representation, this represents an irreducible representations, where all the characters are 0 except character of identity and character of sigma x y. So, you can ask a question as to how many times B 1 G appears ? How many times B 2 G appears?

So, you can ask how many times each of these representation appears in this irreducible representations? It is not hard to see. You can just look at it and you can immediately see that. So, B 1 g is sigma x y. So, A g, B 1 g, B 2 u, B 3 u, you can see or you can take B 2 g, B 3 g, A u and B 1 u. So, you can take these four and they appear exactly once.So, you can write this in two different ways. So, this is 4. So, you can see that if you want 4 here, so you have to take this, this, this, this, and this.

So, these representation can be reduced. So four dimensional representation is equal to A g plus B 1 u plus B 2 u plus B 3 u. So, just to confirm if I take these two and add them up, then I will get 2 here 2 here 0 0 2 here 2 here 0 0. So, then if I add these two, then I will get 2 here, minus 2 here which will cancel this 2. So, we will get 0 4 0 0. So, that is what I will get which is exactly the same as these characters. So, these four dimensional representation can be written as A g plus B 1 g plus B 2 u plus B 3 u.

So, that means these are the only representations that will have non zero projections. So, these are representations that will have non-zero projection of these basis. So, you can calculate projection in A g irreducible representations and since there is only one element, there is one dimensional irreducible representation, so we will calculate the projection onto A g. This you can show is sigma 1 plus sigma 2 or this operation on sigma 1 plus 2 plus sigma 3 plus sigma 4, this is just sigma 1 plus 4.

I am not bothering writing the pre factor l i by h 1 by 1 by 8 factors, so they will be constant. So, I would not bother to write that, but basically this will just be sigma 1 plus sigma 2 plus sigma 3 plus sigma 4. Similarly, projection operation of B 1 g of sigma 1 plus sigma 2 plus sigma 3 plus sigma 4, this you can directly see. In this case, the character here is 1, so we will always have sigma 1, the character of sigma x y 1. So, you will still have sigma. So, you will have sigma 1, so this will look like sigma 1 minus sigma 2 plus sigma 3 minus sigma 4.

So, the way to do this is you have to look at how each operation acts on these sigma and then you can work out this as a projection operation. Then, you can work out the remaining 2 projection operations. P, I will write it in slightly shorter form B 2 u equal to this P B 3 u is equal to this. So, this is sigma 1 minus sigma 2 minus sigma 3 plus sigma 4. This is sigma 1 plus sigma 2 minus sigma 3 minus sigma 4.

So, the point is we can work out all these projection operation and so these are the four. So, when you take sigma 1 plus sigma 2 plus sigma 3 sigma 4, you projected onto the A g irreducible representations, that projection is just itself function. If you projected onto B 1 g, you will get this. You will get sigma 1 minus sigma 2 plus sigma 3 minus sigma 4. If you projected onto B 2 u, you will get this and if you projected onto B 3 u you will get this.

So, these are the four symmetry adapted linear combinations that you can construct for SLAC. So, these are the four symmetry adapted linear combinations that you constructed from sigma 1 plus sigma 2 plus sigma 3 plus sigma 4. So, this completes the exercise, how to construct S L A C using the S orbital's of hydrogen atom. Now, the next exercise is slightly more tricky. This involves a two dimensional representation, so let us consider P t C L 4 2 minus.

Now, this is P t C L 4 minus. The P t C L 4 unit is planar, So, it is planar and this belongs to point group D 4 h and this belongs to point group D 4 h. Now, D 4 h has sixteen operations sixteen operations. It has ten classes, so sixteen operations and ten classes, so there are ten irreducible representations. Now, we will focus on one irreducible representation, which is a two dimensional representation E 2 E u. What we want to do is the same thing that we did last time. We want to construct suitable basis for E u using these, using sigma 1, sigma 2, sigma 3 and sigma 4. So, we will use the four orbital's of sigma 1, sigma 2, sigma 3 and sigma 4. We will construct suitable basis for E u. Let us do this. We will do this instead of going through the whole laborious procedure.

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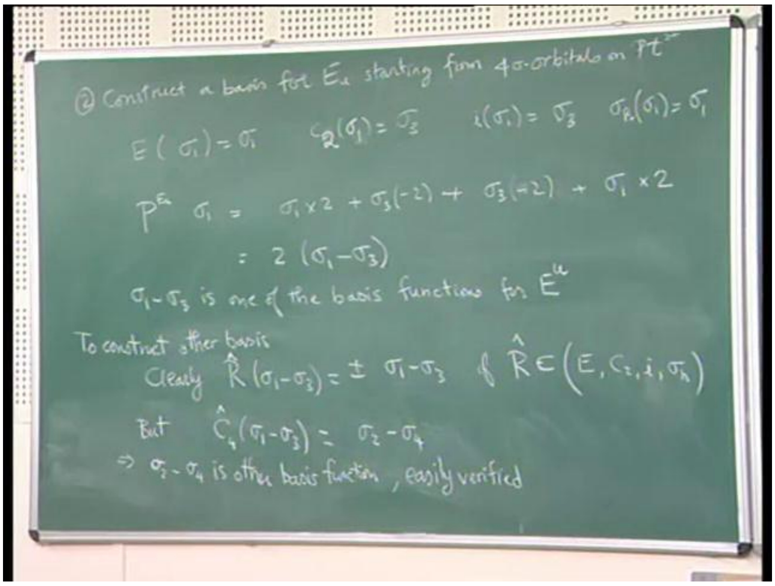

I will just mention that what you want to do is to construct basis for E u starting from four orbitals on P t. So, the four orbital's are connected to P t. So, let us take sigma 1. So, in order to do this let us just use the coordinates system, where the x axis goes along one of the C l, y axis goes along the C l and z axis is perpendicular to the plane of the molecule. So, now let us look at sigma 1. Now, if you operate, so in this case what you want to do is to give the result of all the operations on sigma 1. So, clearly E of sigma 1 equal to 1 and then you have C 4. Well we do not care about C 4, let us look at C 2. So, in order to find the projection operation, you need to know how each operation acts on sigma 1. Now, if the character of the representation is 0, then you know that it would not contribute to the projection operation. So, we are going to use the incomplete projection operation. So, if the character is 0, then we will say that anyway since it does not contribute to the projection operation, I do not need to bother how C 4 acts on sigma 1. So, I will just see how C 2 acts on sigma 1.

So, when the identity operates on sigma 1, you just get sigma 1. C 2 has a non zero character. So, when this operates on sigma 1, now C 2 when it operates on sigma 1, we choose C 2. So, it takes it to sigma 3. So, C 2 operates on sigma 1 as sigma 3 C 2. C 2 will take sigma 1 to sigma 3. C 2 is like rotation by 90 degrees about the x axis and rotation by 180 degree about the z axis.

So, sigma 1 will come all the way to sigma 3. What about I, the inversion operation? When it takes on sigma 1, it will give you sigma 3 and similarly, when sigma h operates on sigma 1, we will get sigma 1. So, the projection operation on E u of sigma 1, can be written using the incomplete projection operation. This can be written as sigma 1 times character of E. Character of E is 2 plus sigma 3 times character of C 2. Character of C 2 is minus 2 plus sigma 3 times character of i. Character of i is minus 2 and sigma 1 times character of sigma h which is 2.

So, then this is just twice sigma 1 minus sigma 3. So, therefore we can immediately say that sigma 1 minus sigma 3 is a basis. So, sigma 1 minus sigma 3 is basis for E u and sigma 3 is one of the basis functions for Eu. Now, to construct other basis, so in principle if you want to construct the other basis you will need the other matrix element. So, we worked with the incomplete projection operation. So, we used only the characters, but we need the full matrix element.

But actually we can do it in another way. To do this, what we will see is that we take sigma 1 minus sigma 3 if you operated by all these ten classes. You operated by members of all the ten classes. Actually you have to operate it by all the sixteen elements. You look at what you end up with in each case. Now, if you operate sigma 1 minus sigma 3 by E, you will end up with sigma 1 minus sigma 3.

So, clearly R of sigma 1 minus sigma 3 is equal to plus minus sigma 1 minus sigma 3, if R is equal to R s contained in E, C 2 and C 2 double prime. No, sorry. E C 2 i i sigma h. So, these four operations will give you exactly sigma 1 minus sigma 3, okay? Now, this is this is very obvious, because these are the operations that have non zero projections. So, in order to find the other basis, we can use one trick. We can operate on sigma 1 minus sigma 3 by some other operations.

So, lest operator by an operation that does not belong to this sets. So, let us operate by C 4. So, C 4 operated on sigma 1 minus sigma 3. So, C 4 will take sigma 1 to sigma 2. So, it will take sigma 1 to sigma 2 and it will take sigma 3 to sigma 4. So, now you can immediately look at this and you can say that probably C 2 minus C 4 will be an other basis functions. So, this implies sigma 2 minus sigma 4 is the other basis function. You can just guess this based on the fact that C 4 takes in onto this.

If you look at sigma 2 minus sigma 4 then when it acts on identity, this is easily verified because, when you operated by identity you will get sigma 2 minus sigma 4. When you operated by C 2, you will get minus sigma 2 minus sigma 4. When you operated by I, you will get minus sigma 2 minus sigma 4. When you operated by sigma h, you will get sigma 2 minus sigma 4. So, clearly this is the other basis function.

So, without doing too many calculation we have been able to arrive at these basis functions. We use some logic here, in the sense that you know we started with a sigma 1 and we ended up with the sigma 1 minus sigma 3. So, we guessed that sigma 1 minus sigma 3 has to be a basis. Then, what we did is we looked, how the operations so clearly C 4, when it operates on sigma 1 minus sigma 3 gave something that is orthogonal to sigma 1 minus sigma 3. So, we guessed this and then we can easily verified that sigma 2 minus sigma 4 is another basis for this representation.