Chemical Applications of Symmetry and Group Theory

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Lecture – 26

Hello and welcome. We are on the day first of week 6. In the last class, we studied learning about symmetry adapted linear combination. What is this essentially symmetric adapted linear combination? We started in giving some brief example, but let us have a look at it in bit detail.

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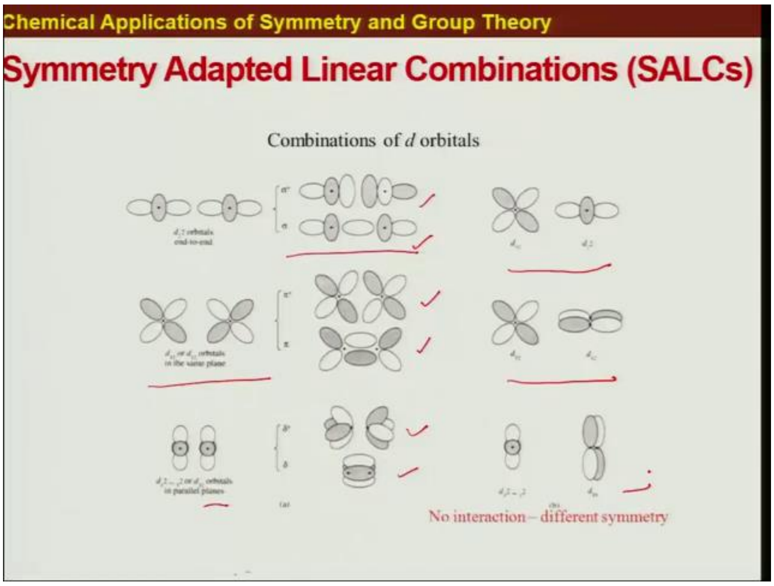

When ever in a molecule, we have certain atoms and each atom will have their own way functions and this way functions are, you know also looked at as orbitals. Different, you know way functions of different atoms will combine, whenever they are energetically preferable and also symmetrically allowed. What does that mean?

Let us have a look at it. For you know, various metal complexes the D orbitals, they come into the, you know in the play. So, is not that you know, 2 atoms have been any 2 D orbitals can combine. There are certain symmetry restrictions. For example, if we have a look at the pictures, that are shown on the screen, 2 digit square orbitals, they can combine which is symmetrically allowed and they can give rise to 2 molecular orbitals like this, depending on which way they are combining. That can give bonding and N type bonding kind of orbitals, more with your orbitals. The Z of sigma and sigma star, that are formed out of the combination 2 digit square orbitals. They form through a linear combination of those 2 digits squares atomic orbitals.

Here we have another example, where either you can take A D XZ to D XZ orbitals or 2 D YZ orbitals and if you take two D XZ orbitals and this is my D XZ plane and this is also other D XZ orbitals in the same plane. They can combine, they can combine in 2 different ways, 1 is in this fashion, and another is in this fashion. Depending on that you get either A Phi bonding or Phi N type bonding molecular orbitals. Again D X square minus Y square can combine with D XZ orbitals because they are in the parallel plane. They can have an overlap; D can form like delta bonding; delta bonding and delta and N type bonding of kind of orbitals, where as if you look at the right hand side panel of this screen, you can see that D YZ and D Z square, they cannot be combined.

Thus symmetrically they are completely different and are D YZ and D XZ and D X square minus Y square and D X Y. Because of the different symmetry of these orbitals, there will be no interaction; no interaction means, no bond formation. No bond formation means, no result and way function or no result in orbital formation.

Now, we need to find out at, which are the orbitals in a given molecules that can form a linear combination to give rise to molecular orbitals, meaning, the orbitals that are formed, they should comply with the symmetry molecular point group.

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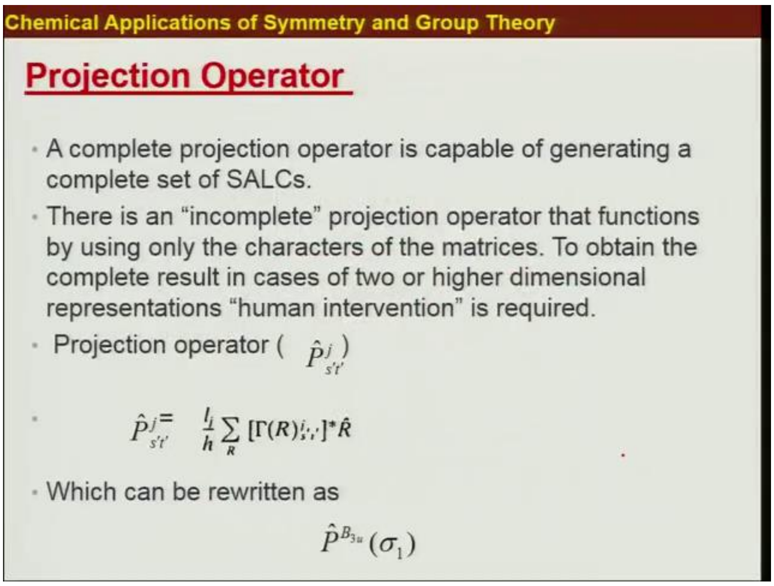

How to find that out, that we started with in the last class, we said that there is truth called projection operator. Projection operator can give us as the information about which, are the orbitals that can linearly combine and give symmetrically allow you know, molecular orbitals. We studied in the last class; a complete projection operator is capable of generating complete set of SALC.

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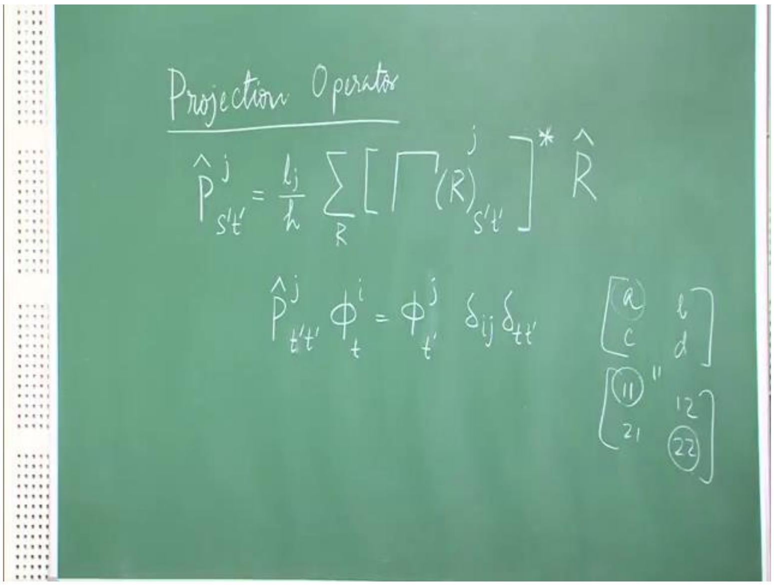

What we did? We formed this projection operator and we derived it sincerely and this is the form of that projection operator, that we formed using the general principle and from there, we also said that, this is the special case when 1 talks about the purely diagonal element of the, you know matrixes of a representation and there by this particular special case of projection operator will find out, whether this Phi t prime belonging to a particular J illusive representation, occur within the orthonomal set, say Phi. You know I is one of which is here as Phi t.

If you apply the projection operator on to any arbitrary function belong to a orthonomal set, then either this function itself will be this one or it will contain this function in that case in this particular function, will be projected out from that set by this projection operator, otherwise this function will be abolished or if this function contains this Phi t prime and many other functions also then all the other functions will be abolished and this 1 only projected, that is why it is a projection operator.

You start with when, you know li dimensional set having orthonomal you know function and take them as basis and you can construct the li number of projection operator and this complete set of projection operator can give the total information about you know, what are the particular function that you know, can act as the basis of the you know, whatever the ire illusive representation one is concerned about and in the molecular of orbital picture, what you can think of such a projection operator constructed form an exhausted, you know in list of orbitals function list of functions and if you form all the projection operator, then the total you know, site of projection operator will give you the overall symmetry adapted linear combination that are possible.

Now, this is about complete projection operator. This term will be when more clear as we move ahead and since we are talking about complete projection operator, there is also another something called incomplete projection operator, which is less efficient than this complete projection operator while we deal with complete orthonomal set and forming the you know, position operators involving the each and every element of the you know, of any given representation and you get the total information about the SALCs whereas, the incomplete projection operator, that is you know that deals with the you know the trace of the you know, matrixes that of prompt while forming the representation.

We will talk about that a little while from now. This is the same thing that is written over the board and we can write the explicit ire illusive representation while replacing this generalized term J. Here just for an example, we can write this as B 3 U, suppose I am concerned about a particular character table of say D 2 8 and in the function that you can choose as any of the bond vector or you can choose as any of the you know, atom orbital is anything.

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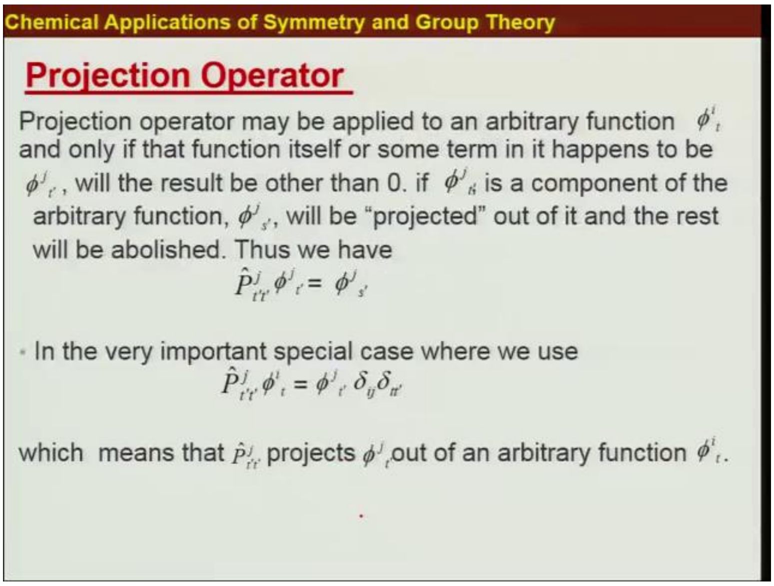

You know by that the projection operator may be applied to be an arbitrary function, say Phi t and only if that function itself or some term it happens to be Phi t prime, the result will be, you know non 0 if Phi t prime is a component of arbitrary function. 5 is prime, that will be projected out of it and the rest will be abolished. We have this term in this as a special case, where we talk about the projection operator involving only the diagonal elements of the representation. t prime t prime is a diagonal element.

Uultimately this P t prime t prime corresponding to A J ire illusive representation that will project this, you know Phi t prime out of an N arbitrary function as Phi t.

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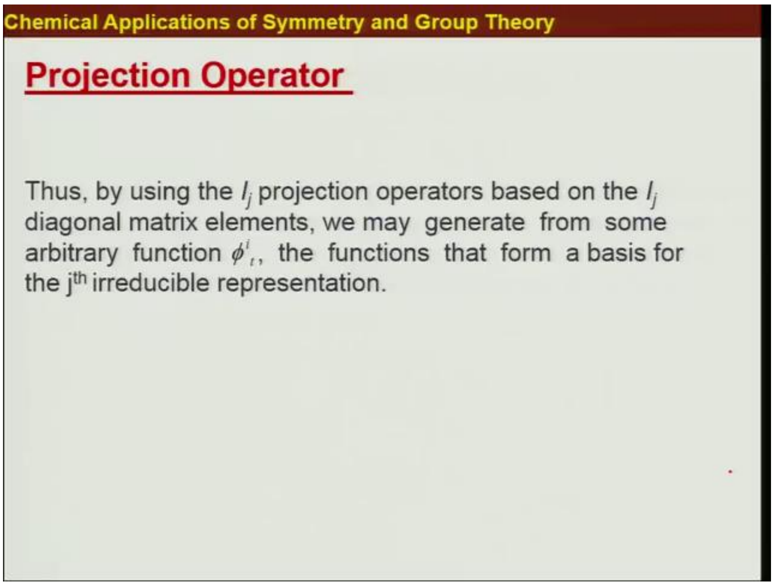

Now if I you know, what we started with li know, of or you know you can call it l j number of orthonomal functions. If you take a set of you know, l j number of orthonomal function, then you can actually produce l j number of projection operator because using that l j number of orthonomal functions, you can form and you know the number of diagonal elements that will be found with also. You know, we can use that particular set of the projection operator to completely find out, you know you can use any general arbitrary function Phi t correspond to any particular ire illusive representation I and the function that form a basis for the jth ire illusive representation which you termed as Phi t prime t.

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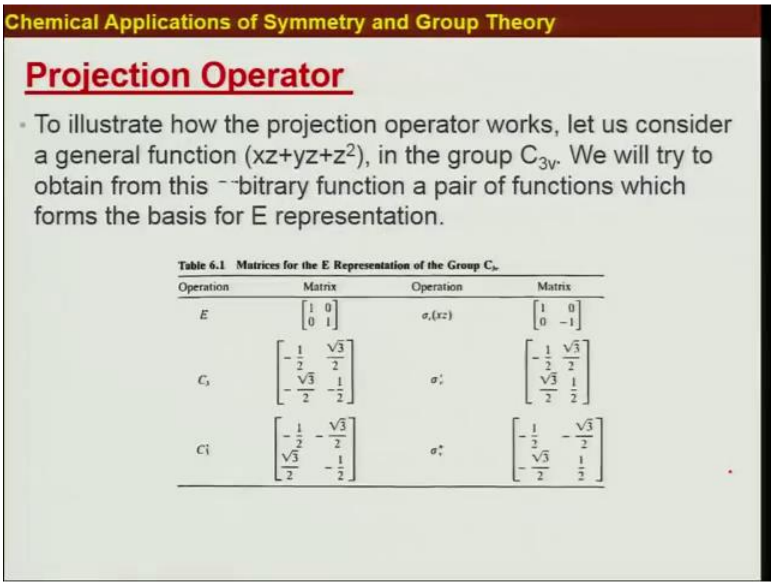

How does the projection operator work actually? Before way into exact formation of symmetry adapted linear combination, let us take simple example and see how the projection operator helps finding out that, which of the of any given arbitrary function, which part of A actually form the basis for any given ire illusive. Here we have an example where we consider the group C 3V and we take an arbitrary function which is as XZ plus YZ plus Z square. This is any arbitrary function, now what we will try to do? You will try to, you know get from this arbitrary function we would like to have a pair of function which will form the basis for the ire illusive representation E, that is 2 dimensional ire illusive representation that C 3V point group as we would like to find 2 functions, you know which would like to take out from this arbitrary function XZ plus YZ plus Z square and that those 2 functions will act as the basis for the representation E.

Here we have all the matrix representation of all the symmetry operation that C 3V point group has this 1, we have already dealt with earlier. So, must be familiar with, you know here talking about complete projection operator like. When I talk about complete projection operator, I will be always dealing with the matrix elements. Matrix elements are specifically as a special case, we will take all those diagonal element with that sort of purpose.

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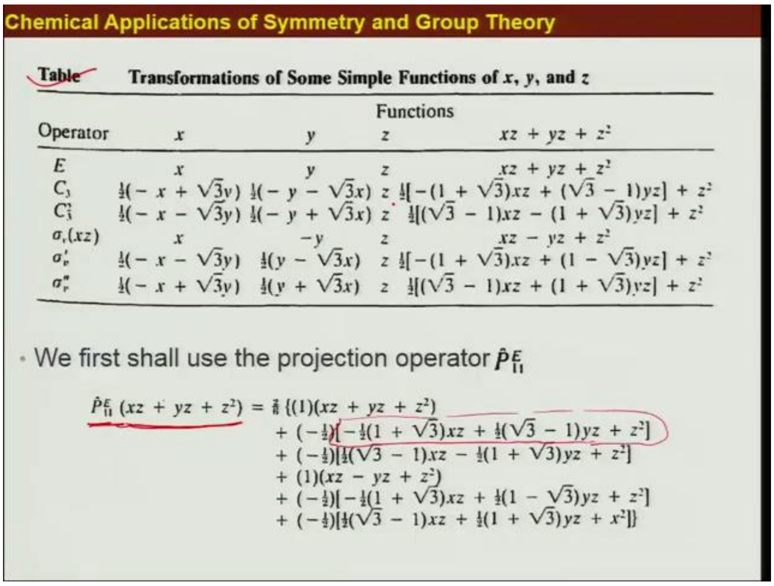

Now, what we have to do? We have to first form the projection operator. Projection operator has the form that you can see on your screen on there. You have to find out dimension of that ire representation. Here for representation, E l j will be equal to 2 H for C 3v, it will be equal to 6 because it has order 6 then you have to get the matrix elements. This is the representation and if essentially we are taking the elements of the representation.

Here we have found on the screen that each and every, you know every symmetry operation has their matrix representation. They are 2 by 2 matrix, correct. Now, you have total, you 2 diagonal elements in that, each and every matrixes. So, what you have to do? You have to select first the 1 element because for any given make fix, which is 2 by 2. You have, say A B C and D. This particular 1 is essentially termed as 1 1 1 2 2 1 and 2 2. That is all in matrixes algebra, we termed this we use the terms. What we have to do? We have to find out this t prime t prime, you know, matrix projection operator form for this P J t prime t prime diagonal element. We will be concerned with this 1 and this 1.

Here is a 2 diagonal matrix and we will be 2 2 dimensional prior ire illusive representation because we are concerned with E. Therefore, we have 2 projection operators because we have 2 diagonal elements. First what we have to do? We have to form the projection operator for this term 1 1 and apply that on the function, that we choose. Here we have like XZ plus YZ plus Z square that is an arbitrary function. We have to operate this projection operator corresponding to this 1 1 element on to the arbitrary function XZ plus YZ plus Z square and then, we have to form the projection operator involving the term 2 2 matrix element 2 2 and again do the same thing. We will get 2 functions out when we operate these projection operators. These 2 projection operators, on this arbitrary function, alright - what we have to do is written here.

First we have dealing with this the P 1 1 term, correct. If you know can correctly identify this, you know this symbol P superscript E and subscript 1 1 and you can correlate with the general form that we have earlier use, the set P J t prime t prime, then you are find if you have any difficulties, go back and again check the previous part that we have talked about and then come back to this portion again. Now, we are going to operate this projection operator on this arbitrary function XZ plus YZ plus Z square and see what it gives out.

In order to do that, what do you have to do? You have to; you know get the form of this projection operator that I just said. li is to H is equal to 6 and then if you look at the form of the projection operator over there, you get the matrix elements corresponding to particular symmetry operation. So, you start with say E then you go for C 3 then you go for C 3 square, then you go for sigma V XZ sigma V prime sigma Beta whole prime that way, alright. You see, how we have done this 1, how did we operate this projection operator on this function? li by H is common for all and then you have selected the matrix element here you see this is for the first term, is for identity operation.

Here we have this term 1, if you quickly go back, you will see that, this 1 1 element of the operation E is 1, alright and then you need to know how this identity operation changes the function. E does not do anything. X remains, XY remains, YZ remains, Z and then overall the function XZ plus YZ plus Z square remain as such, alright. So that therefore, you have, you know multiplication by the matrix element term that is A 1 and then whatever is happening to the function, due to the application of symmetry operation on that function. It returns the same 1, now you move on because you have A some over all R. You have to keep doing each and every R, the symmetry operation and then all together you have to add.

I have just told you about the E. Next step you have to go to the next operation that is say C 3. Here on this table, you have all the transformation property this particular table you have all the transformation properties of XY and Z axis upon this symmetry operations for C 3V. These are the transformation terms and at the end, you have actually the overall transformation of the function XZ plus YZ plus Z square. What you can do? You can verify this table yourself and I will suggest you to do. So here coming back. What do we have to do first? We have to find out a 1 1 element for the C 3V operation. Let us quickly go back to this 1 and C 3, the 1 1 element, this minus half alright and let us look here. We are first multiplying by minus half and then you to be multiplied by you know resultant of the operation of C 3 on to the function XZ plus YZ plus Z square and this particular term that is given here is, it can be found to over here. You can see, that is you know this particular part.

In that way you keep going for C 3 square and sigma V and sigma prime and sigma V double prime. When you complete this sum, you have got your result for the, you know operation projection operator on this arbitrary function and this projection operatory is specifically for the each ire illusive representation which is 2 dimensional ire illusive representation corresponding to the C 3V point group. After you get the, somewhat you will get, you will get you know, some you know terms with containing XZ, some from containing YZ, some containing Z square, ultimately if you can rearrange them properly. You get the co efficient corresponding to XZ, co efficient corresponding to YZ, co efficient corresponding to Z square because these 3 terms, they are in my arbitrary function.

My intension will be to a, you know rearrange the result of this projection operator on this function to also express as co efficient of this 3 functions. You know individually components individually XZ, YZ and Z square.

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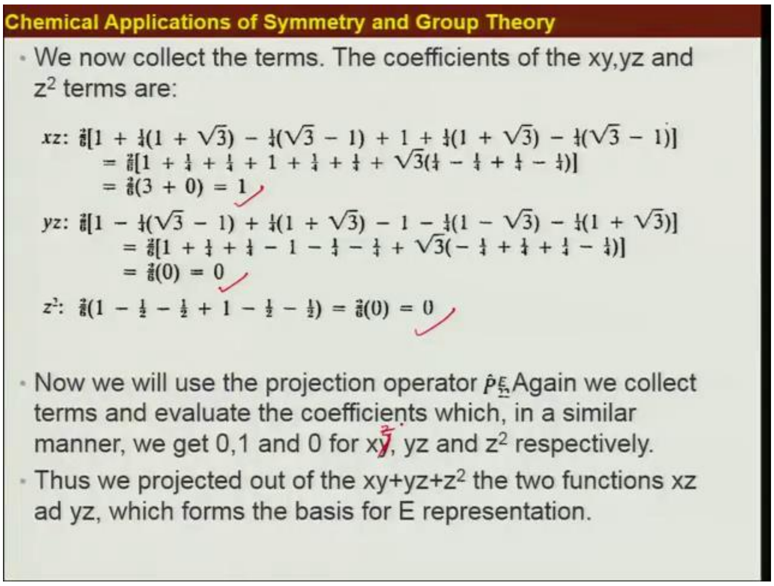

That is what is shown here, when we know, we collect all these terms and separate the co efficient, then I get the co efficient of XZ to be 1 while co efficient of YZ 0 and that of Z square to be 0. My projection operator P 1 1 corresponding to the ire illusive representation E for C 3V is projecting out XZ as the basis for e representation out of the arbitrary function XZ plus YZ plus Z square, alright. We have to get the complete result by using the, you know all the projection operator that can be formed explicitly because we are dealing with the complete projection operator.

The next projection operator will be taking the other diagonal element of this 2 by 2 representation. That will be corresponding to 2 by 2 diagonal element of each and every symmetry operations. If we just quickly look at the representation for E, the 2 by 2 element is also again 1. It will be no different and for C 3V C 3 again, it is minus half for C 3 square minus half and so on. You get those particular elements out and then multiply that with the resultant of the symmetry operation on the particular arbitrary function. Very similar way when we do it and ultimately you collect all the terms and find out the co efficient, we get the co efficient for YZ to be equal to 0 S is equal to N and the rest of the 2, that is X Y and Z square, they give us 0; that means, when we apply P 2 2, it projects out this YZ, you know that can for the basis for the representation E.

Now if we compile the total result, that we have complete set of projection operator meaning P 1 1 and P 2 2 for the representation E all together, it is giving us XZ and YZ.

This means that XZ and YZ out, that arbitrary function XZ plus YZ plus Z square can form the basis for E, which is not surprised right because E is a 2 dimensional representation. We will have two different functions acting as a basis. This 1 will be XZ. You know XZ and YZ will form the basis for representation E and also you see that Z square is completely abolished by this projection operator. So, it will tell you exactly which are the functions that can from the basis of any particular ire illusive representation and whichever is unnecessary, that whichever do not form the you basis for the particular representation. They will be automatically abolished. You will get 0 results when you operate projection operator on the function, for that particular component all the time. Here Z square give you know, 0 contribution in both the cases for P 1 1 as well as P 2 2, alright.

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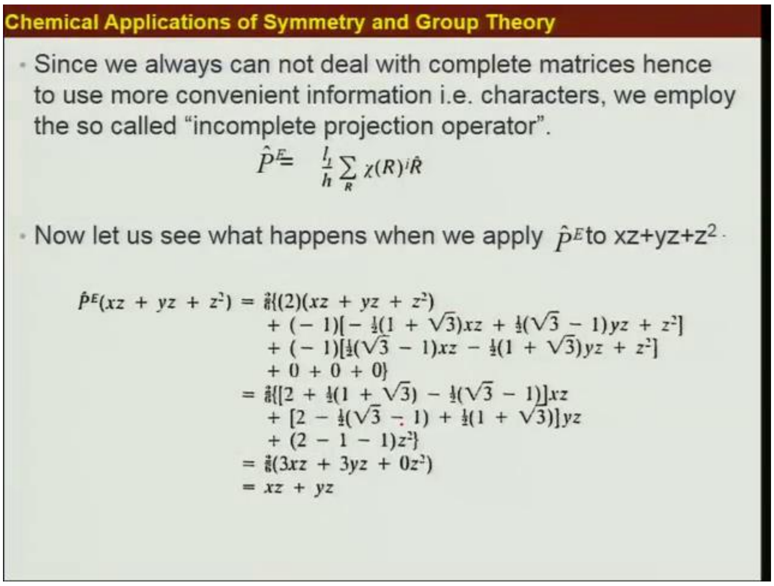

That is about complete projection operator. Now this complete projection operator, it deals with the, you know diagonal element. For a 1 dimensional representation, things are easy because for 1 dimensional representation, the matrix is also 1 dimension. It is kind of trivial, but the moment you go for higher dimensional ire illusive representation, say it 2 dimensional 3 dimensional thing become bit complicated because getting the matrix representation finding the particular, you know elements and then doing it, if this white cumbersome and it cannot be, you know finding this completely set of projection operator. It is not really can be done by a machine alone. It needs so called human intervention alright. You know, it will be a like someone dealing with this problem has to construct the, you know completed to compute the total position of patterns if it on a particular function then again, you know go for the next 1. Every time someone has to instruct it continuously and all together it is really, you know cumbersome, but you know getting the character of the representation is always easy because you have the character table quality.

Just have a look at the character table, you get it and ultimately what you are doing if you think about? You are taking any representation, whatever the dimension be it and you are just taking the diagonal element to form the projection operator and then collecting all the diagonal, you know position operators corresponding to all the diagonal element. You are forming the total set or complete set of projection operator which is known as complete set of projection operator. Now if you look at this 1, if you look at the tries of the representation that actually contains the information that, you know that can be found from each individual diagonal element that we have already talked about and that is why, this tries is also called the character.

It should be pretty fine if we take the character and try to form, you know a projection operator out of that. In some sense it will be incomplete, but it will be extremely useful now. It will be incomplete when you are particularly going for extremely, you know complicate ire illusive representations, but otherwise for actual practical purpose is this incomplete projection operator, which involves the characters, only should work absolutely fine and in the next class we will talk about this incomplete projection operator and we will try to derive this incomplete projection operator and use it and you know, we try to vulgate the points that I just discussed.

We will stop here today, and in our following class we discuss more about this thing. Till then have a good day.