Symmetry and Group Theory
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture - 47
Projection Operators

Now we are going to learn about this very useful tool called projection operator which is going to make our life much simpler than what it is for the rest of the course. What had we discussed the previous day? Symmetry adapted linear combinations, right? What are the problems we discussed? BH 2, CH 4 and that is it right? So in CH 4 what we did is, how did we get the symmetrical linear combinations? First part is easy, right?

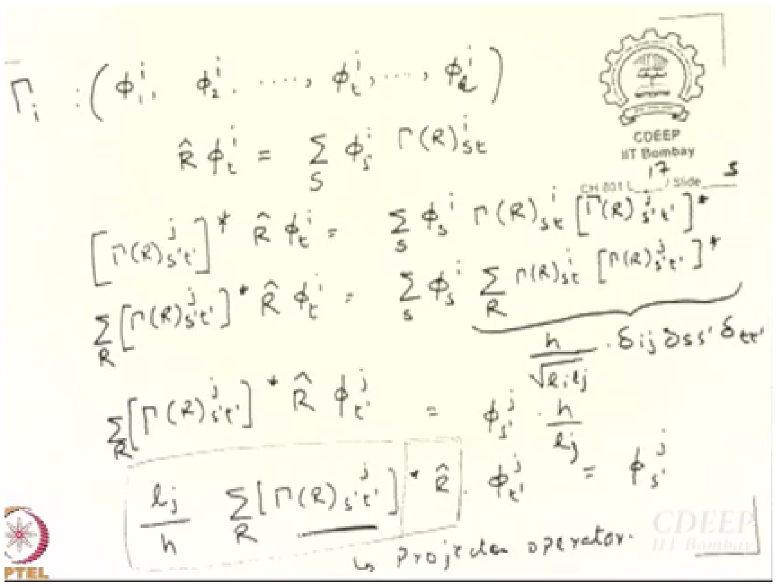
You take the atomic orbitals of the pendant atoms, make a reducible representation, break it down into constituent irreducible representations. That much is fine. But then how did we generate the SALCs? So we did it by inspection, is it not? We did it essentially by inspection, right? Now that is not going to really work when you try to tackle bigger, larger systems. So we need something which will make our life a little easier and that something is as we learn today, projection operator. So we want to eliminate that. What we want really is SALC for dummies.

I will say that this is the formula, use it, we will use it and we will get the result, alright? So but to make anything for dummies, somebody somewhere has to do a lot of behind the screen, beyond the spotlight work. Otherwise you cannot generate things that will be only for dummies, okay? We want to develop a machinery by which one should be able to generate the SALCs without having to worry too much, okay? That is what we will do today.

We will develop what are called the projection operators. What do projection operators do? Projection operators project as the name suggest, right? Projection operators should project. What should it project? As we will see, the projection operator is going to take any function and it is going to project parts of the function that belong to a certain symmetry species and thereby we are going to generate the SALCs, alright?

And to do this again we use the power of great orthogonality theorem. In today's discussion I am going to follow Cotton's book but you might find it more useful to read this from Bishop's book. The treatment that we had done earlier, in Bishop's book if you read, if you take the trouble of reading it actually I think it is easier to understand. In Cotton's book once again it is a little bit of hand-waving is there. But let us go ahead.

(Refer Slide Time: 03:03)



Let us consider a set of functions which belong to an L dimensional irreducible representation, okay? So let us say phi 1, phi 2, phi 3. Let us put a general identifier, phi t etc., phi l alright. And we are saying that they jointly form the basis for some irreducible representation. If it is the ith irreducible representation right we are used to this notation ith irreducible representation so let me just to remember that these functions all form the basis of the ith irreducible representation, let me also put the superscript i on every function.

I hope that is not very difficult, right? So I have l number of functions, phi 1 i, phi 2 i, etc., up to phi l i, which jointly form a basis for the ith irreducible representation of our point group. So far so good, okay? What happens when I perform a symmetry operation on any one of these functions? I take the general one phi t i and make a symmetry operation operate on it. What should you get? Okay when are you going to get plus minus phi t i? When the representation is one-dimensional, right?

Or in some special case where it turns out by some accident that out of the l representations one is by itself, but that is not going to happen. At least not for all the symmetry operation. For one symmetry operation it may be possible, okay. So what would be then the most general expression? It would be a linear combination exactly. And if I may remind you what happened, think of the xy vectors in say C 3v point group.

What happens when C 3 operates on x and y or on x for example. C 3 is your axis, right? This is xy, this is C 3. So I operate C 3, 120 degree rotation. So what does x become? What is R x? X + B is right. What is a, what is b? Since I have told you 120 degrees you should be able to tell me what is A and what is B. And what is cos 120? Minus of x. so x becomes R x right? C 3 x is equal to minus of x then it is root 3 by 2 y. Similarly, you can work out what is C 3 y.

That will also be linear combination root 3 y to x – 1/2 y is it not, right? So you know what the matrix is going to look like okay? So in general it is going to become a linear combination, okay? If you remember our discussion of function space, when you perform the symmetry operation what happens is the length does not change, right? But since the angle changes, the components along the original orthogonal set that defines the space, those components are going to change, right? Initially, y component have x + 0, x component have x is x, x is 1.

Now in the transformed vectors x component, y component both are (()) (06:52) is it not? So let me write a general summation. Will you allow me to write it like this? Sum over S phi S i gamma R S t i. Okay it is a little different from what we are used to seeing. We always write the coefficient first and the function later, right? But it is a linear sum. Suppose x = I mean R x. R x is equal to what do you say, C 3 x. What is C 3 x in C 3v?

Minus 1/2 x + root 3y to y, okay? It will look a little odd but I am perfectly right if I write it is x into 1/2 + y into root 3 y2. Who is stopping from writing it, right? I am perfectly justified if I write the coefficients again and the function first. It is just that we are more used to writing the coefficient first. I am sorry, yes but this is only a row of the matrix. If you take the gamma R S t right, so I have only written a row.

And so next if I can write R hat phi t + 1 i then you will get another one. So on and so forth I can generate the whole matrix. Instead of the whole matrix I am only taking, I am only focusing on phi t i and its transformed avatar, alright? So I am not considering the full matrix and I am perfectly fine in a linear combination if I write the coefficients again. Of course, when we write something in an odd manner, there must be some reason for it.

Here also I have a reason for writing it in an unusual manner and the reason will become clear very soon. Are you okay with this? Are you okay with this, can I go ahead, right? So now, the reason why I have written it on the right hand side is that because I want to eliminate it. That is very clear, okay? How will I eliminate it? It is a matrix element of the transformation matrix. I can multiply it by its complex conjugate, sum over all R and then our great orthogonality theorem will allow me to write a single number in place of that sum.

What is great orthogonality theorem? You take a matrix element of the transformation matrix, multiply it by the complex conjugate of any element of the same transformation matrix or of another transformation matrix is also okay actually, right and sum over all R. Then what you get is 8 h divided by square root of l i l j del i j, del s s dash del t t dash, Kronecker delta, multiplication of 3 Kronecker deltas which tells us thus that these matrix elements behave as a set of orthonormal vectors, remember great orthogonality theorem. We are going to derive great orthogonality theorem at the end of it.

So let us come back to what we are doing now. What I will do is I will multiply this left hand side and right hand side by say gamma of R, s dash t dashed j. Okay what is R, R is a symmetry operation, okay? What is gamma? If I write nothing else, gamma is the irreducible representation. But if I write gamma of R right okay let me write it like this gamma of R with superscript i that is the transformation matrix corresponding to R in the ith irreducible representation.

And then when I write s t as a subscript then it means the sth s t element of that transformation matrix, understood? So R symmetry operation, gamma R, gamma i is the ith reducible representation. Gamma R i is the transformation matrix corresponding to R in the ith irreducible representation. Gamma R i s t is the s t element, remember what it is called, s t element or s t eth element whatever it is. You understand what I mean. The element of the transformation matrix, okay? Now may I proceed?

Now see this s t i these are all general indices is it not? Are they not all general indices? I have not said that s = 5 or s = 2 or anything. They are general indices. They can take different values, all the possible values that are there. How many values of i will be there? Number of classes, very good. That we will learn from great orthogonality theorem is it not? Number of irreducible representations is equal to the number of classes. What about s and t?

What will be the limiting value of s and t, l? Dimensional E t, dimension not order. Dimensional E t of the ith irreducible representation will be the limiting value of S and t, okay. Does s always have to be equal to t? No, it can be anything. You can say 1, 2 element, 3, 5 element whatever. All I am saying is the maximum value of S is l i, maximum value of t is also l i. Only maximum values are defined, okay? So you have understood all s t and i's? Surely, question?

Have you understood what is i, what is s, what is t and what are the limits? It is important to understand that. But now when I just tried gamma R s dash t dash j what I am essentially saying is that s dash t dash j these have some specific value, okay? I am taking one of the all the different possible matrix elements okay and I am multiplying both sides by that. So this is a specific matrix element. So you can write 1, 3 and 5 here for example okay.

These are not general indices, these are specific indices alright. And to make it more fun I am going to put a star on it because this is our star. This is what will help us construct the projection operator, okay? So we should give it due credit and put a star while not forgetting that star means complex conjugate. But most of the time we are not going to use the star as you will see, okay fine. So multiply, what we get on the left hand side?

This multiplied by R hat phi t i is equal to sum over s phi s i gamma R s t i. This is annoying. Gamma of R s dash t dash j star, okay. I have just multiplied both the sides by some element, okay? How will I get Kronecker delta? Ah, first of all you have to sum, do not forget that.

Kronecker delta will not come just like that. Only when you sum over all the symmetry operations will the right hand side start looking like the left hand side of great orthogonality theorem, is it not?

So what we need to is we need to sum over R gamma R s dash t dash j star R phi t i will give you, I hope nobody has an objection if I take this out and I put the summation here. I can do that, right? Gamma R s t i then gamma R s dash t dash j star, okay? See if that is alright or not, alright? What is this equal to? h by square root of l i, l j del ij del ss dash del tt dash and I am myself impressed that I have been able to write 3 deltas that look all different.

All the deltas are different from each other but that is not intentional, okay? So how do I simplify life a little more? You put i = j specific value, put s = s dash specific value, put t = t dash specific value. What does the right hand side become then, this part? h by l i, l j square root of l j l j. So it is h by l j okay? Left hand side becomes sum over r gamma of R s dashed t dashed j star R hat. Now see, in whatever I have written so far nothing has changed, is it not?

By putting this Kronecker delta nothing has changed in whatever I have written so far. Did you notice that? Now the change will come. Here it is already in terms of some specific s dash, some specific t dash. So up to R hat nothing has changed. Also, what is this? This whole thing is like an operator is it not? R is a symmetry operation and you are multiplying it by some matrix element and this is having it over all R. So this whole thing is like an operator.

So this is the mother of projection operator. Projection operator is going to come from here, okay. What should I write here? Phi t dash j okay is equal to this becomes then phi s dash j h by l i or l j right. This is the mistake that I always make and then later I get kind of confused. Phi s dash j h by l j right? What I am going to do, summation, there was sum over s. Sum over R is gone anyway right?

Sum over R product of the matrix elements has been replaced by your h by root over l i, l j del ij del ss dash del tt dashed. That summation over R is gone and then what I have done is output s =

s dash = t dashed i = j. So out of this summation, the only term that survives is when s = s dash. That is why I have written phi s dash j. Suchev is your question answered? What is the question?

Left hand side because I want to make this Kronecker delta is equal to 1. So when will this delta tt dash become equal to 1? When I put t = t dashed, that is what I have done; t dash is a specific value, t is a general value, okay. Just let me finish this up. So what we have on the left hand side? If I write l j/h sum over R gamma R s dash t dashed j okay star of that R hat operating on phi t dash j = phi s dashed j. What has happened, what just happened?

I have taken this operator. I will use a pencil. I have taken this operator here, made it operate. This is also within the operator, sorry. I have taken this operator, made this operate on a wave function and this is why we have to substitute i = j, a wave function which is a basis for the jth representation and I have generated another wave function which is also the basis of the same representation. I want to work within the same representation that is why.

Understand what has happened? You take some function, see this operation that I have written. This operation is a property of what? What? What do you mean, why, what does this have to do with linear independence? Yes, so what I am doing is I am operating this on some arbitrary wave function and I am projecting the, okay I understand. This can be a linear combination also. You take an orthonormal basis function and you take linear combination of the basis elements that also forms a basis, right?

So let us say we are working with a linear combination and we are going to do that. So if this is a linear combination you can project out the component. If this is a component then you can actually construct the linear combination. Let us wait until we come to the example. But this is the operator, alright, fine. Tell me whose property is this? S dash t dash right? So it relates these two. So this thing is called the projection operator.

In fact, it is called the complete projection operator and we are not going to use it. Let me write it once again. And let me tell you something. We do not really care about the l i h as well. Even though in the definition everywhere l i h is written we do not really care about the l i h. That is only a number as we will see that number is irrelevant because in any case whatever SALC we generate we are going to use the, we have to normalize it. So number does not matter. So I would not even write the number even though that is going to be at variance with what is written in all the textbooks.