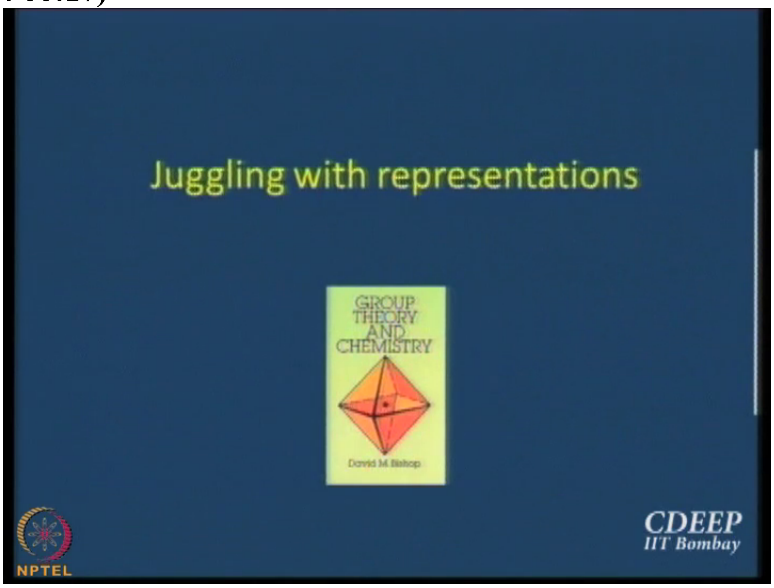
Symmetry and Group Theory

Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology-Bombay

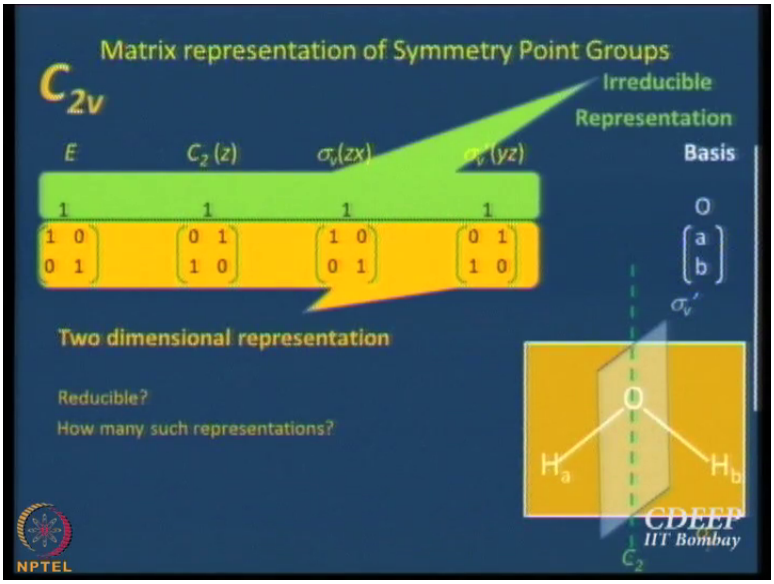
Lecture No. 23
Equivalent Representations

(Refer Slide Time: 00:17)



Alright let us get along with today's proceedings, now we have been talking about functional spaces and all in doing so you are not forgotten what the representation actually are. Today what do what we want to do is remind ourselves what representations are and then go back to the abstract treatment that we have started. Now this is the slide that we have been referring to again and again right. We have constructed the transformation matrices of C2v using Oxygen and two hydrogen atoms as the basis.

(Refer Slide Time: 00:57)



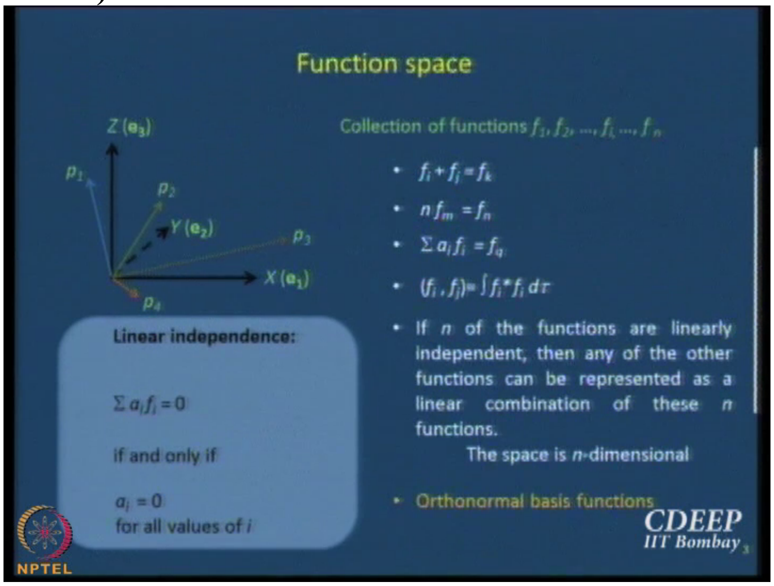
And we got 3 by 3 matrices 1 for each operation and then you saw that we can block factorised these matrices and we get the 1 by 1 block which is 1111 and that is associated with oxygen atom and we got 2 by 2 blocks for this 2 hydrogen atoms right. This was I think our first exposure towards representation. What is the representation then? 1111 is the representation 1001 0110 1001 0110 this is another representation. What is the representation? Can we say it very simply like this there is a collection of matrices matrix representation right?

Can I say it very simply like this that it is a collection all the transformation matrices corresponding to a particular base. Does it make sense? 1001 0110 1001 0110 these are 4 matrices, what is the base for this matrices that 2 hydrogen atom this 4 Matrix makeup a 2 dimensional representation right. The representation is essentially is a collection of matrices; what kind of matrices? Transformation matrices when I say collection it is a complete collection. Collection of all the transformation matrices for a particular basis is called a representation does that make sense right that is a representation fine.

And we ask this question how many reducible representations are there, how do I know whether representation is reducible or not. How many reducible representations are there? Number of reducible representation is of course infinite. So, these are the question that we started with and then what we did was there is no easy way of getting the answers for this. So, we have started developing this kind of abstract general treatment using the concept of function space.

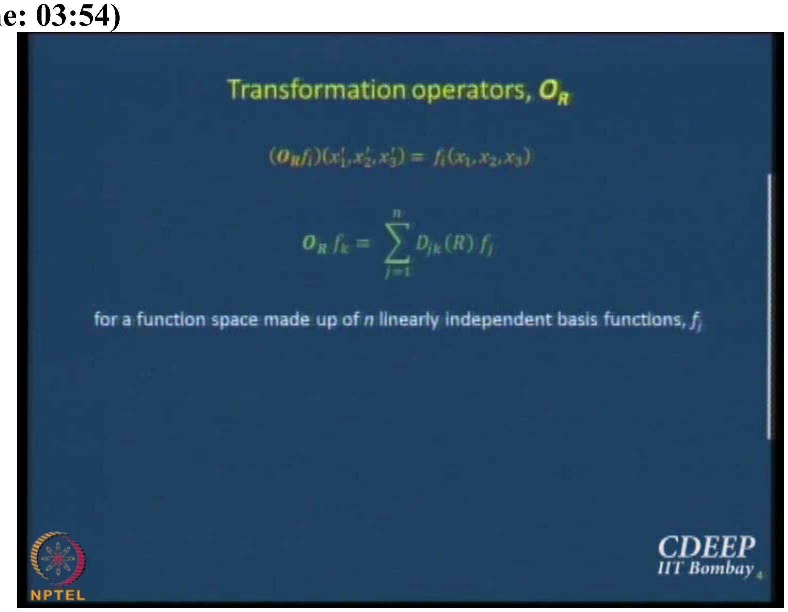
Functions will satisfy all this criteria right and we are specially interested in orthonormal basis function. We are interested also in these functions that span a particular space.

(Refer Slide Time: 03:26)



These are to be linearly independent. It is necessary that all linearly independent functions are also orthonormal? No, if they are orthonormal then there are some added advantages but there is no hard fast rules that if set of functions is linearly independent then they have to be orthonormal. If they are orthonormal are they always linearly independent? Yes right but the converse is not true, very good.

(Refer Slide Time: 03:54)

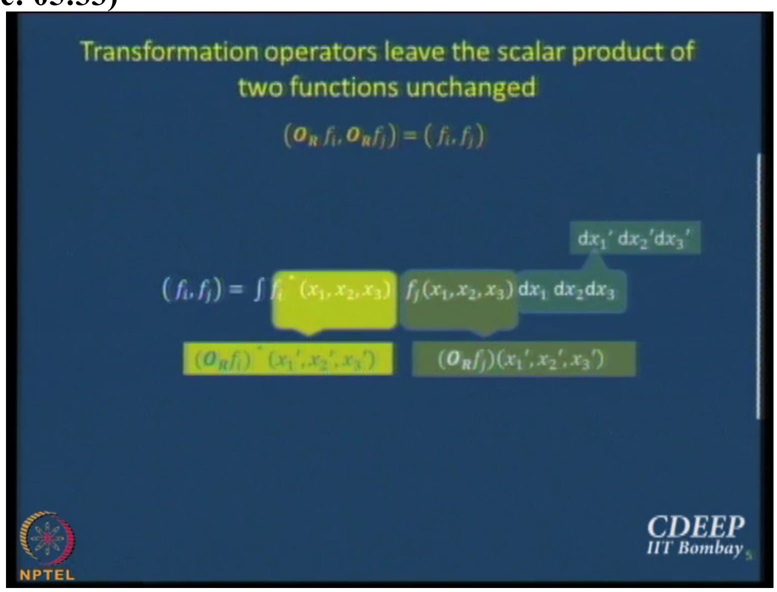


Then we have introduced these transformation operators right this is something we need to remember very well what you said is that using the transformation operator we essentially written that the transformed function in the transformed co-ordinate as the same value as the original function in the original coordinates. This is something that we have discussed at length. And we also realised that I can write this ORfk where fk is the kth function of the f set.

ORfk transform function fk = sum over j from 1 to n Djk of R fj right all of you ok with this. When I am summing over j, am I summing over the column or the rows. I am going down the column or across the column? I am going down the column right. How this is justified? Because how do you get D do not forget this. How do you get DR? I get the DR matrices by transformation of the coordinates. Now I am talking about transformation of functions. What is clockwise for the one is anticlockwise for the other.

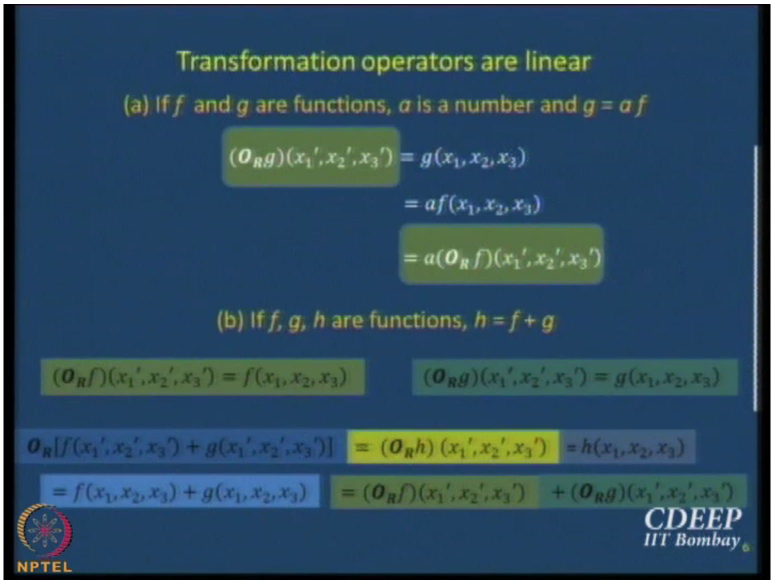
That is why the rows and the column get interchanged when I talk about the functions ok. Please do not get confused the think that we are making wrong multiplication. Actually I was confused that there is like that last week but then is falling in place fine.

(Refer Slide Time: 05:33)



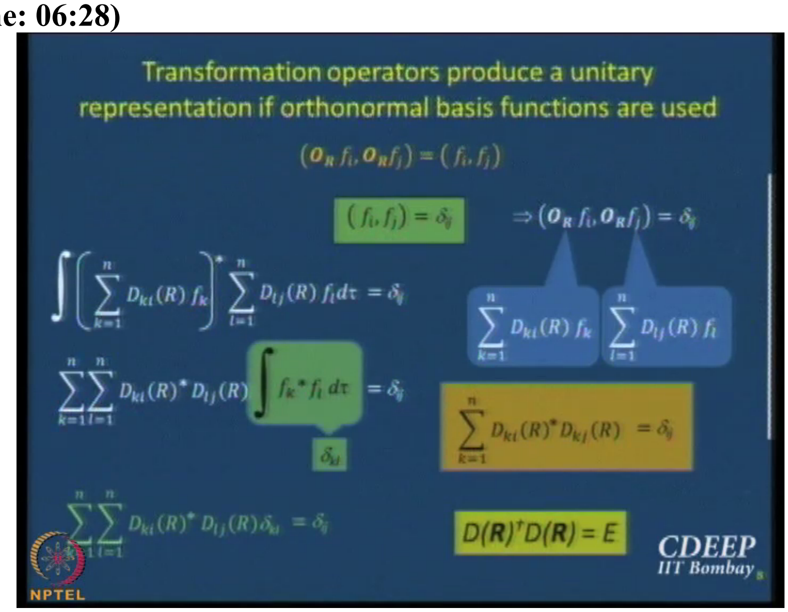
These are things that we have learnt already properties of transformation operators. First of all these transformation operators leave this scalar product of the two functions unchanged and we saw how. Scalar product of two functions remained unchanged upon transformation.

(Refer Slide Time: 05:53)



This is how we are going to use today. It is important to understand that the transformation operators are linear. What is the meaning of transformation operators are linear? It means if g= af where g and f are functions and is a constant then OR of g that is OR operating on af = a multiplied by OR of f right ORg = kORf we are going to use this today.

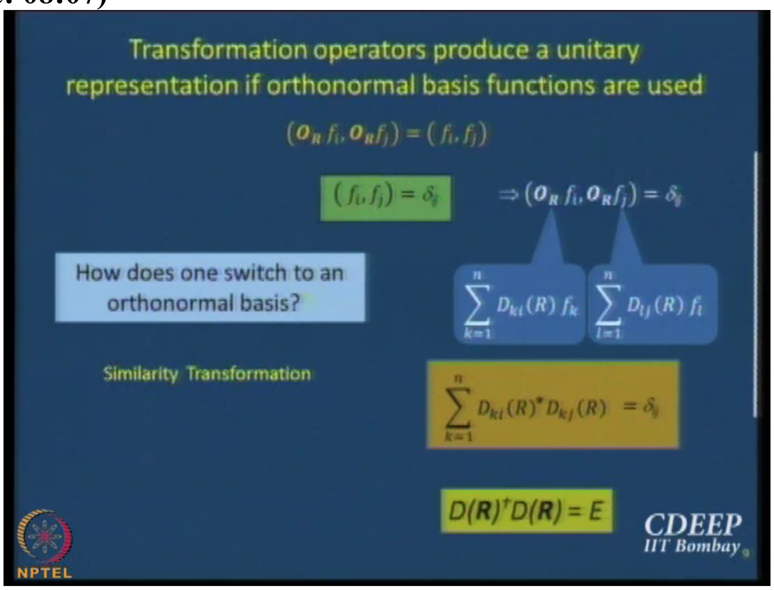
(Refer Slide Time: 06:28)



And this is where we have stopped last day. He said that the transformation operators that we produce a unitary representation if orthonormal basis functions are used. Right now it might seem that we are taking a random walk in some strange function space actually we are not. All these are going to be required when we finally put our story together this is very important property of transformation operators. Transformation operators produce a unitary representation if orthonormal basis functions are used.

What is the meaning of unitary Representation A dagger A= E unitary matrix, that is a property of what? Unitary matrices I am asking what is the unitary representation? Representation in which all matrix are unitary, please do not get scared by terminology ok. Unitary representation is one in which all the mattresses or unitary and you already know what is the definition of unitary mattresses A dagger = A or A inverse? A inverse, if it is A dagger = A, what is it? Hermitian and when it is orthogonal then A transpose = A or A inverse? A inverse ok please do not forget this definitions.

(Refer Slide Time: 08:07)

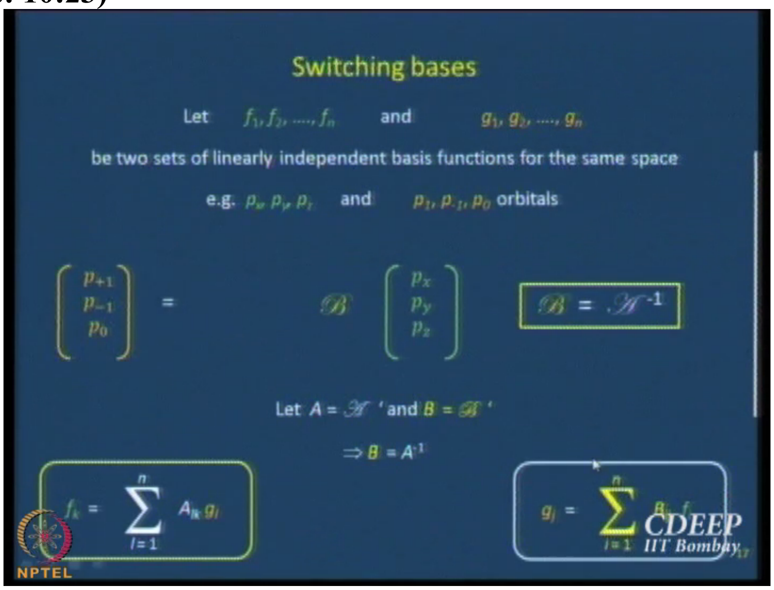


Now the point is this we are saying that transformation operators produce unit representation if orthonormal basis functions are used right. But who has said all the bases that you work with are orthonormal, this not necessary you can work with other bases right. The question is whether it is possible to switch from some given basis to orthonormal basis. Why do you want to make the switch because if we can do that, then you are a representation will become a unitary representation. Why in all instance you say unitary representation because life becomes simple when the inverse of the matrix simply its adjoint.

Life becomes simpler when the inverse of the matrix is simply its transpose right. But maybe that is asking for too much right we cannot expect that all R matrix are real all the time. So, it is better to talk about unitary representations. If the orthogonal representation well and good we have to work little less fine. Now how do I switch to a orthonormal basis as you see we do this switch by using similarity transformation. There are other methods. If you read a book on matrix algebra to read these appendixes of Bishop's book then you can see something called Schmitt Orthogonal method.

That is too much math there is no chemistry so we are not going to talk about it. Similarity transformation that is very useful to us and we now start seeing why? But the similarity transformation can do is that it can perform switch of basis back with one basis you can go to another. In next 2 minutes we are going to learn how? Please remember this; what the similarity transformation essentially does is that it switches from one basis to another. One set of functions to another. So let us see how.

(Refer Slide Time: 10:23)



If we have to switch then you need to set of functions right. Let us say we have two sets of functions f1 f2 f3 so on and so forth up to fn and g1 g2 g3 etcetera up to gn right. These are linear two sets of linearly independent basis functions for the same space, make sense. Can you think of such sets, can you think of two such sets ok? Start like this xyz linearly independent of course I can say that as a human I can say right and left and for the same north. So let us say another co-ordinate system like this right.

Those 3 vectors are actually linearly independent and they span the same space right this side as well as this side both are going to span same Cartesian real space right. I can say this are f1 f2 f3 and these are g1 g2 g3 right nobody has said, you are saying that this is x that is y but who has said that you should not turn it around. It all depends on which reference you use ok. These two kinds of xyz, x dash y dash z dash kind of basis functions can be used right. Let me you something it will be little more tangible to all chemist.

Let me use P orbitals. Can you think of two different sets of linearly independent basis function what P orbitals? I think we have discussed briefly earlier. What are the 3P orbital's you know? px py pz right, so that is one set say f1 f2 f3 px py pz. Is there any other way in which I can write that P orbital's P + 1 P-1 P0 that is right. Will you agree that they span the same space? Actually we are talking about P orbital's right. No matter whether we denote them as + 1 or-1 0 or xyz they span the same space.

Are there linearly independent? Yes, if you have Px Py can you evaluate Pz you cannot they are linearly independent to satisfy these conditions to be f and g sets. How will you draw the co-ordinate axes is that imaginary, P0 is the only real orbital in the second set, P0 is a real orbital and non zero there is no issue. But P+ and P-cannot even draw them in the real space know. The space that we are talking about here it is not Cartesian space. It is the space of P orbital's it is not free of space, understand. So space is not something it should be taken on face value.

By space we just me the collection, remember what is function space? It is a collection of vectors, collection of functions ok that is what I mean fine. So now can you express Px as; let me do the difficult one first. Can you express Pz as linear sum of P + P-and P0? Yes, 0Px + 0Py + Pz 001. What about Px and Py? I want to write an equation like this ok. And if I believe what Atkinson has to say if it is workout in the page 337 the Atkinson's book this edition that this is a matrix PX = 1 by root 2 P + 1, -1 by root 2 P-1, Py = i by root 2.

Then, yes that is it right. This is workout in Atkinson's please go through it, the matrix that Bishop as written is different; I do not know why I believe Atkins because he worked out very nicely. You can go through the working out. So this is the matrix that we have let me call it curly A. I have a non curly A also. That is why I have to force to call it curly A. This is where I got confused reading bishops book because Bishop conveniently jump a step.

That is why lot of people asking what the hell is going on. Let us call it curly A, I can also write it in other way. I can write P+ P- P0 as the linear sum of Px Py Pz, I think I will get other matrix. So I can write it like this P+1 P-1 P0 = curly B multiplied by Px Py Pz and without going through a formal derivation will you believe me if you say b is a inverse. It is quite easily done right B = A inverse it is not very difficult to see that. Now comes the trick I do not want to work with curly A and curly B.

I want to work with normal A and normal B and this is how I define them. Let A be A transpose and B be; let me say it again. Let A be curly A transpose and B be curly B transpose, too many B's. Let us say A is transpose of curly A and B is transpose of curly B that sounds better alright. Why am I taking the transpose because if I take the transpose later on life become little simpler there is no other reason. This is the step that Bishop has jumped and he has only written please note the subscript and gone ahead.

Please note what? What am I supposed to know not very clear this is what you are supposed to know. But this later, that is what you are saying B = A inverse ok I think nobody has problem with that. Transpose of inverse and inverse of transpose then work it out quite easily B = A inverse. Now if I want to write it in the in terms of the matrix element what will I write? Basically I call this f, I called this f and I call this g ok. Will you allow me to write it like this fk = sum over l = 1to n. What is A here? It is just the extension of the matrix that we using.

Here for the example we have taken P orbital's where n = 3. Now if you extend the same type of discussion to n dimensional space right n dimensional basis. Then I can write it like this f is one kind of function and g is other kind of function, but f as to be written as linear sum of the g's. Since I am using the transpose here fk the kth function = sum over l = 1 to n Alk gl, when I say some over l to n Alk I am I going down or I am a across. I am going down right this is what my confusion it is ok.

Actually I am going across curly A instead of writing that I will taken the transpose of curly A of course the rows becomes the column that is why it is written in this manner is that ok. Any case now you have become expert in multiplication by columns by column. Even the definition of OR is like that is it not. Please do not get confused here the reason why I write sum over l A lkgl is that I am working not with actual transformation matrices but their transposes.

Why am I working with transposes because believe me you see that life becomes simpler little later you work with A and B in set of curly A and curly B. Until now this is ok fk = sum over l to n Alk gl is that correct. Then I can write g in the same manner, I am sorry, if it is a diagonal matrix then what will I get. What will be the results be? When it becomes f1 = something into g1, f2 equal to something into g2 so on and so forth. Similarly I can write gj my notation here is little different what is used Bishop because I want to have one consistent notation.

So I change this i's j's and k's little bit not much. Similarly gj = sum over i = 1 to n Bij fi, what is gj? The jth element the jth g function let us put it that way. What is fi? It is the ith f function. What is Bij? Bij is the coefficient of the ith f function in the jth g function usually it is other way around. Why it is other way around because you are working not with the actual matrices but there transposes. So now we have got these expressions what are you trying to do you are trying to learn how we can switch basis alright.