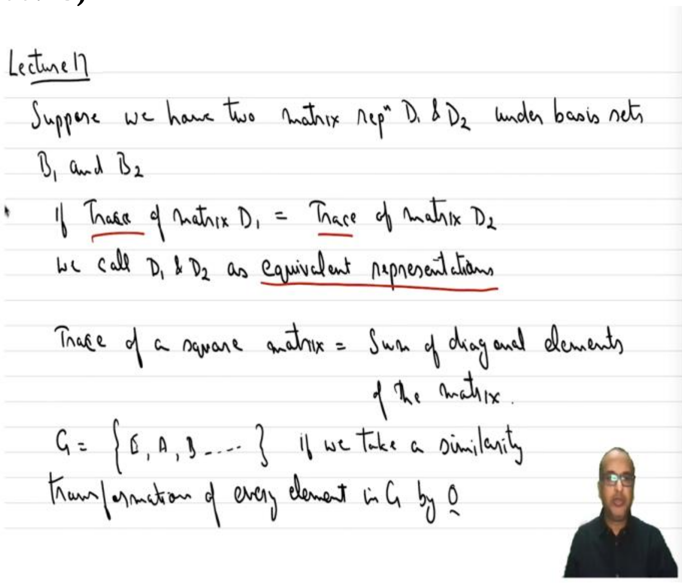
Symmetry and Group theory

Dr. Jeetender Chugh,
Department of Chemistry and Biology,
Indian Institute of Science Education and Research, Pune

Lecture – 21
Unit Vector Transformation

(Refer Slide Time: 00:15)



In the last lecture, we have seen how to write matrix representations for a point group and we also saw that the number of ways of writing a matrix representation for a particular point group is limited by our imagination of having a particular basis set. So, if you can choose a large number of basis sets, you can have a large number of matrix representations. Now, let us consider 2 such matrix representations under basis sets, let us say B1 and B2.

So, let us consider suppose, suppose B1, B2 are basis sets of same order that is the number of vectors which are chosen in the basis are same. So, the dimensionality of the matrix for D1 and D2 will also be same. Also if trace of the matrix D1 is equal to trace of the matrix D2, we call the representations of D1 and D2 as equivalent. Now, this is very very important here. So, because we are saying that the trace of the matrix D1 is equal to trace of the matrix D2. So, in such cases we call the representations as equivalent.

So, what is trace? By the way, so, those who do not know what is trace, so, trace of a square matrix is equal to sum of diagonal elements of the matrix. So, now, let us say that we take a similarity transformation. So, let us consider a group first G, where group elements are E, A, B and so on. Now, if we consider if we take have every element under G by some other matrix called Q.

(Refer Slide Time: 03:21)

$Q^{-1} A Q = A'$ This new set of matrices is also a

$Q^{-1} B Q = B'$ representation of the group G.

$\vdots \qquad \vdots$

Let us calculate the product $A'B'$

$$A'B' = (Q^{-1} A Q)(Q^{-1} B Q)$$

$$= Q^{-1} A \underline{Q Q^{-1}} B Q$$

$$= Q^{-1} A B Q$$

if $AB = D$

$$A'B' = Q^{-1} D Q = D'$$

So, in that case we can write Q inverse A Q will be equal to let us call it as A prime. Similarly, Q inverse B Q let us call it as B prime and so on. So, now, what we are trying to see is that this new set of matrices is also a representation of the group. So, how do we show that. Let us calculate the product AB or A prime B prime. So, we will see Q inverse A Q, Q inverse B Q and we can write this as Q inverse A Q Q inverse B Q.

Now this term goes to E. So, we can remove this then we will have Q inverse A B Q, and let us say if AB = D. Now, we can say A prime B prime = Q inverse D Q and now this can be called as D prime. Thus we can show that if a B and so on D are representations of a group, then upon similarity transformation, we obtain an alternate matrix representation, which also is a matrix representation for the group G. So, that is easy to see.

(Refer Slide Time: 05:36)

→ Similarity transformation does not change the trace of a matrix

If $A' = Q^{-1} A Q$ then $Tr(A) = Tr(A')$

Trace $(AB) = Tr(BA)$ even if AB do not commute with each other.

$$AB = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & & & \\ \vdots & & & \\ a_{n1} & & & \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & \cdots & b_{1n} \\ b_{21} & & & \\ \vdots & & & \\ b_{n1} & & & \end{bmatrix}$$

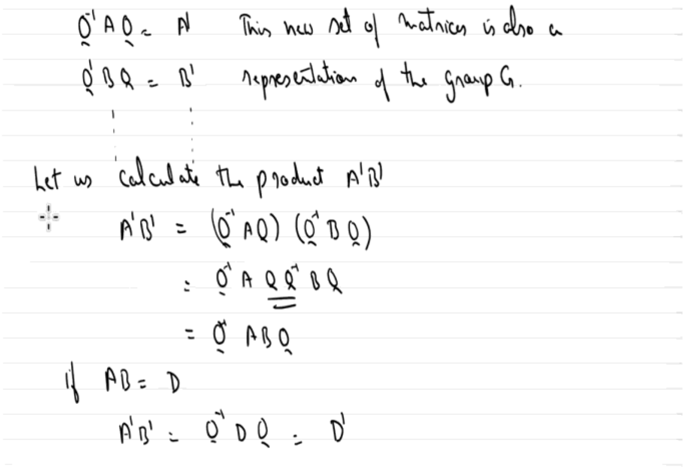
$$AB = \begin{bmatrix} a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31} + \cdots a_{1n}b_{n1} \\ \vdots \\ a_{n1}b_{11} + a_{n2}b_{21} + a_{n3}b_{31} + \cdots a_{nn}b_{n1} \end{bmatrix}$$

Now, let us move ahead and try to show that similarity transformation does not change the trace. So, what we are trying to show is similarity transformation does not change the trace of a matrix. So, this is what we want to prove. So, that means, what we want to prove is that if A prime = Q inverse A Q then this is I am just writing the same statement mathematically then trace of A should be equal to trace of A prime.

So, to prove this first we will have to prove that let us start with proving trace of A B = trace of BA, and that is true even if A and B do not commute with each other. See, these are matrices and it is not necessary that the product A B will be equal to product BA. So, even if the product is not equal, the trace would still be equal. That is what we are going to prove first to be able to prove the above statement.

So, let us start writing the matrix product in any general form. So, we can write this as two different matrices. So, we can say that this is a11 this is a21 and so on an1, this will be a12 and we can say that this will be a1n. Similarly, we can write this as b11, b12, b1n. So, I am just writing a general matrix ab, b21, bn1. Now, to write the product of this I can write it as a11, so, I will take this row and this column and multiply the corresponding elements to write the first column or first row. So, a11b 11 + a12b21 + a13b31 this you are all are very well aware of and the last one will be a1nbn1, this is my first element of first column first row. So, similarly, I can say that, I can write the last element in this as an1b11 + an2b21 + an3b31 + annbn1, and similarly here if I go I can write the other elements. So, this will be the general product.

(Refer Slide Time: 09:45)

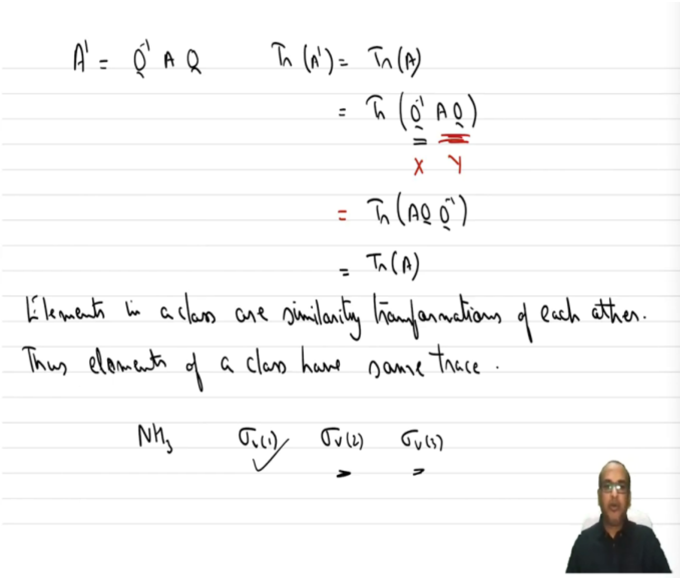


So, let us say if I want to write this product in short notation, So, I can write it as ij and I can say that any element of this product matrix can be written as ai1b1j + ai2b2j + ainbnj. This is easy to see. So, we can also say that this can be written as aikbkj where k goes from 1 to n. We can write it as a summation. This is a general element ABij, because we are interested in determining the trace, so, and for the trace we need to have the diagonal elements.

So, how to write the diagonal element, diagonal element will be where indices i and j will be same. So, basically we can write ABii which will be equal to summation k goes from 1 to n, aik and bki think this will be my diagonal element. Trace of AB is equal to summation of diagonal elements where i goes from 1 to n. So, I can say summation i of summation k aikbki, double summation of a ik and b ki.

So, because these 2 are numbers so, I can always aik and bki are numbers individual numbers of the matrix, remember that these are the matrix elements these are not matrices anymore, so, I can always exchange these terms. So, this will be AB. So, I can also invert the summation and I can write it as bki and aik. Now, this because the summation of i is also from 1 to n and k is also from 1 to n, so, I can easily write this as trace of BA. So, irrespective of whether we are given that A and B are commuting or not, we have shown that trace of AB is equal to trace of BA. That is a very important result.

(Refer Slide Time: 12:50)



So, now, let us try to prove the thing which we wanted to, to start with, that similarity transformation does not change the trace. So, trace of A prime is equal to trace of A. Now, this is very straightforward. So, trace of A prime will be equal to trace of Q inverse A Q and now treat this as maybe a matrix. Let us say X and this as this complete product as Y. So, I can always write it as trace of AQ into Q inverse, we have just now seen that trace of AB is equal to trace of BA.

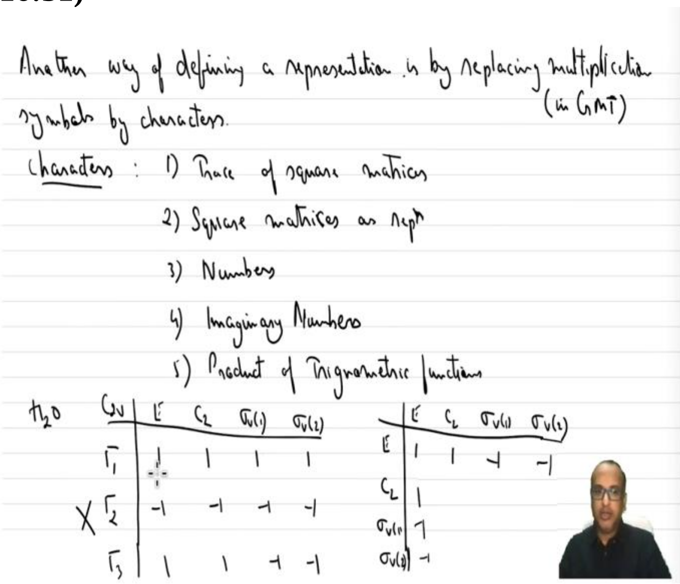
So, we can say trace of XY is equal to trace of YX. Now, this implies that Q Q inverse will be equal to E, so, this will be trace of A. So, we are very easily shown that trace of A inverse is equal to trace of A. Now, why is that important, because we have shown that similarity transformation does not change the trace and we know that elements which belong to same class are similarity transformations of each other.

So, let me write it down. So thus if we have determined the matrix representation of one of the class elements, we do not need to determine the matrix representation for rest of the class elements because the trace of the two elements will be equal. So, if we want to work with only trace and we will see later that we do not need to actually work with the complete matrix, we can work with trace itself to look at the various properties of those symmetry operations or group elements.

So, then in that case, we can actually save time and write just the matrix representation for one of the class elements and take the trace as to be same. So, for example, in case of NH3 molecule, we saw that writing for sigma-V1 was very trivial whereas writing because N-H1 bond vector was lying along YZ plane, whereas, writing for sigma-V2 was not asked we will and we had to actually carry out the axes transformation to be able to write the matrix representation for sigma-V2 if you follow our previous lectures.

So, now, in this case, because these sigma-V1, sigma-V2 and sigma-V3 all belong to same class, and if we have written the matrix presentation for sigma-V1, we can just take the trace of this and that trace will be equal to trace of matrix for sigma-V2 and sigma-V3. So, we do not need to write matrix representation to find the trace here. So, we can just take the trace and put it equal to trace of matrix for this. So, that makes our calculations very easy, this is just another way to work around.

(Refer Slide Time: 16:31)



So, now, we have seen how to write matrix representations and what are different ways of writing matrix representations and now, let us move ahead and see what are different ways of writing characters or traces. So, we have defined here, so, here we have defined trace of a square matrix as some of the diagonal elements. This is also called as character. So, character or trace. So, I will be intermittently using the term either trace or character, both of them means the same thing.

So, another way of defining a representation is by replacing multiplication symbols in GMT by characters, so, what do I mean by characters? So, characters can take any form. So, let us define the characters, what are the different types of characters? We have seen that trace of square matrices can be characters. So, let us see trace of square matrices, we can also write square matrices as representation, right.

Well, we can also write numbers given that they follow the rules of GMT, then these numbers can also be imaginary or real, these can also be product of trigonometric functions. So, why are we discussing this? Let us see that, let us again take the example of water. So, under C2v point group, we had E, C2, sigma-V1, sigma-V2. Now, let us say that one of the representation we have seen that using x, y, z basis, we got 3 cross 3 matrix and we wrote that matrix as the representation.

Now, I am saying that I can choose numbers also as long as those numbers follow the rules of GMT. So, what do I mean by follow the rules of GMT? Let us say I define E as character 1, C2 as character 1, sigma-V1 as character 1, sigma-V2 as character 1. Now if I write GMT using those characters, that is, if I write E, C2, sigma-V1, sigma-V2. Now here also I will have to write the same thing. So, now if I am writing 1,1,1,1, 1,1,1,1 all the products will be 11. Now, we see that C2 into C2 is given by 1 and the character under C2 was 1.

So, and we know that character under E was 1 we know that C2 into C2 is E and E is given by 1. So, it does follow the rules of GMT. Similarly, here if we see that sigma-V1 into C2, whatever product it should give, it is giving us 1 and then we are getting it sigma-V2, 1 under sigma-V2. So, basically all the products are following the characters which are defined by E, C2, sigma-V1, sigma-V2. So, let us take this is let us call this as one representation, let us call this another representation as let us say that now, I am choosing -1, -1 for all.

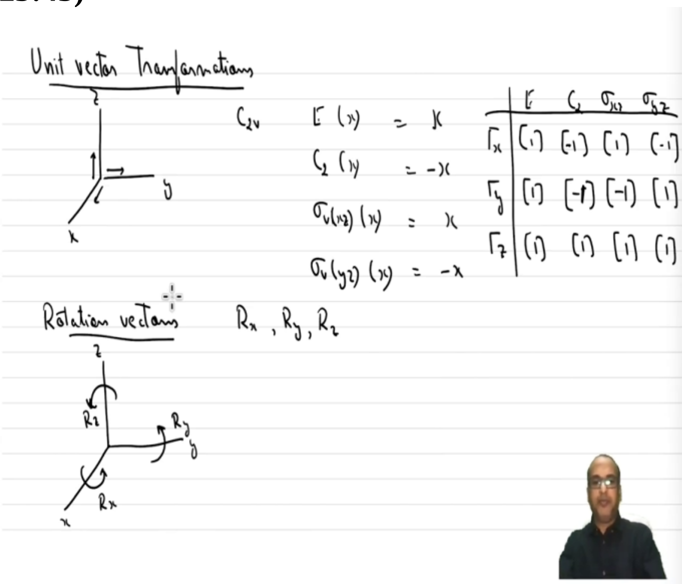
So, in that case I will have, so, what do I have, so, -1 into -1, I should get +1 thing. So, let me just rub this off and write the products again using -1 as the character for all 4. Now, if I do E into E that means, I should get E here, but if I do -1 into -1 what I get here is a +1 what I get is +1. So, that means, now, it is not following the GMT table. So, the products are not giving me the correct representations if I choose -1 as the character for all 4.

So, that means, this does not form a representation under this C2v point group. So, let us write more types, let us see, if I have 1, 1, -1, -1, let us take 2 of them as negatives and 2 of them as positives. So, we will see what is the meaning of all of this later, but let us say this is one way of writing representation. So, let us say now, if we do E into E, E into E will be 1 into 1 which will be 1, C2 into E will be 1 into C2, which will be 1 sigma-V1 is -1 sigma-V1 into E will be -1, so, as follows.

Similarly, here this will also follow. So, now, if you see if you calculate rest of the products also, you will see that it will follow all the products nicely using this. So, similarly, we can define other representations, where these numbers or these characters are defined by any of these can be either trace of the square matrices or square matrices itself or the numbers like we have seen they can be imaginary numbers also.

And they can also be product of various trigonometric functions like we can have cos theta, sine theta and so on so forth. So, this is another way of defining how to write representation. So, let us now quickly see if we can move to unit vector transformations.

(Refer Slide Time: 23:43)



So, why are we, why do we want to write, what is the unit vector transformation. Unit vector transformations are the unit vectors along coordinate systems. So, if we have x, y, z as coordinate system, this is my unit vector along x. This is my unit vector along y this is my unit vector along z and now we can write transformation matrix representations for different point groups.

When we choose basis as individual unit vectors instead of taking x, y, z completely as the basis set. Now, we can take unit vectors as the basis set, and write down our representation for example, under let us again write C2v point group. So, if I want to write the matrix under, let us say x as my basis, C2 also x, so I am transforming using sigma-V1 or sigma-Vxz for x sigma-yz for x?

So, what do I get here I get x here x will be replaced with -x this will be x and this will be -x. So, sigma-xz on operating on x will give you x back sigma-yz operating on x will give you -x. So, if I now want to write the matrices the matrix corresponding matrices will be let us call this representation as tau-x. So, this will be 1, -1, 1, -1. Now, similarly, if we want to write for tau-y, E operating on y will give you y.

So, the matrix will be 1, C2 operating on y will give you -1. So, matrix will be -1 sigma-xz that will give you -y and sigma-yz will give you + y, symmetric should be formed. Tau-z will give you, what does it give you, E operating on z will give you z back, C2z operating on z will give you a z back, sigma-xz on z will give you z, sigma-yz on z will give you z. So, basically we will get square matrices of order 1 and we can see that these characters are the same characters as we defined by trial and error method.

So, if you see this tau-1 actually matches with the tau-z character here. So, these are called as unit vector transformations and we will see that when we discuss reducible and irreducible representations, this will be very useful. So, in a similar way, there is also rotation vectors which can also be taken as the basis set. So, rotation vectors are called as Rx are denoted as Ry, Rz and what are these. Basically, these are if I take this, so like we said these are the rotations.

So, let us consider this as anti-clockwise rotation when I am looking from x-axis positive side of the axis towards origin. So, this vector rotation vector is called as Rx vector. Similarly, if I have to write Ry, so, this will be Ry and for Rz this will be Rz. So, in all three times I have what I have done is I have drawn anti clockwise rotation vector, when I am looking from the positive side of the axes towards origin.

So, now, if I carry out these operations on to these vectors, what kind of characters do I get? So, I think let us stop here and then let us discuss that in next class because you have already spent close to 30 minutes. So, we will discuss unit vector transformations using rotation vectors in next class. Thank you.