Symmetry and Group Theory

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Lecture -19
Matrix Representation of Point Group

So, welcome back, let us start with lecture 16. So, in last lecture we have seen matrix representation when we use xyz coordinates or orthogonal set of coordinates, we transform orthogonal set of coordinates. So, now let us see if we can use the same principle to develop matrix presentation for our point group.

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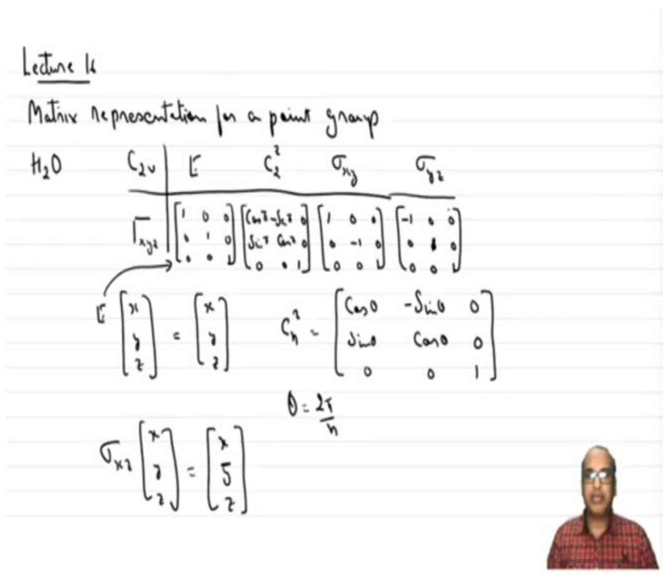

So, matrix representation, so, we will see here when our symmetry operations lie along axis systems or the orthogonal coordinate system, it is much easier to write a matrix representation and so, we will take both examples where the symmetry operations lie along the axis system and where it does not lie. So, that will cover both the cases. And then, let us take an example. So, let us start with a water molecule where the point group is C2v.

And we notice symmetry operations are the group elements in this case are E, C2 will say z, sigma-xz and sigma-yz. So, in this particular case, let us call this representation. So, now I am not writing a group multiplication table but the format of writing is similar. So, here on the left hand side I am using a symbol tau. And I am using the basis set, basis set it is the set of vectors which are chosen for defining a particular matrix.

So, in this case, we have chosen xyz. So, I am writing tau xyz. So, now, let us see what do we have in place of E, what matrix do we have? So, we know that E does not do anything and it has to be 3 cross 3 matrixes because we have 3 bases in this. So, it has to be a unitary matrix of order 3. So, again to remind you, if I am doing this operation, E on to x y z, I am getting x y z back. So, that tells me that my E is nothing but the identity matrix of 3 cross 3.

Now in same way if I am doing C2z, we have seen how to develop a rotation matrix. So, we have cos theta, - sin theta, 0, sin theta, cos theta, 0, 0, 0, 1. So, we will just say theta is 180 degree in this case, so, let me just write down C2z we defined as not C2z let us try to see Cnz cos theta, - sin theta, 0, sin theta, cos theta, 0, 0,1 this was done in last lecture. So, any rotation by 2pi / n, where theta = 2pi / n.

So, in this case our theta will be pi, because n will be equal to 2. So, 2pi / 2 will be equal to pi. So, we will have these values. So, this is very easy because our rotation axis is lying along one of the axis. So, let us continue with this. So, cos pi, what is cos pi? So, I leave it for you cos pi, sin pi with a negative sign, 0 then we have sin pi, cos pi, 0, 0, 0, 1. Now, let us see what happens to sigma-xz and sigma-yz.

So, that also we have seen sigma xz that means the only y goes to negative. So, if I am doing this operation sigma-xz on to x y z, what I will have is x will remain as x, y goes to minus y, z remains z. So, I can say that this is 1, 0, 0, 0, -1, 0, 0, 1. Similarly, in case of sigma-yz, x will be negative, 0, 1, 0, 0. So, this is a very straightforward way of writing a representation in terms of a matrix where we are using orthogonal coordinate system as our basis sets. And fortunately, our symmetry operations are lying along those axis systems.

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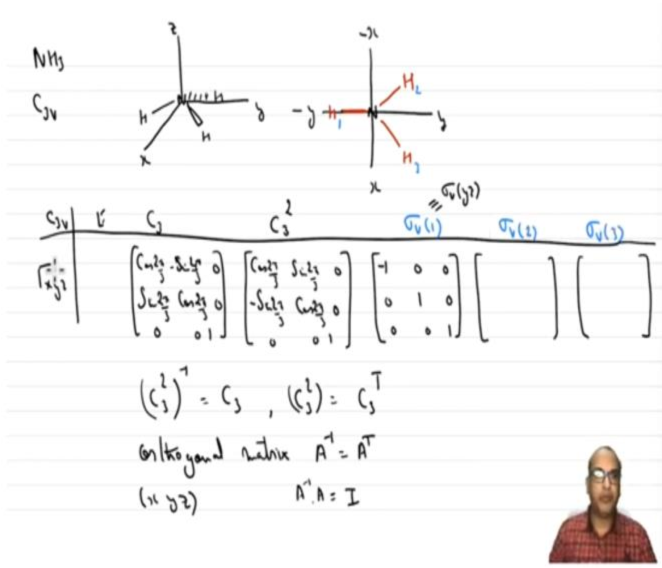

Now, let us look at an example of NH3. NH3 is a C3v point group. So, let us draw the axis system. So, let us say we have nitrogen at the axis and this is along yz plane, H, H. so, if I am looking from the top, because I am not really interested in z, it is not going to change. So, let us just look at it in 2D format. So, it will be easier to understand. So, this is my nitrogen let me draw the bonds with red color. So, one of the NH bond is actually lying along yz plane.

Another one is somewhere here, this one is somewhere here. So, now, you see it is not these 2 bonds are not lying along xy system, along the coordinates or along the planes. So, it will not be straightforward, as was in the case of water to write the matrix representations. So, let us see how to do that. So let us start with writing C3v, so again, it is tau xyz, so I am not going to write for E because again, E will be the 3 cross 3 I matrix. So let us start with C3.

So, C3 in this case will still be OK because C3 is lying along z axis. So, C3 will still be cos will still go with the same formula just at the angle will change. So, in this case, it will be 2pi / 3. So cos 2pi / 3, -sin 2pi / 3, 0, sin 2pi / 3, cos 2pi / 3, 0 and you can see this will be 1 / root 2, - root 3 / 2, 0, root 3 / 2, 1 / root 2, 0, 0, 0, 1. Similarly, you can also write for C3 square, because again C3 square is lying along the z axis, so writing the C3 square will be easy.

So, I must also tell you that C3 square is an inverse of C3. So you can just transpose this matrix and write for C3 square, why we will see in a minute. So the minus sign comes here cos 2pi / 3, 0, 0, 0, 1. So I said C3 square is inverse of C3. And in this case, the inverse can be written as simply C3 square is equal to C3 transpose. By transpose, I mean changing the rows into columns and columns into rows.

Why is that because, this is an orthogonal matrix. So far orthogonal matrix, the inverse If A is an orthogonal matrix, we can say that A inverse is equal to A transpose, Where we can say A inverse A is equal to I, or E in this case, so why it is an orthogonal matrix because our basis sets are xyz. So, that makes this this rotation matrix as an orthogonal matrix. So, this is true for all orthogonal matrices that the inverse can be written as transpose. So, we can simply transpose it and get the inverse.

Now, let us write for sigma. So, again writing for sigma is easy for sigma 1, you know we have sigma-V1, sigma-V2 and sigma-V3. So, let us see one by one how to write for different sigma, so, for sigma-V1 we know that it is lying along yz plane we can see that here so, because it is lying along sigma yz plane, so, we can say that this is equivalent to sigma-V(yz) and we have seen that in the case of water how to write for sigma-yz.

So, only x becomes negative and rest of the elements are same as E, because y and z does not change this. So, that is again easy. Now, let us consider the difficult case of sigma-V2, how to write this one? once we have figured this out, we can also we can write this one very easily from group multiplication table because we know that the product of these 2 are we will figure it out how to write first let us first focus on sigma-V2.

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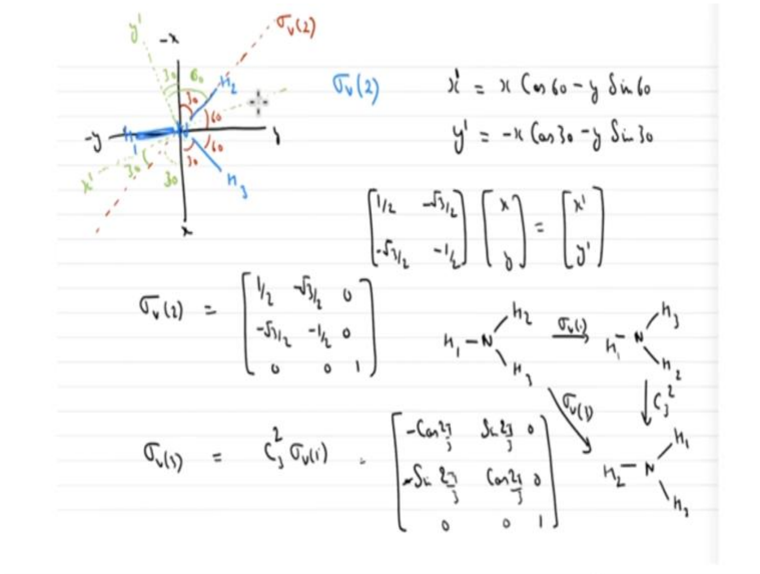

So, let me draw this molecule again in the plane. Now, let us mention all the angles, this angle is going to be this complete angle is going to be 120. So, this will be 60 degree, this will be 60 degree and this complete will be 120. So, this will be 30 degree, this will be 30 degree and we are trying to write for sigma-V2, a plane which is actually passing through this N-H2 bond. This is my sigma-V2.

Now, we have to see, to be able to write this, we have to see how the axis system is changing upon application of the sigma-V2, so, that we can write the new axis system in terms of old axis system the way we did it for rotation and how it changes. So, let us see what happens to xy. So, if I use this reflection for y, y comes somewhere around here because this is NH this the sigma-V2 is making an angle of 60 degree with this plane with this y axis.

So, we can say that the y will be going somewhere here, let us call it as y prime. Now, this angle will be 60 so, this this will be 30 degree, this complete will be 60, because this was 60, so, this will be 60, so, it is not to the scale. So, you can see that it is not. Now, what about the angle between sigma-V2 and x, what will be that angle. So, that angle will be this will be 30 and this x will be reflected into a new x, x prime.

Let us call it as x prime and this angle will also be 30 degree, this has to be equal to this angle. So, again this is not the angles are not drawn to the scale. So, if you actually draw it to the scale you will see that it is much easier to look at. So, now, we have defined the new axis system x prime and y prime which comes as a result of reflection by sigma-V2. Now, let us try to write down x prime y prime in terms of x and y.

So, it is easier to see if we can say that x prime which is this can be returned in terms of x as x cos 60, because this angle is now 60 degrees, so we can say that x prime can be written in terms of x cos 60, -y sin 60. This is a simple trigonometry. So, I do not think I need to explain this. So, all you are doing is you are taking a projection of x prime onto x axis and -y axis. So, length of this prediction will be x cos 60 and this will be minus y sin 60.

Now, similarly, we can say that y prime, so this is y prime, Now, again, try to put the projections onto x and y original axis system and this will be equal to we can say that it is making an angle of 30 degree with x, so we can with minus x, so we can say minus x cos 30. And it is making angle for minus y, this will be minus y sin 30. So, we can say, if we want to write this whole thing in matrix form, we can say that cos 60 will be equal to 1 / 2.

And let us write down x y which changes to x prime y prime, similar to what we did for rotation. So, half minus of sin 60 will be minus root 3 / 2. Now, cos 30 will be root 3 / 2 with a negative and sin 30 will be half with a negative because negative sign is there. So, if you see x and y are changing to x prime and y prime with this relation. So, this should be the matrix corresponding to sigma-V2 and z we can now include z. So, z does not change because that is lying along this plane. So that does not change.

So, we can just introduce it by writing 1 over here. So how do you write sigma-V2, so now can be written as complete sigma-V2 can be written as 1 / 2, - root 3 / 2, 0, - root 3 / 2, - half, 0, 0, 0, 1. So this last column and row are added to show that z does not change. So, we had already written for sigma-V1. Now we also have for sigma-V2. Now let us see for sigma-V3, how do we write for sigma-V3? So can we say that? Let us do this operation.

So, can we write sigma-V3 in terms of product of sigma-V1 and sigma-V2. So, let us say if we have NH3, I am showing it from the top. So, if I am doing sigma-V1, I get 3, 2. And if I am doing sigma-V3 will give you N, H3, H1, H2. So, H1 and H2 will be reflected. Now, if I want to go from here to here, to identify what are the factors of sigma-V3, all I have to do is see H3. So, I have to take H3 here. And then H1 here. And H2 here that tells me it is a C3 square, rotation anticlockwise.

So, if I am doing C3 square rotation using this, so, I can write it like this that sigma-V3 = sigma-V1 followed by a C3 square. So, we already know what is sigma-V1, we know for sigma-V1 is here, we know for C3 square is here. So, we can write the product and basically what it is, so we have cos 2pi / 3 will become negative. So, it is easier to know so we have this matrix we can write as cos 2pi / 3, sin 2pi / 3, 0.

And then we had C3 square as minus of sin 2pi / 3 here, -sin 2pi / 3, cos 2pi / 3, 0, 0, 0, 1. So, what I have done is I have just done the matrix multiplication for these 2 to obtain sigma-V3, otherwise, indirectly, you can also write for sigma-V3 by doing a axis transformation to by using a reflection along this plane but which is again will be tedious, you will have to do the axis transformation, write the new matrix and do this but we will come out to the same.

So, we have now seen how to write matrix representations for a point group where our symmetry operations are lying along the coordinate system and where our symmetry operations are not lying along the coordinate system. So, in the former case, it is literally easier like we saw in the case of water, whereas in the case of NH3 or other complex molecules, it will be more tedious to write. So, how many such representations are possible?

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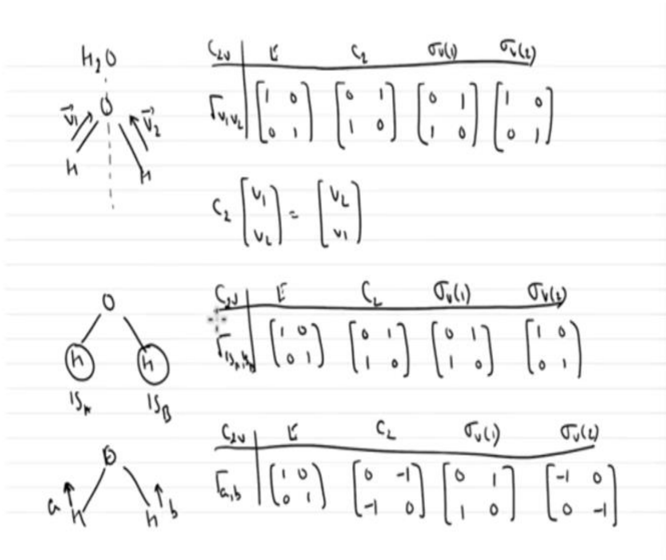

Let us ask ourselves, so, let us, again take an example of water. So, let me draw this, let us say if I change the basis set now, to something else. So, earlier, my basis set was xyz, so I got a 3 cross 3 matrix representation. Now, let us say if I am choosing this vector v1 and this vector v2 as my basis set. So, what I mean to say is that E, C2, sigma-V1, sigma-V2, let say tau v1v2. Now, this will be a 2 cross 2, because my basis set has 2 vectors.

So, this will be 2 cross 2 identity matrix 0, 1, 1, 0. Now, for C2 we see that if we apply C2, v1 will be replaced with v2 and v2 will be replaced with v1 in other words, if we do C2 matrix on to v1 v2 what we get is v2 v1. So, I can say that this will be 0, 1, 1, 0 simple to write. Now, let us say for sigma-V1 let us say that the sigma-V1 is the plane which is reflecting v1 v2. So, again it will be v1 will be reflecting v2.

So, we will have 0, 1, 1, 0, v1 will be replaced with v2 and v2 will be replaced with v1, sigma-V2 is the plane where all 3 items lie. So, the vectors will not move. So, basically it will be like identity here, so, you can say 1, 0, 0, 1. So, this is another representation for same molecule but in 2-dimensional space, where the space is defined by the basis vectors v1 v2. Let us write another representation for water, where now the basis set is the S orbitals on to water.

So, 1SA and let us call it as B, 1SB. So, if we do that what do we have? So, as you can see this will be exactly same as above. So, again S orbital's will be replaced with each other in C2 operation. So, we have 0, 1, 1, 0 sigma1 will also reflect 1SA. So, with 1SB, so, we have 0, 1, 1, 0 and 1, 0, 0, 1. Let us try it one more representation with same molecule. But in this case now, the vectors are actually perpendicular to this plane of water.

So, these are the 2 vectors, let us call it as vector A and vector B, which are now perpendicular to this plane defined by the water plane. Now, in this case tau-AB, this will be again same. Now for C2 what happens if I am doing a C2, A will be replaced with B, B will be replaced with A but in addition to this, their directions will also change. So, if I am doing a C2 rotation B will come here but with A direction downwards, similarly, A will come here but with a direction which is downwards.

So, in such a case to represent, so, what I have to do is I have to write it as negative, so, 0, -1, -1, 0. So, now you can see that the representation from here to here is different. Here the vectors were in plane and parallel to the bonds, here the vectors are perpendicular to the plane. So, it changes. Now, let us write for sigma-V1. So, for sigma-V1, it will be A will be replaced with B without any change in the direction of the arrows.

So, we will write 0, 1, 1, 0 and for sigma-V2. So, again, sigma-V2, A will not be replaced with B but A will be changed into direction. So, it will be a negative unit matrix. So, A remains at A but changes at sign by doing sigma-V2, similarly B remains at B but changes its sign. So, we can say that there are multiple such representations possible.

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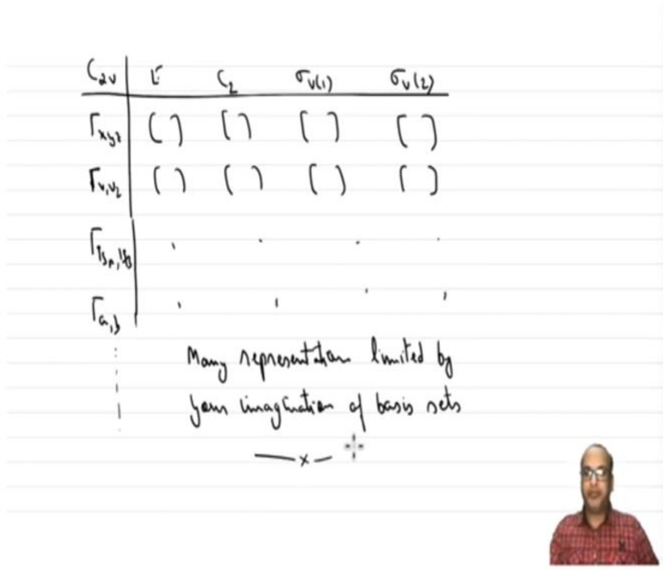

So, if we now try to list all the representations down what we have looked so far, so we have seen E, C2, sigma-V1, I am not going to write all the matrices again but I will just try to make a point that let us say if I have sigma xyz, I get a 3 cross 3 matrix. If I have v1, v2 vectors which are in plane, I get 2 cross 2 matrixes which is a different representation than the above. Now, if I have 1SA, 1SB, I get a different representation and above, if I have A, B vectors which are perpendicular to the plane of water, I get different vectors.

So, I can keep on choosing different basis set, I can keep on getting different matrix representations. So how many such representations are possible? The answer is many representations which are limited by your imagination of basis sets, which are chosen to carry out the transformation under different symmetry operations. So that is all for today. So, we will see more of this matrix representation in next class. Thank you.