Mathematics for Chemistry
Prof. Dr. M. Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 26

We have seen the basic definitions and some basic properties of groups, we have seen what is meant by sub group. Today, we are going to start while start looking at another property of a group call the class of a group; in order to do that first we will define something called a similarity transformation.

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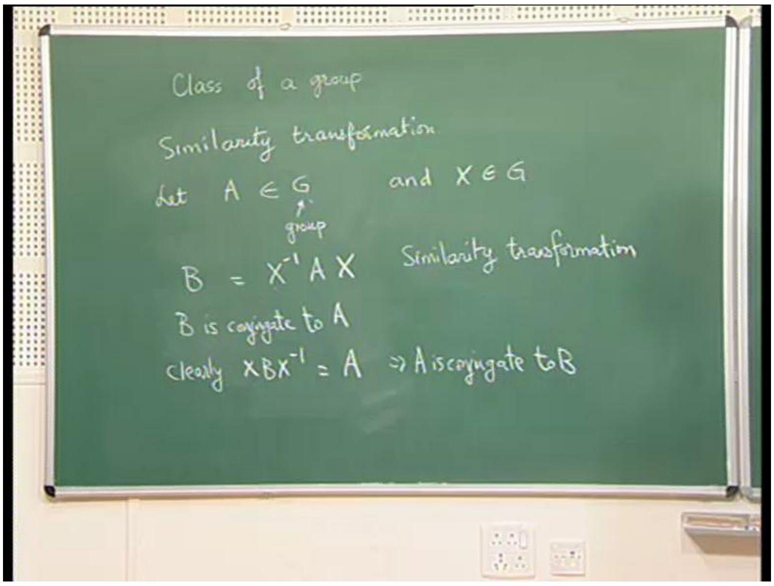

So, we will define something called a similarity transformation, in order to define this, so let A be a member of G, this is the group. So, A is the member of the group and X is also a member of the group, then B is equal to X inverse A X this operation where you multiply A by X on the right and X inverse on the left is called a similarity transformation; and B and A these 2 elements B and A are set to be conjugate to each other.

So, we say B as conjugate to A or you can also say you can easily show that if B is conjugate to A, then A is also conjugate to B. So, you can show that by just now if I pre multiply by X, so clearly X B X inverse, so I multiply on this side by X. So, here I multiply by X X times X inverse is 1, then I multiply on the right by X inverse, so here if

I multiply on the right by X inverse then I just get A. So, therefore A is conjugate to B, so B is conjugate to A then A is conjugate to B.

So, implies A is conjugate to B or you can say that A and B are conjugate elements. Now suppose we consider an element A. So, implies A is conjugate to B or you can say that A and B are conjugate elements.

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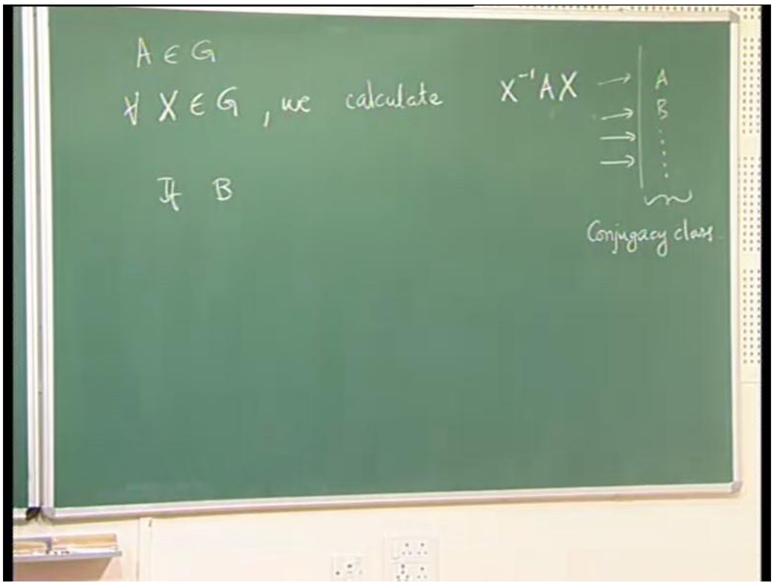

Now suppose we consider an element A so A contained in G and let say the for all X contained in G, we calculate X inverse A X. So, for all X this is X X contained in G. So, for all the elements of G we calculate X inverse A X, so A is the same. So, A is the 1 element of G, so then this will lead this in some cases it will just yield A in some cases will B it in some cases it will give you something else. But, this set of elements for different choices of X this set of elements is called the conjugacy is called a conjugacy class.

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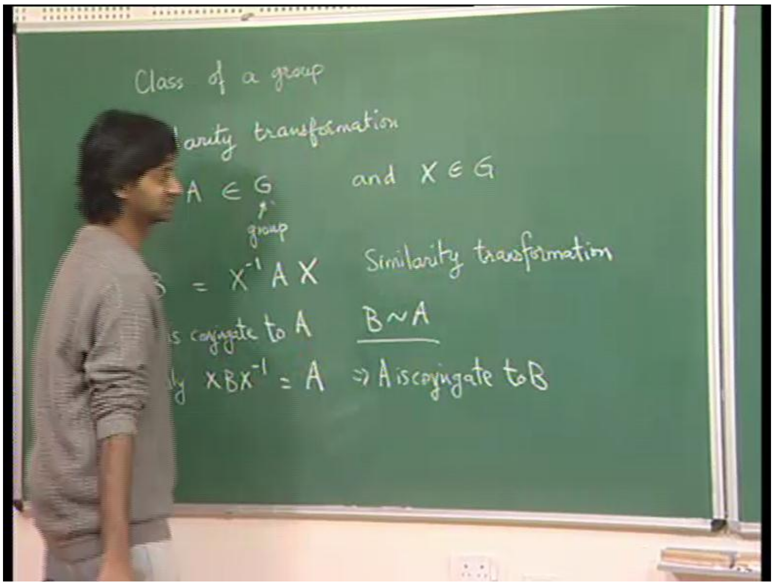

So, the conjugacy class consists of all elements that are conjugate to an element the other thing I should mention is that if B is conjugate to A, so I will just B is conjugate to A, we write it as B is conjugate to A this is the notation.

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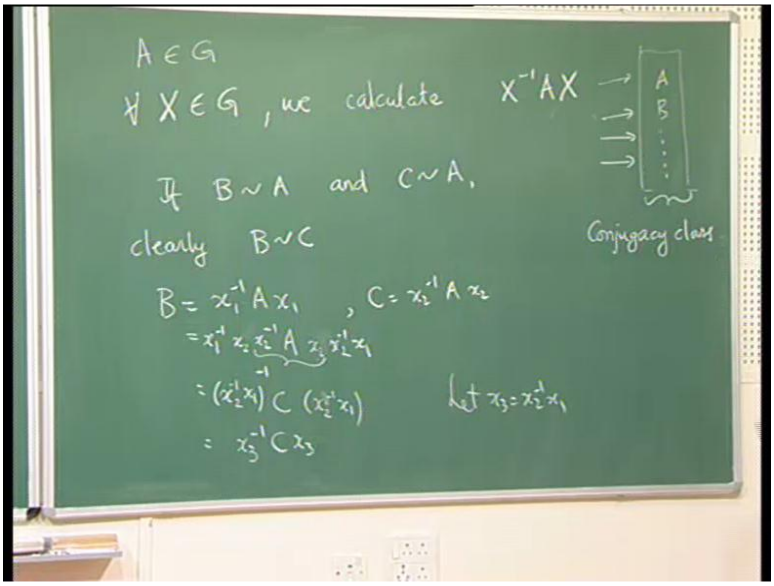

So, if B is conjugate to A and C is conjugate to A clearly B is conjugate to C, so let us show this. So, if B is conjugate to A that is B is equal to X 1 A or X 1 inverse A X 1 and C is conjugate to a implies C is equal to X 2 inverse A X 2. And I can easily do the following I can put an X 2 inverse X 2 here so I can just say that B is X 1 inverse and then I will just multiply by 1. So, I multiplied one in the form of X 2 inverse X 2 A, then again I multiply by 1 and I multiply in the form of X 2 inverse X 2 X 1.

So, I just multiplied by 1 here, multiplied by identity here, an identity here because X 2 inverse X 2 is just identity. So, I can always multiply by identity it does not change anything here also I multiplied by the identity. So, this is equal to X X 1 inverse X 2 inverse that is same as X 2 X 1 the whole inverse times X 2 A X 2 inverse I should out done it the another way I will just do this as I will put X 2 X 2 inverse here and X 2 inverse X 2 here X 2 X 2 inverse, so I will just do it in this.

So, this X 2 inverse X 1 the whole thing inverse, and then this whole thing is just X 2 inverse A X 2 that is C and here you have X 2 inverse X 1. So, what I have is if I call X 3 X 2 inverse X 1 then B is equal to X 3 inverse C X 3 implies B is conjugate to C, so what we showed that if you see if we had B is conjugate to A and C is conjugate to A then clearly b is conjugate to C. So, then the set of all these elements that are conjugate to each other they form something called a conjugacy class.

So, are conjugate to each other, so this idea of conjugacy class will be very useful when we are describing the groups of interest to (( )) symmetric. So, let us take an example to make the idea of both classes and subgroups clear.

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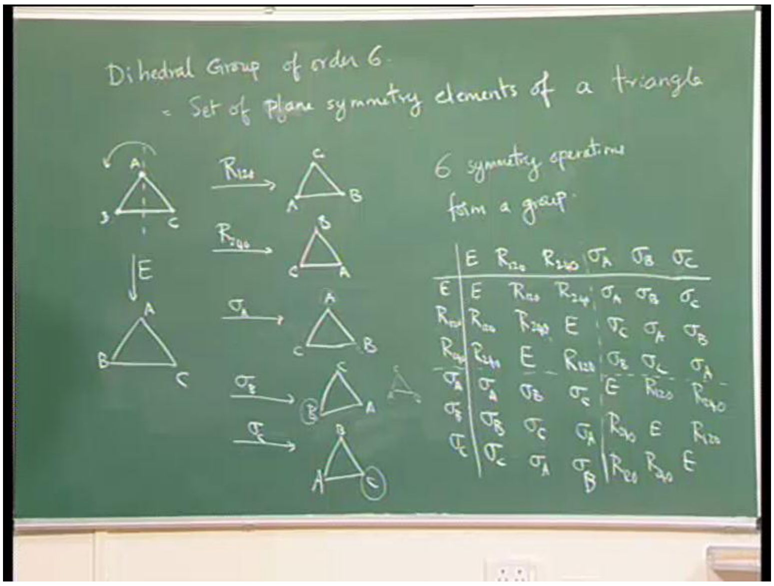

So, the example I will take is the dihedral group of order 6. So, what is this corresponds to, this corresponds to the set of symmetry of plane symmetry elements of a 3 sided of a triangle actually a 3 sided polygon is a triangle for regular triangle. So, basically suppose I had a triangle and let me call this A B C, now I can I have various symmetry operations of for example, if I rotate by 120 degrees 20 degrees to this way in the sense then I will get C A B and then I can rotate by 240 degrees then I will get A B C. Then I can consider reflection about a plane passing through A and the midpoint of the other 2. So, that will give me A C B and I can consider 2 more reflections sigma C B C A C B A.

So, there are 5 operations and then the 6'th operation is the identity operation by you don't to anything. So, this also the identity operation, now these 6 operations which will be taken to form a group. So, the 6 symmetry operations form a group and we can write the multiplication table of this group, so we have E R 120, R 240, sigma A, sigma B, sigma C and I have E and I choose to define my sigma A as rotation with respect to this point with the with respect to the top point.

Sigma B is rotation with respect to this point and sigma C is rotation with respect to this point. So, it is always this point so even if I do sigma B twice I will always reflect sorry these are the reflections. So, I will always reflect about a plane about this plane. So, clearly you can look at this and you can say that you can write the first row similarly, you can write the first column, so this part is easy then you ask what is the product of these 2 operations.

So, that means, you operate first by R 120 and then again by R 120 and then it is very obvious to see that if I rotate 1's by 120 degrees and I again rotate by 120 degrees that corresponds to rotation by 240 degrees. And rotation by 120 followed by 240 is nothing but the identity and you can fill in this part quite easily. So, this part is fairly easy, now suppose I do sigma A and I again do sigma A. So, I reflect about this plane and then again reflect about plane that is nothing but the identity.

So, this is identity similarly, this is identity and this is identity. So, this much you can write fairly easily. Next you have to consider what happens when you do sigma A first and then R 120. So, what I am going to write here is R 120 sigma A that is means I operate first by sigma A and then by R 120. So, if I operate by sigma A then basically I get A C B and then I follow it by R 120 degrees then I will get B A C so B A C and notice that C is where it is B and A are switched. So, that corresponds to sigma C.

So, this is sigma C similarly, you can show that this is sigma B and this will be, now if I do R 120 and I follow it by sigma or I do sigma B followed by R 120 you can easily show that this will be sigma A. So, I do sigma B and then rotate by 120 degrees and A is where it is and B and C are swapped. So, it is sigma A you can show this.

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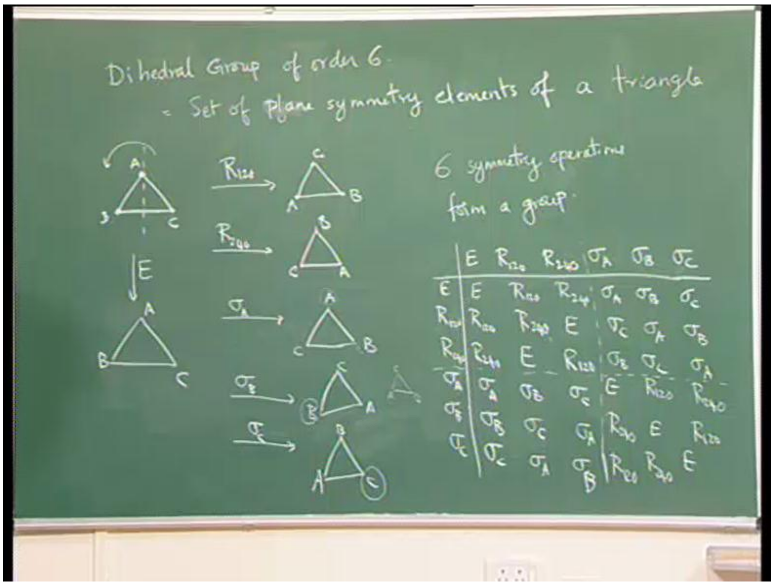

This is not hard to show, now what if I do it in the reverse order. So, first I rotate by 120 degrees and I then I do sigma A. So, first if I rotate by 120 degrees then I get A B C, now if I do sigma A if I flip it about this then I have C A B. So, now B is where it started, so it corresponds to sigma B and this will correspond to sigma C this will correspond to sigma, so if you do R 120 and then followed by sigma B. So, R 120 and then you do by sigma B about this then you have A here B here C here, so that is sigma C.

This will be sigma A, sigma A this should be sigma B that we see and now what about sigma A sigma B. So, first you do sigma B and then you do sigma A. So, first you do sigma B that will correspond to this. So, you will get this, now if I reflect about this then I have C A B, so I have C A B and you can clearly see that this corresponds to rotation by 120 degrees. So, this is R 120 this will be R 240 this will be R 120, so you can verify this multiplication table of this group this is dihedral group of order 6.

Now let us we want to identify the sub groups and the classes of this group, so we want to identify the sub groups and the classes. So, let us start with the sub groups, now a sub group is a part of a group that itself looks like a group. Now, if you just look at the multiplication table and you look at these elements E R 120 R 2 40, so these...

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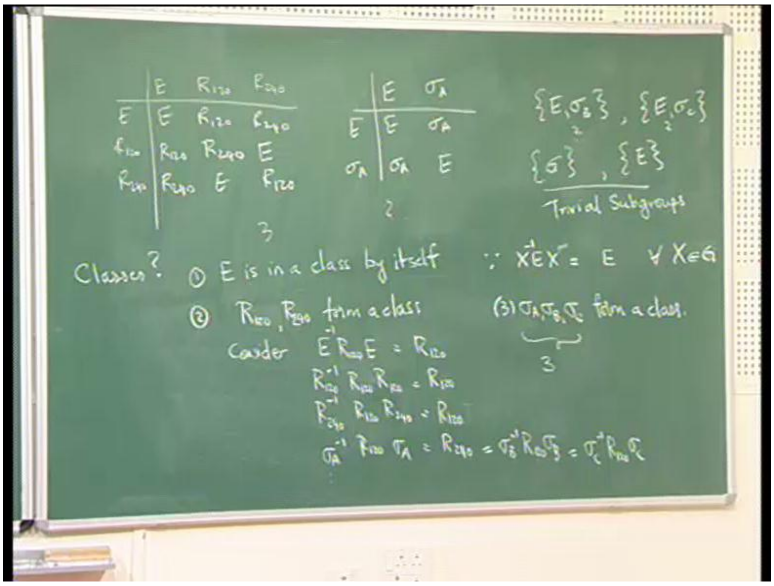

So, if you just look at E R 120 R 240, so clearly this is the group because it has because inverse of R 120 is R 240, because R 1 nothing but the identity. So, it has 3 elements it is a group of order 3 are there other groups in here, so well you can always construct a group like E sigma A because sigma A inverse of sigma A is sigma A itself inverse of sigma A is just sigma A because sigma A square is identity. So, this a group similarly, E sigma B, so these are all the sub groups.

So, all these will be the sub groups of this group are there any other sub groups of this group and I do not see any other sub group. So, I do not see any other sub group because if you involve any 2 sigma’s then you get rotations. So, you have to involve rotations and the only other sub group is the entire group, so G and in addition. So, there is always this trivial sub group which is G itself and identity. So, these 2 are the trivial sub groups, so for every group the identity will be a sub group and the entire group G itself is also be a subgroup.

So, these are the sub groups in addition there is 1 2 3 4 we have identified 4 sub groups the orders of the sub group this is a sub group of order 3 and these 3 are sub groups of order 2 and notice that the order of the sub group divides 6. So, 6 is the order of the group order of the sub group divides the order of the group. So, the sub groups this is how much we can say about the sub groups, now what about the classes.

So, statement I will make is that E is in a class by itself because X E X X inverse X E is equal to E for all X containing G. So, you take E for any group this is true for any group E is always a class in itself because X inverse E is just X inverse. So, X inverse E X is just is always equal to E. So, the only the element that is conjugate to E is E itself, so R 120 R 240 form a class and you can verify this because suppose I take R 120 and I multiplied on the right by sigma.

So, for example, consider, so suppose I take E R 120 or E inverse R 120 E, E inverse is just E identity the inverse of the identity is I is the identity R 120 into E. So, this is R 120 then you consider R 120 inverse R 120, R 120 then you consider R 240 inverse R 120, R 240 then you consider sigma A inverse R 120 sigma A and then similarly, you will do for sigma B and sigma C. So, this will give you that the set of all elements that are conjugate to R 120.

Now, R 120 inverse R 120 is E. So, E in to R 120 is just R 120, R 240 inverse R 120, R 2 40. So, R 120 into R 240 is identity in to R 240 inverse is just R 240 inverse which is R 120. Now what about sigma A inverse R 120 sigma A. So, first you operate by sigma A and then R 120. So, that gives you sigma C, so you have sigma C multiplying sigma A inverse sigma A inverse is just sigma A. So, sigma C into sigma A is R 240 similar, to sigma B and sigma C you will get R.

So, if I do sigma B I will just write it here sigma B, so if I do sigma B inverse that is just sigma B R 120 sigma B R 120 is sigma X. So, sigma A into sigma B is just R 240. So, this is also equal to this and similarly, this is equal to sigma C inverse R 120 sigma C, that means now if you look at all the elements that are conjugate to R 120 you only get R 120 and R 240.

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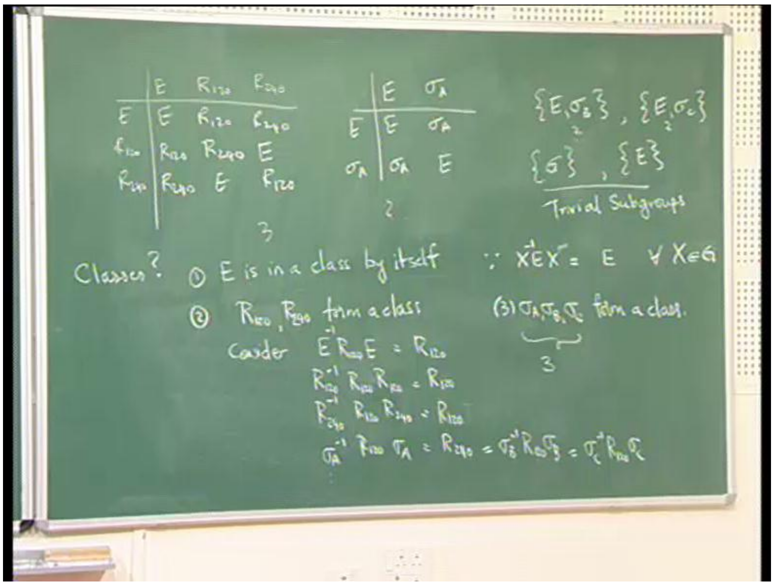

So, therefore, R 120 and R 240 they form a class, and last part similarly, you can show that sigma A, sigma B, sigma C form a class. So, this is a class of order 3 this is a class of order 2 this is a class of order 1 and you can see that each of these is divisor of 6. So, order of the class also divides order of the group, so this exercise is an explicit calculation of the sub groups and classes for a group for a very simple group. This is not the same as the groups that will be discussing when you are talking about symmetry operations.

Because, this is for a plainer figure and we are looking only at symmetry is in a plain but the next thing we want to do is to consider the symmetry operations in various molecules. So, that will be the next thing that we consider, so next we will talk about symmetry operations and symmetry elements for a molecule for a typical molecule. Now these are the symmetry operations and symmetry elements that are considered and these are the one set are relevant to various for describing the spectral signatures.

So, it helps to classify molecules based on what symmetry elements they have, so that is what we are going to do today. So, we are going to describe what are the various symmetry elements and symmetry operations.

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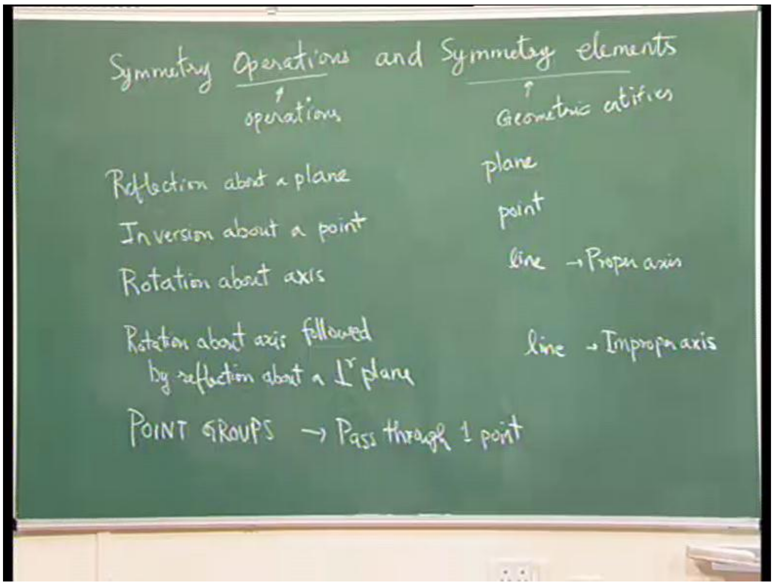

So there is a distinction between symmetry operation and symmetry element sometimes, the same symbol is used for both of them. Symmetry elements are typically these are geometric entities these are as I said operations. Now there are 3 relevant symmetry elements and or actually there are 3 relevant symmetry elements and corresponding to that there are 4 relevant symmetry operations and 4 symmetry operations and the corresponding symmetry elements are the following.

So, first is reflection about a plane this is the corresponding symmetry element is your plane, second is inversion about a point and that the symmetry element is a point, the third is rotation about axis here the so you have a line or the axis. And the fourth is rotation about axis followed by a reflection about a perpendicular plane. So, suppose you have an axis is the unique plane that is perpendicular to that axis and so we will do this and here the symmetry element is a line.

So, these are the 4 operations and that will be considering this is sometimes called a proper axis and this is called a proper rotation, this is called an improper axis or an improper rotation. So, these are the symmetry elements off or any typical molecule and these are often referred to as point groups. So, the set of all these symmetry elements for a molecule they form a point group and these all pass through, because they pass through one point.

Therefore, when I say rotation about an axis followed by a reflection on a perpendicular plane the axis passes through the point which might be the center of the molecule the plane also passes through that point. So, the perpendicular plane also passes through that point. So, all these elements they all pass through one point, this will become we look at examples, so that is what we are going to take up next and why did you can show that the set of all symmetry operations for a molecule that forms a that forms a group.

So let us look at the symmetry operations 1 by 1 and we will do this taking various examples. So, that things become clear, so the first operation will consider is reflection about a plane.

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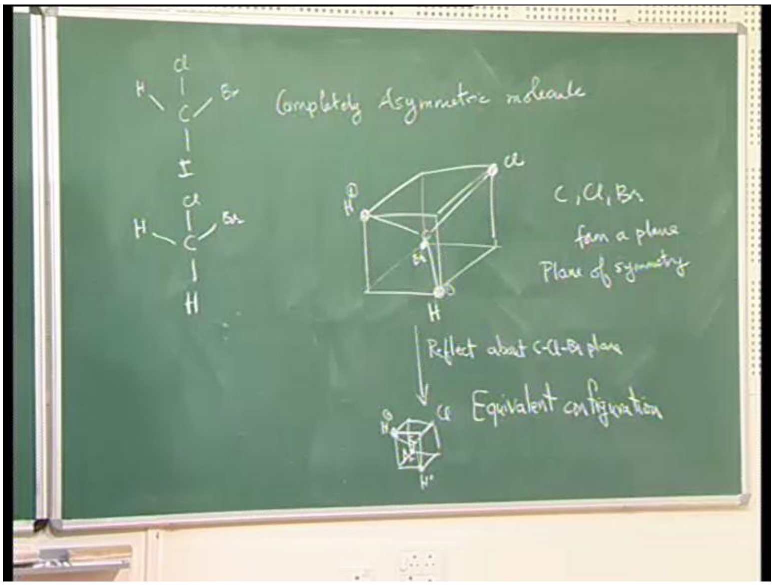

Now consider molecule let us take molecule of the form let us say C c l B r H I. So, this is a completely asymmetric molecule only symmetry operation is the identity operation and you called this molecule totally asymmetric. Now suppose I had the case where I had C c l B r H and I had a second H, now what are the reflections that are there in this molecule. So, let us look at. So, in order to see the reflections it is easier if you draw the tetrahedral in this form.

So, we need to draw the molecule in a way in which we can easily see the symmetry elements the most convenient way this is tetrahedral geometry where, C is the center of the tetrahedral and then you have one H you have another H you have c l and you have a

B r is the all the way behind. Now you can just look at this molecule and you can say that these 3 atoms; so the C c l B r.

So, if I have 3 atoms. So, the points corresponding to these 3 atoms they form a plane, so any 3 atoms. So long as they are not collinear they will form and so these 3 atoms are not they are not a line but they form a plane. So, if I take the plane containing these 3 atoms then that plane you can see. So, that is this plane clearly is a plane of it has symmetry of reflections. So, if I reflect about this plane then this H will come here this H will go here.

So, this plane form a plane this is the plane of symmetry. So, in other words if I had a mirror here 2 sided mirror and I reflected about this mirror then this H will come here this H will come here the atoms in the plane would not change at all. So, then I will get configuration that looks identical to this or that looks similar to this. So, it is equivalent to this, so this if I call this H 1 and H 2. So, if I reflect about this plane about plane what I will get is H 2 H 1 and everything else where it is.

So, the C c l and B r would be at the same place. So, the c l will be where it is, C will be where it is and B r will be where it is. So, the point is when I reflect about this plane all I will do is switch these 2 and so this is an equivalent configuration. And so when you get an equivalent configuration by performing this reflection operation then this is called a symmetry operation. So, that means; this is a plane of symmetry.

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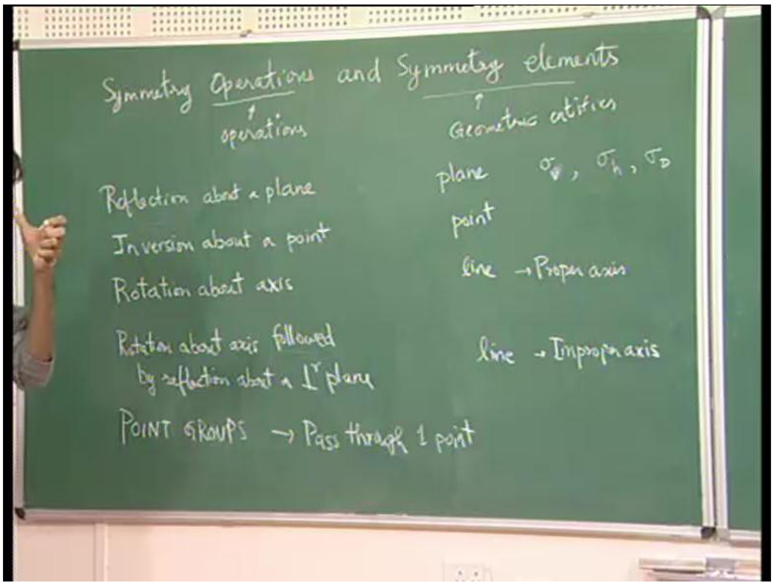

Now, there is a notation that is used as standard notation that is used for the planes you use sigma for the plane and there are 2 kinds of planes here is one that is called sigma D and sigma H for sorry sigma V sigma H and sigma D. These will become clear when we talk about various molecules the definitions of these will become clear this is, sometimes called the horizontal plane. This is called the vertical plane this is called the dihedral plane. So, when we consider specific molecules each over the meaning of all these will become clear.

So, we can see that C H 2 c L B r has a reflection has a symmetry element that corresponds to a plane such that, you reflect about that plane and you get a symmetry operation. Now suppose you had a molecule of this type.

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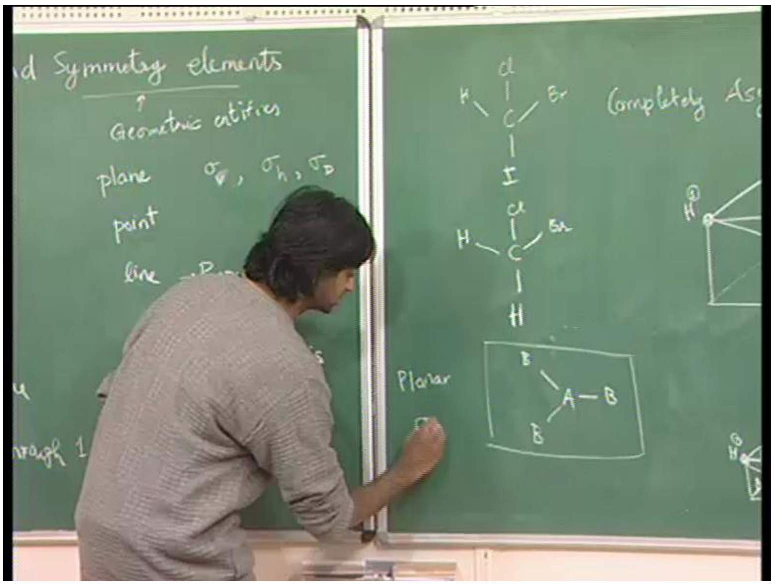

Suppose you had an A B B B this kind of molecule, a planer molecule planer. Now this has 1 plane of reflection if you reflect about this plane if you reflect about the plane containing A B cube then it is that is called a sigma H.

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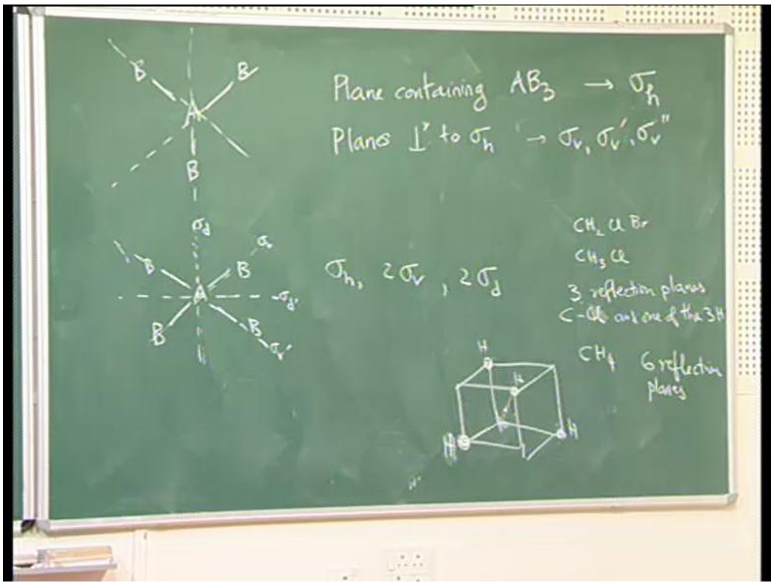

So, now suppose you consider a molecule a planer molecule of this shape A B cube. So, it is a planer it is triangular in shape then what you can see is that it has the plane containing A B cube this plane is a symmetry plane it is referred to as sigma H. Then you have planes perpendicular to sigma H and so you have planes perpendicular to sigma H and I will just I would not write the details but basically there are 3 planes perpendicular to sigma H. So, 1 plane is this plane the other plane is this plane and the other plane is this plane.

So, these are called sigma V sigma V prime and sigma V double prime. So, this is an example, now suppose you had a molecule like A B 4, suppose you had a molecule like this then in addition to these planes. So, these planes are called sigma V, so in this case you have sigma H 2 sigma V's, so you have 2 sigma V planes which are these 2 and you have these 4 of these planes which are or 2 of these 2 planes 2 and these planes are called sigma D or dihedral. So, these are called sigma D which is passing in which passes in between these bonds.

So, they are sometimes refer to this is just nomenclature that is used typically. So, sigma refers to both the plane and the symmetry operations, now you can see that if you reflect about this plane you will get an equivalent configuration. And so this is a symmetry operation these are called sigma D, sigma D prime these are sigma V, sigma V prime this is just the conventional notation. So, this is a notation that is used in group theory, so that as much as I want to say about reflection there are just couple of more examples I want to give.

So, that you know how to count the reflections here lets so we started with C H we had C H 2 c L B r. Now if you have C H 3 c l if you had C H 3 c l then we have 3 reflection planes and it is not hard to see they contain the C H and or C c l and one of the H S the 3 H. So, just to show you this will look like this, so if you had this then here and here if you had these 4 the C is at the center that is make this H H H c l. So, then you can consider various planes.

So, 1 containing c l C and this H, so that will that will go like this and it will essentially when you reflect about it this H will go here and this H will come here. Next you could have a plane containing this c l the carbon and this. So, that will essentially be in between, these 2, so when you reflect about it this H will go here this H will come here then you could have C c l and this H and that will essentially go in between these 2.

So, it will be a plane that goes in between these 2 and what will happen is it will switch these 2 on reflection. So, you have 3 reflection planes for C H 3 c l if you had C H 4 if instead of a c l you had an H here if you had C H 4. So, for C H 4 you can have 4 and you can choose any of the 2 hydrogen's and a carbon atom. There are 6 ways to choose it, so there are 6 reflection planes, so that means, you take a carbon and select any 2 hydrogen's and the plane containing those 3 atoms will be a plane of reflection. So, C H 4 has 6 reflection planes. So, that is how much I want to talk about reflections when we actually do examples it will become more clear.

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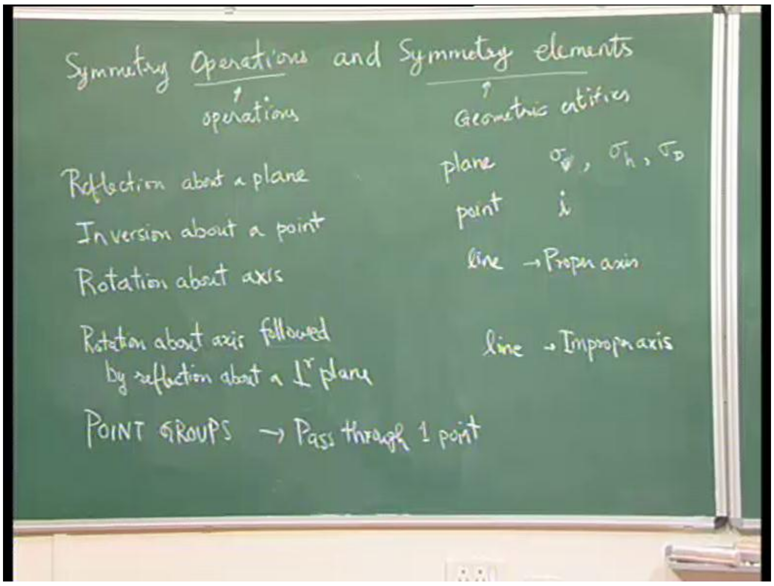

So, C H 4 has 6 reflection planes. So, that is how much I want to talk about reflections when we actually do examples it will become more clear. So, next let us talk about the next operation which is inversion about a point the symbol use for this is i, so me there are some molecules that have this point about which you can do an inversion.

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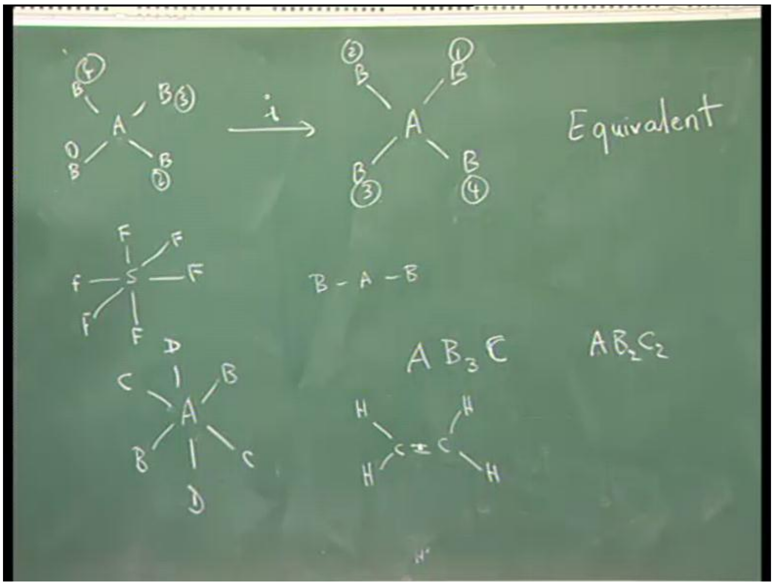

So, the one example is you’re A, so a planer molecule of this form. So, this is the point of inversion when I invert the molecular about this point I put B here this B here this B here this B here. So, if I call it 1 2 3 4 if I do an inversion I will get A B B B B but then I will have 3 here 4 I will have 2 I will have 1 and this is an equivalent configuration. So, whenever a molecule has a property that if you invert about some point you get an equivalent configuration and that inversion that point is a symmetry element an inversion about that point is a symmetry operation.

So, there are some examples of molecules that have a point of inversion for example, S F 6, so S F 6 has a point of inversion. So, this is the classic molecule that is known to have point of inversion similarly, if you just had a linear molecule like B A B then A it has a point of inversion and so on. You can immediately see that if a molecule has to have a point of inversion then other than the molecule on the center all the other atoms should appears in pairs. So, if I had instead of A B 4 I could also had A B B C C D D.

So, this molecule has a point of inversion, so this has a point of inversion because all these molecules are appearing in pairs. So, that is a necessary condition it is not sufficient because not only do they have to appear in pairs but the pairs have to be situated opposite to each other about this central molecule. So, the point is suppose you had a molecule like A B 3 C then you know that this cannot have a point of inversion.

Because, if you take A as a center molecule then either does B and C appear in pairs, if you take B as a center molecule then clearly A and C do not appear in pairs, if you take C as a center molecule then A B do not appear in pairs. But, on the other hand molecule like A B 2 C 2 this could have a center of inversion if A is at the center and B is are situated opposite to each other. If you have something like A B 2 C 2 then it could have a center of inversion.

So, necessary condition is that other than the central molecule the other atoms should appear in pairs thus other than the center atom the atoms should appear in pairs. The other well known example for a point of inversion, now you need not have a molecule at the point of inversion you could have a case like C H the ethylene molecule. Now this has a point of inversion right here this is a point of inversion, so you can see that all the molecule appear in pairs about this the all the other molecule all the other atoms appear in pairs.

So, when you invert about this then this hydrogen goes here, these carbon goes here, this hydrogen goes here, this hydrogen comes here, this hydrogen comes here. So, in the next class we will talk about proper axis and improper axis.

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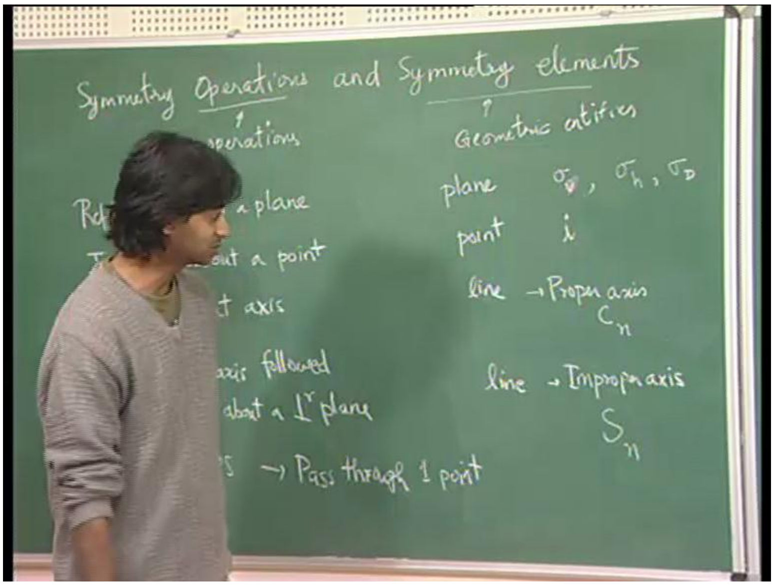

I will just mention that a proper axis is denoted by a C and an improper axis is donated by an S. So, C n and S n is what is what we will use and this is used to signify rotation this is you used to signify that you have an axis about which rotation is a symmetry operation. So, I will just briefly mention these now and then and then we will continue to the discussion in the next lecture.

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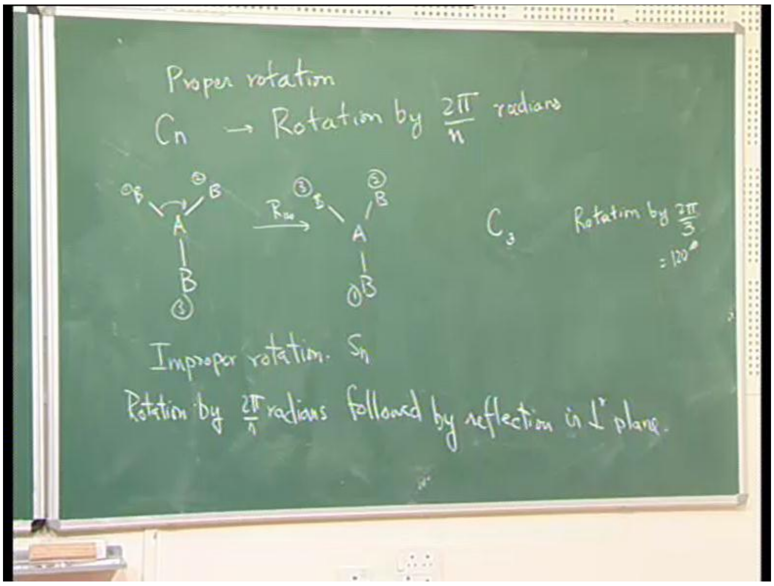

So, proper rotation, so C n means rotation by 2 pi by n by angle 2 pi by n. So, for example, if you had a molecule like A B B B, now if I take the axis that passes through

A, so if I take the axis that is perpendicular to the board and passes through A. Now I can rotate by 120 degrees by 120 then I get an equivalent I rotate by 120 degrees then I get A an equivalent configurations. So, if this is 1 2 3 and I get 3 2 1, so this is a symmetry operation this is denoted by C 3, so 3 3 because C 3 means rotation by 2 pi by 3 2 pi by 3 radians.

So, 2 by 3 radians is equal to 120 degrees 2 pi by 3 is 360 by 3 that is 120 degrees. So, this is proper rotation and we will look at examples, of this soon the other thing is the improper rotation. So, this is rotation followed, so rotation by 2 pi by n radians followed by reflection in perpendicular plane. So, we will this in the next lecture we will look at examples of each of these in more detail now clearly if a molecule has if each of these is a symmetry element if rotation by 2 pi by n is itself a symmetry element and reflection is also a symmetry element then clearly there product will be asymmetry element.

That is actually a very trivial case when you have an S n when you have both C n and a sigma perpendicular but there are cases of molecules where you have S n's where you do not have C n and sigma perpendicular still have an S n. So, this is what this is where we will continue in the next lecture.