Mathematics for Chemistry

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Lecture - 28

Let us look at the list of symmetry operations for molecule, and this will illustrate some of the key things, that we need to keep in mind while writing down the symmetry elements.

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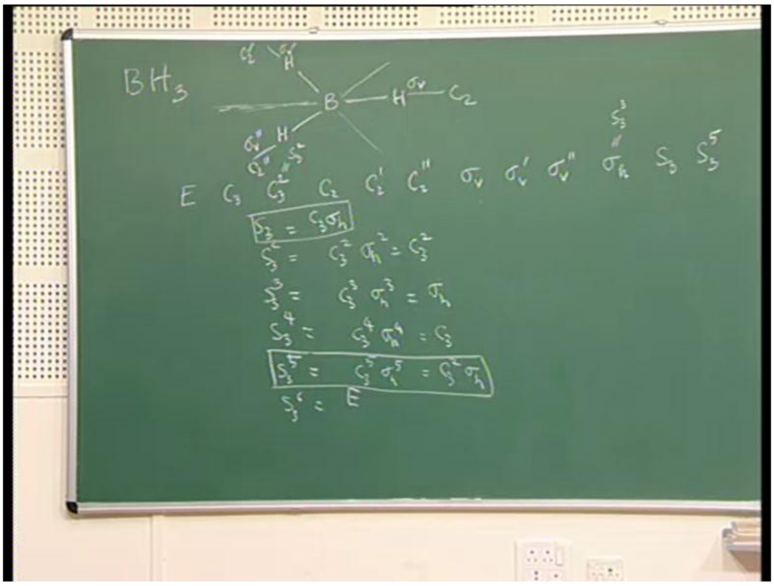

So, let us consider molecule B H 3 - Boron di-hydrate and this is a planer molecule and it is angle, so it is B, hydrogen each of these angles are 120 degrees. Now, let us try to write down the various symmetry elements, obviously the first symmetry element will write is the identity element. Then we notice that this if you take an axis perpendicular to the board, then that is a C 3 axis. So, C 3 will generate C 3 and C 3 square.

These are the two operations, generated by this axis perpendicular to the plane of the. Then, you say that there should be this H axis, so each of these correspondence to a C 2 axis, because you rotate by you go along this axis along the B H bond. If you take that axis that is a C 2 axis and will call these 3 will call them, will just order them, will call this C 2, will call this C 2 prime and will call this C 2 double prime; C 2, C 2 prime. So, C 2 because you rotate by 180 degrees and you get back the, an equivalent configuration.

Also we notice that this plane is a symmetric plane, because you reflect about this plane. These 2 H atoms are interchanged, were as this H atom and the B remain the in their in their original locations, so there are 3 sigma v’s. So, sigma v, sigma v prime, sigma v double prime this, so we just call this 3. So, we can call this plane as sigma v, this plane as sigma v prime, this plane as sigma v double prime.

Are there any more symmetry operations, now we one thing one symmetry operation that is very obvious, is the reflection about since is the planer molecule. It has a plane of reflection, so there is a sigma h. So, the plane containing the 3 atoms is sigma h, since it contains a C 3 and a perpendicular sigma h, that the will be an S 3. So, this axis is an S 3 axis, because you rotate by 120 degrees and then you reflect about a plane perpendicular, you get back an equivalent configuration.

Now what are the remaining operations, so you have S 3, now S 3 square S 3 generates the whole set of operations. S 3 generates S 3 square S a, but S 3 square is same as C 3 square. So, this is S 3 square, S 3 cube S 3 cube is same as sigma h, S 3, 3 times is nothing but sigma h because S 3, 3 times is you can say S 3 square equal to C 3 square sigma h square equal to C 3 square.

S 3 cube is equal to C 3 cube sigma h cube is equal to C 3 cube is identity sigma h cube is sigma h. what about S 3 4, so I can write this as C 3 4 sigma h 4, sigma h 4 is identity, C 3 4 is just C 3, S 3 5 is C 3 5 sigma h 5 this is C 3 square and sigma h. So, an S 3 6 is identity. So, clearly the only two distinct operations, so this is a new operation S 3 and S 3 5.

So, these are the only two new operations, rest of the ones are already listed in this case. So, the only other symmetry operation we need to take is S 3 5. So, you have 12 symmetry operations 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and these are the 12 symmetry operations of the B H 3 molecule.

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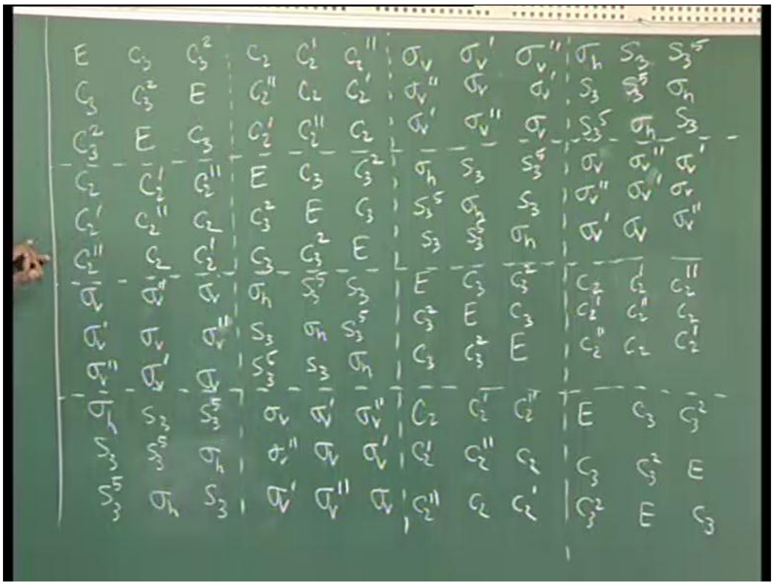

Now, let us make up the multiplication table for this group. So, to make up the multiplication table, you to write all the twelve elements C square and it is instructed to do this once. So, that you do not have I mean if you work this on once then once you have the practice, you can do it for many other groups. So, I will just write the multiplication table it is, I would not bother writing the same grow again. I will just starts straight with C 3, C 3 sigma h, S 3.

So, I just wrote the first row and the first column. So, the first row and the first column is this. Now what comes here is C 3 times C 3 that is C 3 square, here C 3 square times C 3 that is identity, here C 3 times C 3 square is identity, C 3 square, C 3 square is C 3. And now what comes here is C 2 followed by C 3, so remember what does C 2 do, so C 2 will switch these two hydrogen's, and then if you do a C 3 axis. So, then this hydrogen will come here, this hydrogen comes back to where it was, and this hydrogen and hydrogen that was here and sub here, so it corresponds to C 2 double prime.

So, you can verify this, so C 2 will bring this hydrogen over here and then C 2 followed by C 3 will bring it here. So, this hydrogen came back to where it was, but the other two hydrogen's they swapped their positions, because this hydrogen went here, this hydrogen came here. And that corresponds to a C 2 double prime, so you can show that this is C 2 double prime, then this will end up being C 2 prime.

This will be C 2 C 2 prime C 2 double prime C 2. So, and notice that the product of two rotations should be another rotation. So, C 2 followed by C 3 gives the C 2 double prime. Now what about sigma v followed by C 3, so let us look at that, so sigma v will switch these two. So, sigma v will end up switching these two and if you follow it by C 3, if you follow sigma v by C 3 what you will end up getting is will be sigma v double prime.

Sigma h times C 3 is just S 3, S 3 times C 3 is just sigma S 3 5, and S 3 5 time C 3 is sigma h, S 3 5 sigma h S 3. And I can go ahead and now I can do the same thing I can evaluate all of these. So, for example, we just do a few of them, and then will write the remaining. So, what is C 3 followed by C 2, so suppose I do C 3 first, so C 3 will let say bring just hydrogen here then followed by C 2. So, it has come here. So, this hydrogen has come here and that is corresponds to a C 2 prime.

C 2 time C 2 is nothing but identity, C 2 prime C 2 prime is identity, C 2 double prime C 2 double prime is identity. What is C 2 prime followed by C 2? So, if I do C 2 prime, then these 2 hydrogen's are swapped and if I follow it by C 2, then this hydrogen ends up coming here. So, this hydrogen got swapped here and then it came here, and this hydrogen came here, so it turns up to be a C 3 rotation.

This is C 3 C 3 square, C 3 C 3 square C 3 C 3 square. So, this is this part is now next if I do C 2 or if I do sigma v followed by C 2, this will followed by C 2 this will be, nothing but sigma h. So, sigma v followed by C 2 sigma v will reflect in this direction, so it will be directly translated here. And then you do C 2, then it will correspond to rotation by 180 degrees. So, the next effect is the sigma h, similarly sigma 2 prime sigma u prime is sigma h, sigma 2 double prime sigma v double prime is sigma h.

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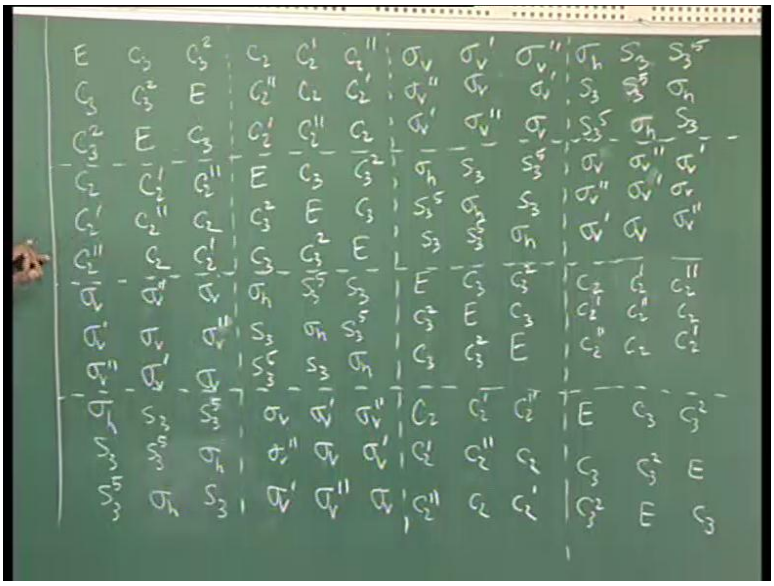

And what is sigma v prime followed by C 2, so sigma v prime that will take this here, followed by C 2, sorry sigma v prime will take this to this followed by C 2; that means, this stays where it is. So, that corresponds to that corresponds to an S 3. So, this corresponds to S 3 S 3 5 S 3 S 3 5 S 3 S 3 5.

And then you can show that sigma h followed by sigma v that is just no sigma h followed by C 2 is just sigma v prime, this is sigma v double no sigma v sigma v prime and sigma v double prime. S 3 followed by C 2 is just sigma h, is just sigma v followed by C 3. And if you just look at sigma v and C 3, you will get sigma v double prime, sigma v prime, this is sigma v, sigma v.

So, we have reconstructed most of the group, and you can do all the remaining part. I would not go into too many, I would not go into constructing the remaining, but essentially you can show that what comes here will be just be, that be the sigma v is the whole region is that sigma h C 3 is S 3 S 3 5 S 3 times C 3 is sigma h S 3 5 from C to sigma h. So, this is S 3 S 3 5 S 3 time C 3 is S 3 5 S 3 times C 3 square is sigma h, we have sigma h S 3.

Now, this will be C 3 followed by sigma v prime, that is same as sigma v prime followed by C 3 and that is sigma v. And so this is the sigma v double prime, sigma v double prime, and so this should be sigma v double prime sigma v. Now what about C 2 followed by sigma v? So, C 2 followed by sigma v is again sigma v followed by C 2, so sigma v followed by C 2 is sigma h. So, we have sigma h, C 2 prime followed by sigma v, so that is same as sigma v followed by C 2 prime. So, that is sigma v followed by C 2 prime is S 3 to the 5, this is S 3 this should be sigma h.

So, this will be S 3 5 S 3 to the 5 S 3. Now sigma v sigma v is just identity, here sigma v double we have these 3 sigma v prime followed by sigma v, so that sigma v prime will take this here, followed by sigma v that will keep this here. So, this atom ended up here and that corresponds to a C 3 rotation. So, this is C 3 C 3 square C 3 C 3 square C 3 C 3 square and sigma v prime sigma h so that is same as sigma h time sigma v and that will be. So, we have to, so sigma v time sigma h and the nothing but C 3 C 2 this will be C 2 prime C 2 double prime. Now, S 3 followed by sigma v that is same as C 2 followed by C 3 and C 2 followed by C 3 is C 2 prime, so it is the C 2 double prime C 2 followed by C 3 is C 2 double prime. And you can go ahead and fill these 3 also.

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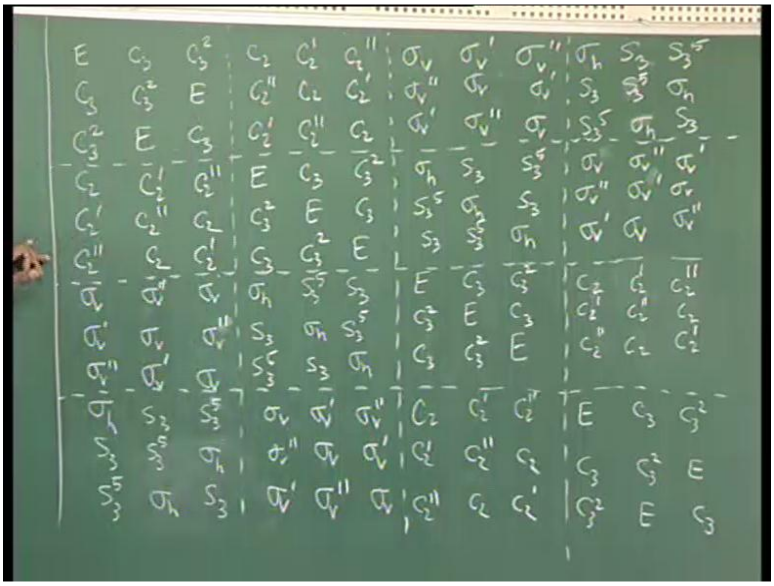

So, C 2 followed by sigma h that is sigma v C 2 prime followed by sigma h is sigma v prime C 2 double prime followed by sigma h is sigma v double prime, is like so sigma h followed by sigma v prime is C 2 prime. This is C 2 double prime so S 3 followed by sigma v so this should be. So, all these are some C 2 operations, you can identify exactly which one it is. So, S 3 followed by sigma v S 3 is C 3 times sigma h.

So, sigma h followed by sigma v is C 2. So, C 2 so the C 3 followed by C 2. So, C 3 followed by C 2 is C 2 prime. It comes in this order C 2 and here we can fill the remaining, so S 3 followed by C 2 prime. So, what we have C 2 followed by S 3 S 3 is same as C 3 into sigma h. So, C 2 into sigma h is sigma v. So, sigma v followed by C 3 is sigma v double prime and then this should be sigma v prime sigma v sigma v prime double prime, so most of the group is done and I just for convenience I will put into this little blocks.

So, and you will immediately see something that is happening. So, notice that within this whole block you only have sigma v sigma v prime and sigma v double prime, similarly in this block you will just have S 3 S 3 5 and sigma h, and this block again S 3 S 3 5 sigma h in this block you have E C 3 and C 3 square and so on. So, like in each of these blocks there seems to be one of these sets, one of these sets that seems to be appearing entirely within these blocks.

So, let us complete this now sigma v times sigma h is C 2, this is C 2 prime C 2 double prime, sigma v followed by S 3 again this should be S 3 followed by sigma v. So, it should be C 2 prime double prime C 2 C 2 C 2 and sigma h sigma h time sigma h is E, sigma h C 3 S 3 followed by sigma h is same as C 3 this is C 3 square sigma h followed by S 3 is C 3 C 3 square. So, this should be S 3 followed by S 3 that is C 3 square identity, identity C 3.

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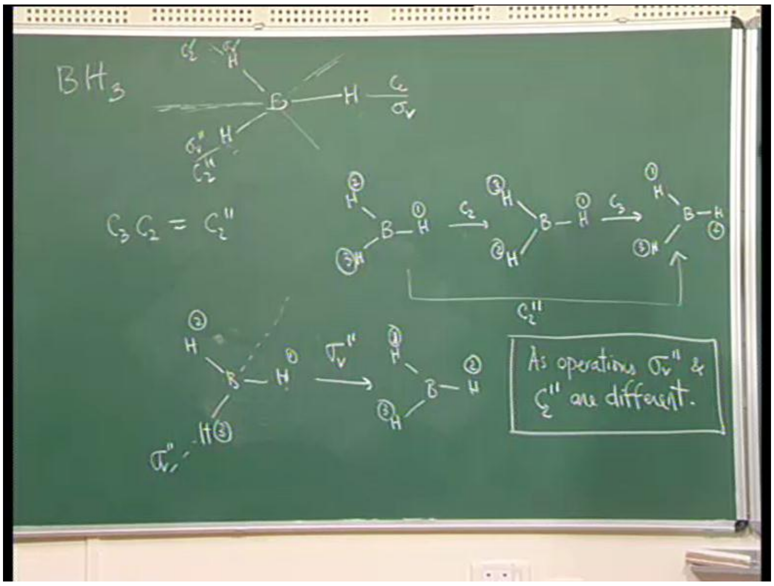

So, notice how the various groups, how the multiplication table naturally divides into these blocks. And again you have a rule that every row and every column has to have each element appearing exactly once. So, if you go down any row or you go across any column each element has to appear exactly once. So, these are the characteristics of the multiplication table, now there are few things that you have to be very careful, when you make the multiplication table.

And I will try to illustrate this like here. So, let us take this example, so I said that C 2 times C 3. So, we said that C 2 followed by C 3 is C 2 double prime. So, what we said is the following next can I lets take this by showing this, so C 3 C 2. Here C 3 C 2 means first you operate by C 2 and then by C 3. So, that is first operate by C 2 and then C 3 you will get C 2 double prime.

So, now let us look at this C 2. So, suppose I have started B H and I call this 1 2 3. So, suppose I operate by C 2 what I will get is B H will this first, H will be where it is. So, this is still H 1. These two will get switched, so this is H 2, this is H 3. So, when I operate by C 2, then I switch this H comes here, that H comes here. Then I operate again by C 3. So, if I do a C 3 operation, then what I get is B H H H, I have 1 here, 3 and another 2. So, I just rotate it clockwise, now notice one thing that I call this I said that this operation from here to here. This operation I called it, C 2 prime and C 2 prime if you look at it. So, C 2 prime means, so sorry C 2 double prime. So, C 2 double prime mean s 3 is where it is, so 2 and 1 are switched.

Now the obvious question that will raise is a following that suppose I did H and this is my sigma v double prime. So, if I reflect about sigma v double prime, so if I perform a reflection about sigma v double prime. Then what I will get is exactly that configuration, this is 3 this is 1 this is 2. So, the B is where it is the H the two H’s are switched.

So, why did I call this C 3 and why did I call this, why did I not call this operation sigma v double prime, why did I call it C 2 double prime, why did not I call it sigma v double prime. So, this is the question that will come. So, if you just look at the configuration, the answer is that if you just look into the configurations for this B H 3 molecule. Then the effect of C 2 double prime and sigma v double prime.

They seem to have the same effect on the molecule. So, whether I since it is a planer molecule whether I reflect or I rotate by 180 degrees, I seem to get the same net effect. However, or it is important to keep in mind at these two as operations they are different operations. But, these two are different operations, so for a molecule that that was not planer their effect will be different, because suppose you had a molecule that was not planer, you had an H you had something coming out here. That would go inside that as in a reflection, it would still stay above the board.

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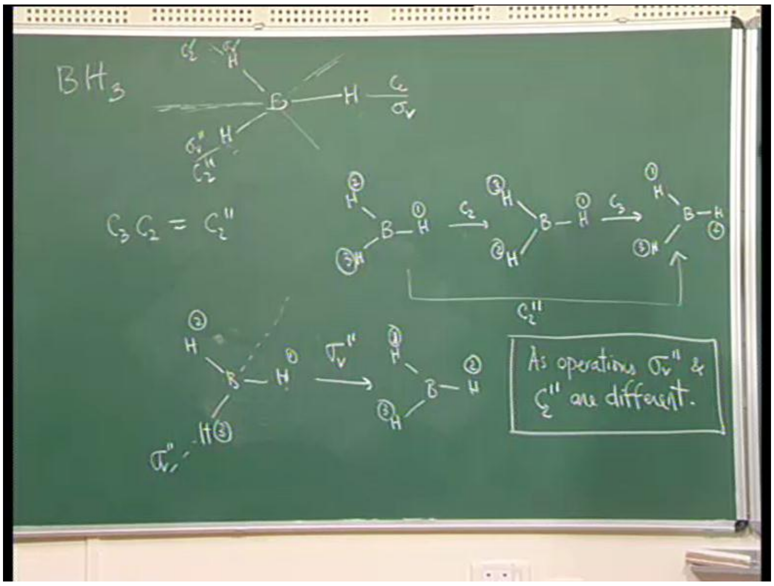

So, as operations sigma v sigma v double prime and sigma h are different. So, as operations sigma v double prime and C 2 double prime are different even though they seem to have the same effect on this planer molecule, but as operations these two are different, but this is a very important thing to keep in mind when you are making the multiplication table of any for any set of operations.

So, will always remember this in mind that when you are doing the multiplication table, you are writing a product of operations not the net effect, the net effect of these two operations can be thought of either a C 2 double prime or as a sigma v double prime, because they have the same effect on this molecule, but as operations these two are different.

And this is a product of these two rotations. So, it should be a rotation and. In fact, you can show that this is C 2 double prime and this is not sigma v double prime. So, remember sigma v double prime and C 2 double prime are not the same operations even though they have the same effect on this planer molecule but sigma v just reflects things from this end to here, where as C 2 rotates it by one 180 degrees. So, if you had anything that was outside the plane outs, that was coming outside at this hydrogen were under a C

2 under a C 2 operation that that piece would go inside, where as in a simple reflection that piece would come.

That piece would still stay out of the board. Now this gets us to a point that how do we what is the good way to see this effect, is there any way in which I can immediately look at product of operation and identify exactly which operation it is? in this case it was easy, because I knew that it is the product of two rotations. So, it should be a rotation, so if I had a choice between C 2 and C 2 double prime, and I will say that it should be, if I had choice between C 2 double prime and sigma v double prime. I would choose C 2 double prime but in general how do you characterize operations.

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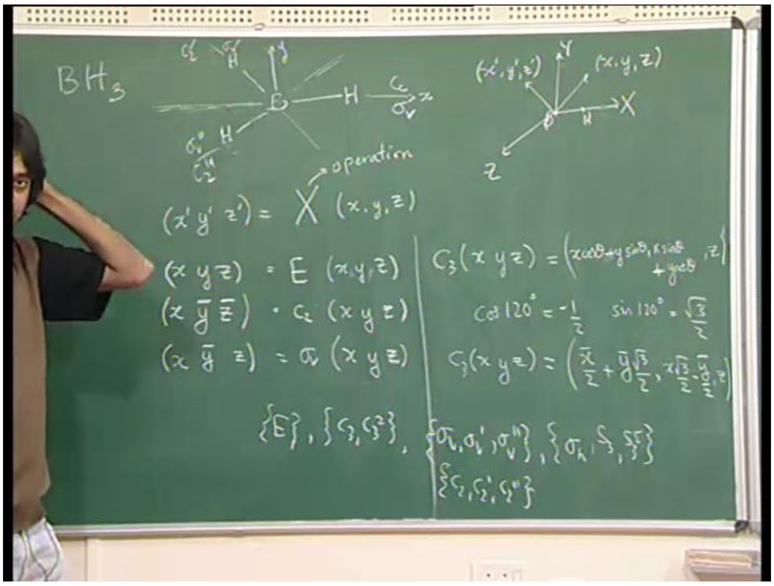

And this is the next part that I am going to do and I will do that right here, so what we should do is we shall take an arbitrary point. An arbitrary point in space, so let us take a coordinate system that is centered at the B atom and you have an arbitrary point x y z or you can take it as vector x y z. Now when you do an operation, when you one of this symmetry operation this goes to some other vector, with the same length, so it goes to some new vector x prime y prime z prime.

So, if you do an operation, so we write this in the following way, x prime y prime z prime is equal to this operation, I will just call the operation x operated on x y z, so this is operation. So, let us take some examples, so suppose x is equal to E. So, E operated on x y z, so that will give you a point E will give you the same point x y z.

And usually the commas are not put on you right. So, x y z goes to x y z under E what about C 2. So, if I do C 2 of x y z, now you are taking an arbitrary point and when you rotate it. So, let us call this the x axis and this is the y axis and this is the z axis is perpendicular to the plane of the board. So, we choose an axis such that this is B and this is H one of the H's.

So, C 2 corresponds to 180 degree rotation about the x axis, x axis y axis and z axis is. So, C 2 when you do a 180 rotation about the x axis, it is not hard to calculate what will happen. So, the x coordinate will remain the same. So, the x coordinate would not change at all since you are along the x axis, so this part is clear what about the y axis. So, when you do a 180 degree rotation y will go to minus y. So, y will go to minus y and this is denoted by y bar and z goes to minus z.

So, z axis if it is forward if you do 180 degree rotation it will go to the other side. So, that goes to z bar. So, this is the effect of C 2, so when I do C 2 on an ordinary point the x coordinate will not change, y coordinate will go to minus y, z coordinate will go to minus z. Similarly, you can do let us say sigma v, so if I do sigma v. Then I am reflecting about this point reflecting in this plane the plane, in which I am reflecting is the exact plane. So, if you reflect about the exact plane, then x and z remain the same x coordinate and z coordinate will remain the same, y coordinate will change the sign, because sigma v corresponds to reflection about the x z plane.

So, this now you can immediately see by this by this notation you can immediately see that C 2 and sigma v are different. So, as operations they are different, C 2 will take a point x y z to x y bar z bar where as sigma v will take a point of x y z to x y bar z. So, there is a fundamental difference between C 2 and sigma v.

Now I will live it as an exercise to you to work out all the remaining operations, I will write a few. So, for each of these you have to identify what is C 3, what is C 3 square. So, for example, what is what will C 3 be, C 3 operator on x y z, the z coordinate will remain the same. What about the x and y coordinate? So, C 3 corresponds to 120 degree rotation. So, if you rotate this vector by 120 degree about the z axis, then you know that your x prime is x cos theta. So, rotation by 120 degrees x prime becomes x cos theta plus y sin theta and your y prime becomes x sin theta minus y cos theta.

So, now cos theta, so cos 120 degrees is equal to half minus half sin 120 degrees equal to route 3 by 2. So, C 3 of x y z is equal to this is minus x by 2. So, it is x bar by 2 plus y route 3 by 2, sorry this is cos theta minus sin theta, this is sin theta plus cos theta. So, this is plus y bar by 2, then this is x route 3 by 2 minus y bar by 2 and z, so this is the solution. So, like this you can work out all the remaining operations, I will give it as an exercise to you to work out all the remaining operations.

So, next will continue will try to identify all the classes. So, you identify all the classes of this group, you can show that the classes are just E. E is one class C 3 C 3 square the 3 sigma v double prime sigma h S 3 S 3 5 and the 3 C 2. So, we already worked it out. So, will stop here and will start looking at more of these operations next time.

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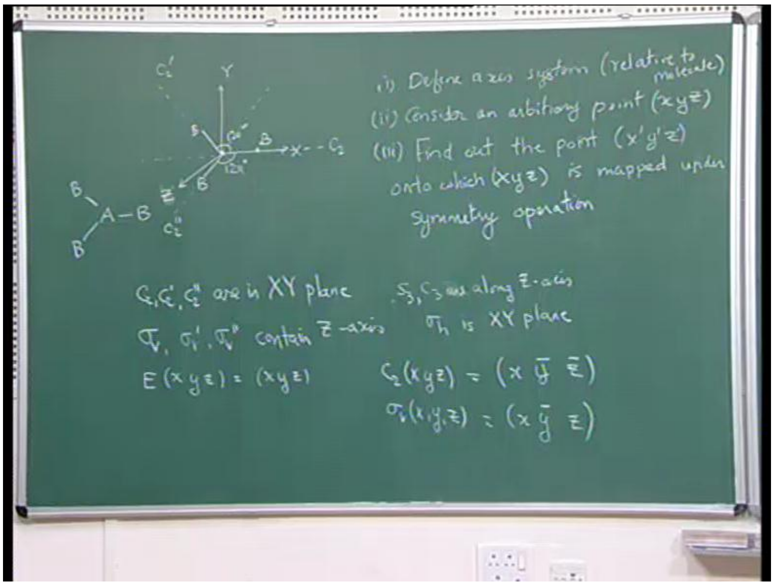

So, what we was saying is that you can represent all your operations as transformations on an arbitrary point. And to do that what we have to do first, is to define our axis system. Then you consider an arbitrary point an arbitrary point x y z and then you operate find out the point x prime y prime z prime to which x y z is mapped, on to which x y zero is mapped under operation under symmetry operation. So, just to repeat what we should do is first is to make the axis system and this is relative to molecule. And I will say exactly what I mean then consider an arbitrary point that is x y z find out the point onto which x y z is mapped to under symmetry operation.

So, in the example that we considered the A B cube planer, now my axis I am going to define my axis. So, that x axis passes through one of the B's the origin is always at the center of the molecule and if this is the x y plane and z is perpendicular. So, the x y plane the other 2 B's are in the x y plane. So, this B and this B are in the x y plane, they make 120 degrees with this with the x axis and 120 degrees here. So, what this means is that our C 2 axis this C 2 axis is located along the x axis.

This C 2 axis is located in the x y plane, this is C 2 prime C 2 double prime both of them are located in the X Y plane. So, this implies C 2, C 2 prime, C 2 double prime are in X Y plane. And sigma v, sigma v prime, sigma v double prime contained z axis, and sigma v will be in the exact plane. Sigma v prime will be in the plane that contains a z axis and it makes an angle 120 degrees with the x axis and similarly, sigma v prime will make an angle of minus 120 degree with the x axis and it contains the z axis.

So, similarly, what else can you say about the other plane, so C 3 is along z axis C 3 and S 3, S 3, C 3 are along z axis sigma h is X Y plane. And now knowing all these we can write the each of the operations the more, so I will just quickly list the operations. So, E operator on x y z gives me x y z which is very obvious, I will write the obvious one's first and then will do the complicated one's.

Now C 2 operated on x y z, so C 2 operated on x y z, it will not change x at all, but y will be mapped to minus y, z will be mapped to minus z. So, this is x y bar z bar, now before we let us do the easy one's as is said let us look at sigma v operated on x y z and sigma v is the exact plane. So, x and z axis will remain the same y axis be mapped to minus y. So, this is x y bar z, so that is sigma v what about sigma h.

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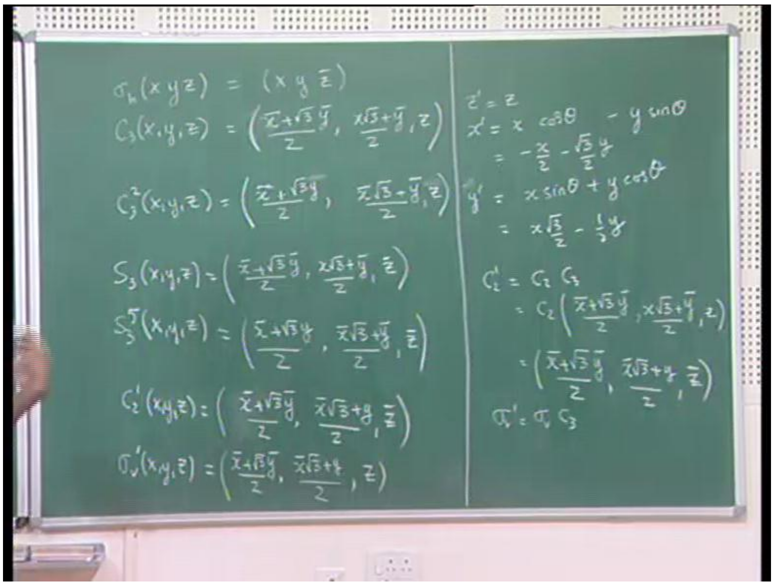

Sigma h is the x y plane, so sigma h will keep x and y the same and plane z will be mapped to minus z, z bar. What about C 3 of x y z? So, this is also not very hard to calculate this is 120 degree rotation. So, suppose you have an arbitrary point x y z, that is rotated by 120 degrees about this axis it will comes to it will come to some x prime y prime z prime and you know the relation between x y z and x prime y prime and z prime prime.

So, you know that z prime is equal to z, since the rotation is C 3 is about the z axis. So, the z coordinate will not change, x coordinate the new x coordinate will be a combination of the original x and y coordinate. So, it is x I will write it here x prime equal to x cos theta minus y sin theta, where theta equal to 120 degrees, so cos 120 is minus half. So, it is minus x by 2 sin 120 is route 3 by 2. So, minus route 3 y by 2 and y prime, y prime is x sin theta plus y cos theta. So, it is x 3 by 2 minus half y.

So, if you put this together x prime is just x bar by 2 plus route 3 by 2 y bar, x bar plus route 3 y bar by 2. y prime is x bar x minus x route 3 plus y bar. So, x route 3 plus y bar by 2 and z. So, this is the result of a C 3 operation, now how will you calculate C 3 prime. How will you calculate C 3 square? So, the first C 3 square, we do not have to do much, we just operate by C 3 twice and will get C 3 square. So, then will just be you can do it in a few different ways, but if you just do the operation again on this, what you will get is the following.

So, you will get x bar minus route 3 y bar by 2 or x bar plus route 3 y by 2. This will be sin theta, so x bar route 3 plus y bar by 2 z bar. So, that is C 3 square it is not hard to show you can do it in 2 ways, you can either operate by C 3 twice or you can just see the operation this corresponds to rotation by minus 120 degrees. So, C 3 square corresponds rotation by 240 or rotation by minus 120, so you can do it in either way.

So, we finished about half the operations 1 2 3 4 5 6. So, the remaining 6 they correspond to sigma v prime and so on. What about S 3? S 3 is just C 3 followed by sigma h. Sigma h just all it does it changes z coordinate, so S 3 of x y z is just this same thing, when you a change the z coordinate to z bar, x bar plus 2 z bar that is S 3 and similarly, S 3 square S 3 raise for 5 x y z this is just C 3 square into sigma h.

So, this is just C 3 square is just route 3 y by 2 C 3 square should just have z sorry now it will become S 3 five will have a z bar. So, this is also not to difficult, now the tricky part is calculating C 2 double prime calculating C 2 prime, C 2 double prime, sigma v prime and sigma v double prime. So, those are the slightly more tricky not a whole not more tricky because you know that C 2 prime.

C 2 prime as is same as C 3 followed by C 2 right. So, if I do C 3 then this will come here and if I follow it by C 2, then this will come here, So, C 2 prime is same as C 3 C 2. So, you use equal to C 2 C 3. So, it is C 2 C 3 is, so you do C 3 first. So, then this B will come here, then you do C 2, then this B will come back here. So, that will correspond to a C 2 prime. So, C 2 prime is C 2 times C 3 or in other words C 3 operated first followed by C 2. So, then you can calculate what is, so C 3 just gives me.

So, this is C 2 operated on x bar plus route 3 y bar by 2 x route 3 plus y bar by 2 z and you operate on that by C 2 and what C 2 will do is to change y bar change y and z to y bar and z bar. So, x remains the same, so this is just x bar plus route 3 y bar by 2 you change the sign of this. So, x bar route 3 plus y by 2 and z bar. So, that is C 2 prime so you have C 2 prime x bar plus route 3 y bar by 2 x bar route 3 plus y by 2 and z bar. So, that is C 2 prime.

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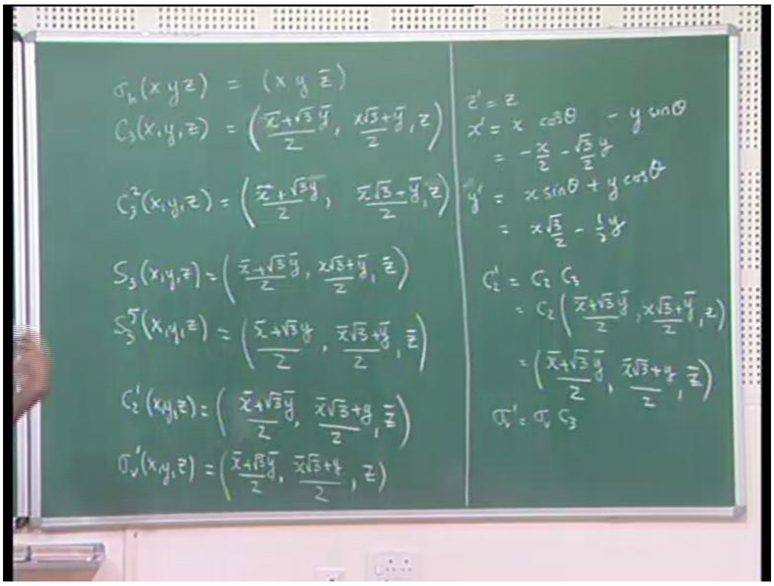

Similarly, you can also write that sigma v prime is sigma v followed by C 3 or C 3 followed by sigma v. So, you can do exactly the same thing and sigma v if you remember if you look at this it only changes y bar. So, it keeps x and z same as you get when you operate by C 3 and it changes the sign of y y bar. So, this is just, so I can write sigma v bar of x y z. This is just, so keep x and z keep x to this and z to this. So, you get change the sign of y.

So, y will become x bar route 3 plus y by 2 and keep the sign of z as it is, so z remains same. So, that is sigma v prime and very easily you can evaluate sigma v double prime sigma v double prime is just C 2 followed by C 3 square C 3 square followed by C 2 will give me C 2 double prime and similarly, C 3 square followed by sigma v will give me sigma v double prime. So, in this way you can you can represent all the operations.

And the nice thing about this sort of representation is that you can take products of operations very easily, you can you can see exactly. If you follow S 3 5 by C 2 prime you can easily show what points did you map on to, you can easily calculate what the result of various operations. So, this is something that will keep in mind will come back to this again when will look at the various representations of a group but what we will say right now is that this is a very convenient tool to study the various operations. And in the next class will start looking at various operations in molecules and looking at various representations.