Symmetry and Group Theory
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Lecture -52
Ascent and Descent in Symmetry - II

So, in the last class we were discussing how we can go from a higher order group to a lower order group by using Descent Symmetry and vice versa by using Ascent Symmetry and then there is a typically group-subgroup relation. And how if there is a group-subgroup relation between two point groups the IR representations or irreducible representations of one point group are also related to another point group.

So, what is the physical significance of that relation, that correlation between the IR representations of two point groups is that if a property transforms as one IR representation in one group, then it will transform to its correlated IR representation in the subgroup. So, and we saw that we try to correlate D4h and C4v point groups and we saw that each IR representation in C4v correlated with 2 IR representations in D4h.

Because D4h had 10 IRs and C4v we had 5 IRs, now let us see if we go one step down, what do we see so we were discussing that there might be a case where degeneracy is lifted, what do I mean by that? I mean that when I go from one point group to other, the degenerate representation in one point group may not remain as the same degenerate representation in subgroup, it may reduce further to two individual one-dimensional representations.

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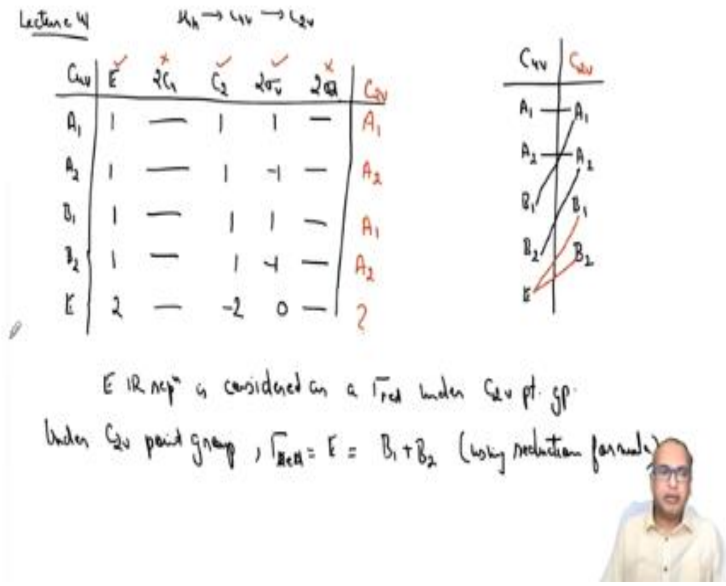

So, we will see that so let us go further down so let us start with lecture 41 today. So, we will start with C4v, writing C4v character table, so earlier we went from D4h to C4v now we will go one step down to C2v, so now for C4v we know that there are symmetry operations which are E, 2C 4, C 2, 2 sigma v, and 2 sigma d and the Mulliken symbols for IR representations are A1, A2, B1, B2, and E.

So, there are 5 classes of IRs present. Now on this side, we will write the lower subgroups which is C2v. Now C2v if you remember that it has only E, C2 and 2 sigma v, there is no sigma d, there is no C4. So, will not be writing the characters under these ones where the cross is there and then so let us write down these characters from C4v character table. So, we are writing in black from C4v character table which is 1, 1, 1.

And then again it is 1, 1, -1 for B1, B2 also it is 1, 1, 1 and 1, 1, -1 and this is 2, -2, 0. So, there is nothing here I am not going to write here because there is no corresponding symmetry operation in C2v. So, now if you see that now if you compare these characters to C2v character table what do you get, let us write down the corresponding Mulliken symbols here, so for 1, 1, 1 we know that it is going to be A1, for 1, 1, -1, again it is going to be A2.

And we have 1, 1, 1 again so it is A1 and it is A2 over here and there is no 2D representation in C2v point group, so we cannot write anything over here so now if you see if we try to draw a correlation between C4v, let me use the black colour for C4v, so if we try to draw this correlation between C4v and C2v, we see that A1, A2, B1, B2, E and we have A1, A2, B1, B2 so now we know that A1 is correlated with A1, A2 is correlated with A2;

B1 is correlated with A1 and B2 is correlated with A2. So, we can see that here directly now there is no B1 and B2 in C2v are not correlated with anything in C4v so far, to any of the 1D representation. Now how do we find out what is E going to be represented under C2v point group? So, how do we do that? It is not as straight forward but it is not difficult also, so what do we do? So, E representation E IR representation is considered as a tau reducible under C 2v point group.

So once you do that now the case is simple so if you consider E as tau reducible you can reduce it under C 2v point group using reduction formula. So, I will write down under C2v point group tau E or tau reducible which is nothing but E in C4v point group reduces to B1 + B2 this comes using reduction formula, which I am not going to show how to do this calculation again, you must have done a lot of practice by now.

So, using reduction formula we know that now E under C4v point group can be reduced to B 1 + B 2, so that means now I can say that my E is correlated with B1 and B2. So, now you see that B1 and B2 both are correlating with E;

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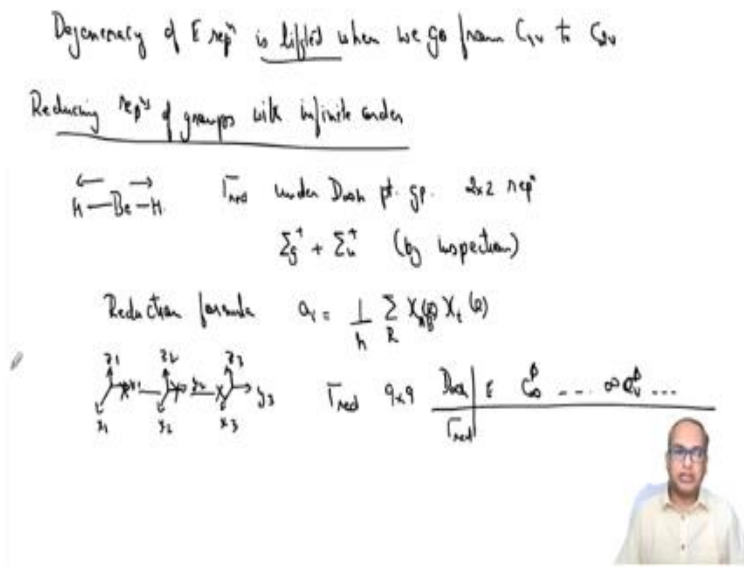

That means that my E representation is now, which was earlier degenerate in C4v, is now, so the we can say that the degeneracy is lifted now when we go from C4v to C2v. So, you can say degeneracy of E representation is lifted when we go from C4v to C2v. So, this is a very important point that degeneracy is lifted, because now consider that any property let us say that let us find out what is the basis set for E under C4v, let me look at the character table and let us find out what is the basis under E.

So, for C4v for E the basis is x, y, so x, y jointly forms a basis. Now what happens here in case of C2v point group. So, x forms the basis for B1 and y forms of basis for B2, so now a property let us say that the px, py orbitals were earlier degenerate in C4v point group, now when you go from C4v to C2v now px orbital and py orbital has their independent symmetry and hence it might have independent energy.

There can be accidental degeneracy, that is the different case but the property which is along x axis and along y axis are no longer have same symmetric criteria under C2v point group, which earlier had same symmetry because they were degenerate they were bound to be degenerate because of symmetry. So, that is a very, very important concept that degeneracy can be lifted and if you go from a higher order point group to a lower order point group.

So, now let us start with the actual reason why we started discussing ascent and descent in symmetry, so the reason was how to reduce reducing representations of groups with infinite order. This was the reason why we started discussing this so if you remember that we were discussing Beryllium Hydride case and we had made these two arrows as to sigma bonds and we took we made a tau reducible under D infinity h point group.

So, now the problem is, so this was a 2 cross 2 representation, so we could easily inspect that this is sigma g +, + sigma u + this was obtained by inspection, why it was obtained by inspection? Because if you notice that the reduction formula, let us write down the reduction formula, so reduction formula a i is equal to 1 over h summation over all R chi A B and chi i R. So, now if you see where this is the character for irreducible representation;

This is the character for reducible representation under symmetry operation R, and this is summation over all R and the important point here is that h is in denominator, which is the order of the group. Now if you have infinity order point group, then you will have infinity here to divide to, so the whole thing goes to 0. So, that means you will not be able to calculate the coefficients for irreducible representations.

As in how what is the number of times a particular a i will come over, so this becomes difficult how to use it. So, in case of for 2 cross 2 representation it was rather easy that by inspection we could do it, so let us assume that let us say if we have a molecule x, y, x and now I am interested in some property which requires me to formulate 3 vectors x y z, x y z, x y z, at each atom. So, I can have this requirement that this is my x 1, y 1, z 1, x 2, y 2, z 2, x 3, y 3, z 3.

Now this tau reducible will be 9 cross 9, so first of all it is not straight forward to construct a tau reducible with 9 cross 9 if we have infinity order because with infinity order the creation so let us say if we have D infinity h over here, and we have E, C infinity, infinity C v phi, sigma v, this is phi and so on. So, it is not straight forward to create the tau reducible itself because it is 9 cross 9 order, what happens to each vector under this infinity order operations is not easy to calculate.

So, then forget about what is the how do we reduce this to IR representation that is even more troublesome.

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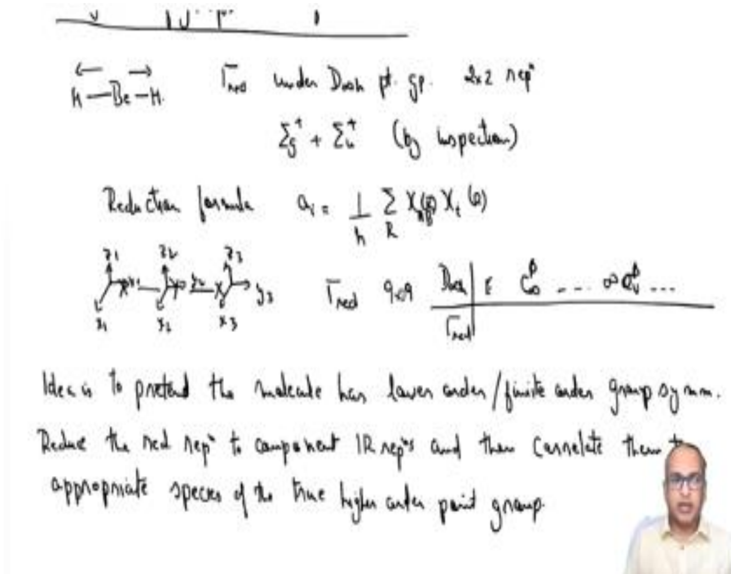

So, then what happens what you do here is so you take this advantage of group-subgroup relation and go to a lower point group, lower point group. So, the idea is to pretend the molecule has lower symmetry lower order or finite order, but you have to choose such orders so that it is subgroup of infinity order point group, finite order group symmetry, now reduce the reducible representation to component IRs and then correlate them to appropriate, we will see this how to do this for this particular example, itself appropriate species of the true higher order point group. So, we first assume pretend that the molecule actually has a lower order point group, which has to be a subgroup of the original point group. So, original point group here is D infinity h, so let us assume that the molecule is actually D 2h symmetry.

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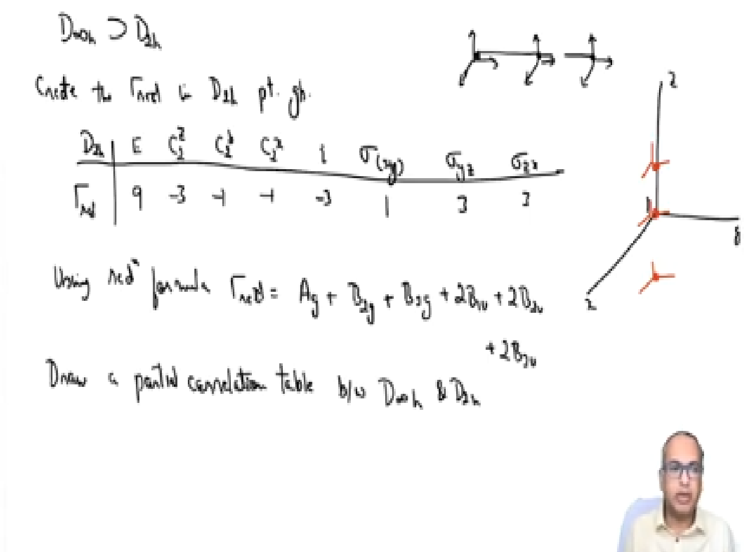

So, we know that it is not but we are just pretending, now we know that D infinity h has a subgroup which is D2h that is that we can easily identify. Now it has to be D2h so now create the tau reducible in D2h point group, so what is D2h? So, let us list down the symmetry operations, so we have E, C2z, C2y, C2x then we have i, sigma xy, sigma yz, sigma zx that is all and this is my tau reducible.

And where are the vectors, the vectors are if there are three atoms in linear molecule these are my vectors, each of this has a x, y, z and now these are my bonds. So, now we will not write the independent matrices for 9 cross 9 for all the symmetry operations what we will do is we will just see which of these vectors will change position and accordingly whether they will contribute positive negative or 0 to this symmetry operation.

So, none of the vectors will change so it will be 9, for C2z, so for C2z, 3 vectors will not change which are oriented in let us say if the molecule is oriented vertically then 3 z vectors will not change and x and y will move, so you will have only let us say if it is C2z how many vectors should not move so there should be 6 vectors which will go to negative side and so we can just draw it the bigger picture, otherwise you will get confused;

So, you have one atom another atom, another atom and I have small vectors which are x y z here, x y z here, x y z here and this is my bigger x y z frame. So, if it is drawn like this so your 3 z1, z2, z3 will contribute + 1, + 1, + 1 each all 3 x is will go to -x is so that will contribute -3 and all the y s will contribute – 3 so overall it will be – 3. Now for C2y if you consider, so C2y is going through this these two atoms are replacing with each other.

So, they will not contribute anything. Whereas the y will contribute + 1, x will contribute – 1, z will contribute - 1. So, you will have – 1. Similarly, here – 1, i will contribute - 3 similarly, sigma xy if you consider so sigma xy you will have + 1 sigma xz will be + 3 and + 3, so this you should be able to calculate out if you do it carefully. Now, I can create this tau reducible in lower symmetry point group in D2h.

And I should be able to reduce this also, so using reduction formula, I can say my tau reducible is equal to Ag + B2g + B3g + 2 B1u + 2 B2u + 2 B3u. So, this was a 9-dimensional representation, so overall it should contain 9 1D representations, so this is 1, 2, 3, 4, 5, 6, 7, 8, 9 so this is correct. Of course, you will have to use the reduction formula to be able to say that that it is correct.

Now, how do we convert these into D infinity h Mulliken symbols? So, we have to correlate all these IR representations under D2h to D infinity h, so what we have to do is, we have to write let us draw partial correlation table between D infinity h and D2h. So, I am saying partial because it is an infinity point group, I cannot draw complete correlation table.

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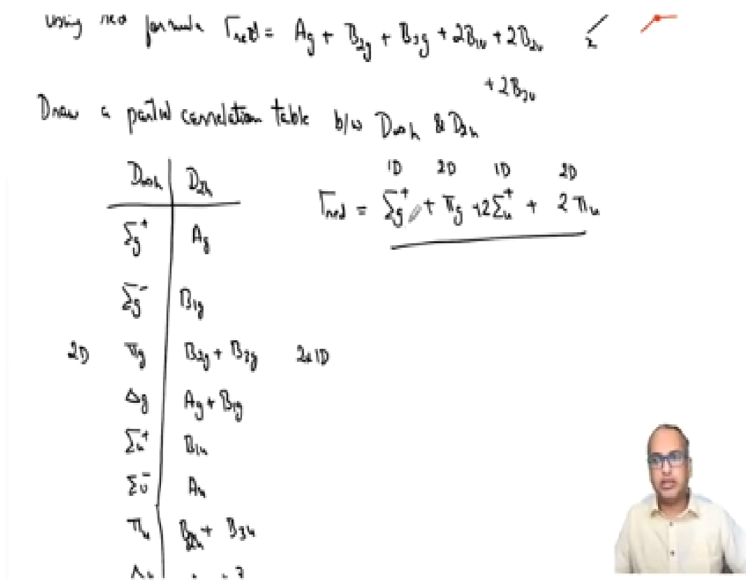

So, let us draw this so of course you will have to do either it will be given to you, you can find out in books or you can draw it yourself so write down the characters and how we have been drawing between before D4h and C4v and C2v use the same principle, I will just draw it for you I will just write it down. So, you have sigma g +, sigma g - then we have pi g we have delta g sigma u +, sigma u -, pi u and delta u.

Now this one correlates to Ag then we have B1g will have B2g + B3g, Ag + B1g, B1u this was Au with B2u + B3u. And this is Au + B1u, so now we know that our tau reducible was let me go up this is my tau reducible so if I correlate back A g to IR representation under D infinity h. So, I have got sigma g +, B2g and B3g together it is pi g so you have pi g. So, now again you see that there is a this is a 2D representation and these are 2 1D representations.

So, there is a degeneracy which is being lifted when you go from D tau h and D 2h. So, this is done now, 2B 1u and 2B 2u so what do we have here two of these B1u, B2u and B3u. So, B 1u corresponds to sigma u + and these are two of those so we have 2 then we have 2 of B 2u + B 3u so B 2u + B 3u gives you pi u. So, we will write 2 of pi u, so now this is 1D this is 2D so you have 1, 2, 3, 4, 5, 6, 7, 8, 9 so total 9 dimensions are coming.

So, because this is 1D this is 2D this is 1D this is 2D, so 1, 1 dimensional 1, 2 dimensional 3, 2, 1 dimensional 5 and then 2, 2 dimensions so 4 so 5 + 4, 9, so now you have got yourself tau reducible. And now next step is whether you want to go for studying Molecular Orbital diagram or any other thing. Like whatever physical property you want to study that you can, but the idea was to how to reduce a representation under infinity order point group;

Which cannot be done directly by reduction formula and what you have to do is you have to go to a, use descendent symmetry go to a subgroup of bigger or infinite order point group find out the reducible representation in that point group, reduce it. And now correlate back the IR representations, back to the higher order point group and find your answer and proceed further as depending on the physical property what whatever you are looking for.

So, I hope this should be very, very clear now and I would suggest do practice it a lot again and will go to next physical property, so chemical bonding is now complete. We will go to next physical property in next class onwards, thank you very much.