Symmetry and Group Theory
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Lecture -41
Tutorial-8

So, welcome to this week's tutorial. In this week we will be looking at few more applications of direct product. So let us see what kind of questions can come in direct product applications what kind of problems you can encounter in direct product applications.

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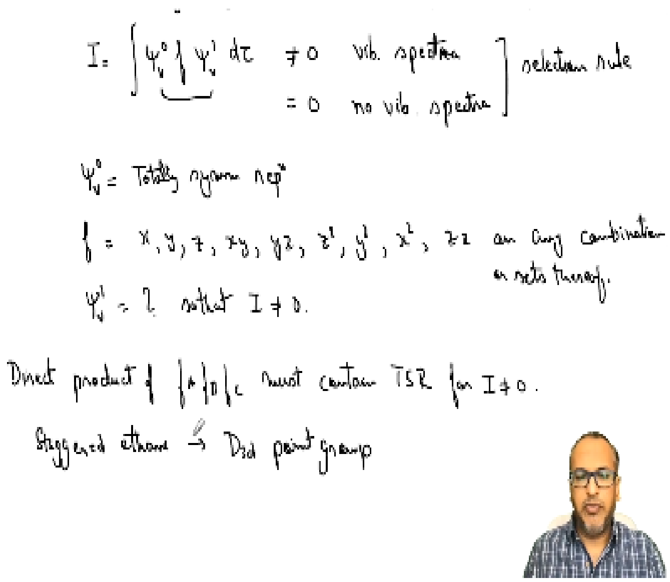

So, let us start tutorial 8. So let us try to solve at least two questions. So, let us say in later part of this course we will be looking at introduction to spectroscopy, so this application is in spectroscopy as we have also learnt in the regular class. So, let us say somebody wants to record vibrational spectra. Do not worry about what this spectroscopy is and what is the use of the spectroscopy, we will come back to it later.

But let us say if we are interested in recording vibrational spectra of staggered ethane and maybe another molecule is any other molecule with square pyramidal geometry. So, now we want to know whether this Vibrational Spectra will come in these molecules or not, and so to know this the kind of integration that we need to solve is of this form, and do not worry about how this integration comes in but let us directly look at the application part.

So, this is the kind of integral that we need to solve if this integration does not go to zero, we will see vibrational spectra; if this integration goes to zero, no vibrational spectra. So, this together is called as Selection Rule. So, now let us take the question is given that psi v 0 belongs to totally symmetric representation, and f belongs to x, y, z, xy, yz, z square, y square, x square, zx or any combination of these or sets thereof.

So, these two things are given so psi 0 is totally symmetric representation, f belongs to any of these functions that means the basis set of this function is known. Now we know that this is totally symmetric representation, now the question is asking that what would be psi v 1 so that I does not go to 0? So, now you try to remember under what conditions the I does not go to 0? What are those conditions?

So, the direct product of all these three, direct products of let us say fA, fB, fC must contain totally symmetric representation for I is not equal to 0, remember that we have studied this. So, now we have to find out what will be your psi v prime for these two are given to you under these two different point groups. So, the first point group is staggered ethane. So, staggered ethane you must know what is the point group of that.

So, staggered ethane belongs to D3d point group, again we have discussed this, so I am not going to discuss this again. So, now let us try to find out what is the character table of D3d? We will see what we have to read out of the character table. So, I will just write down the character table of D3d.

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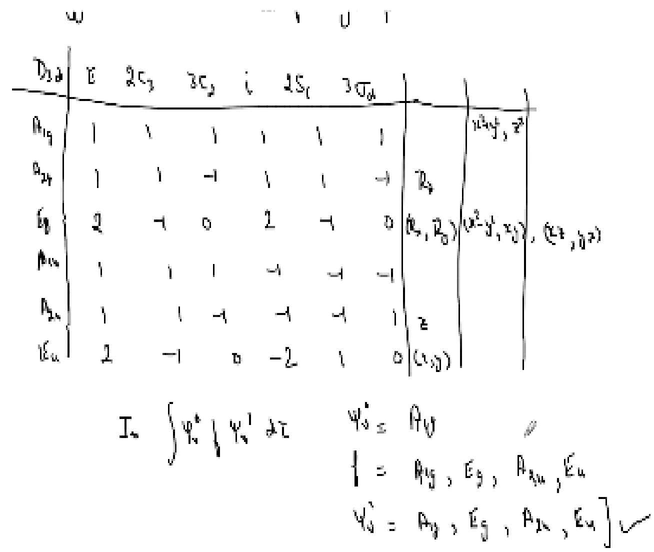

Let me take a look at. So what we have here is E, 2C3, 3C2, i, 2S6, 3 sigma d and we have A1g, A2g, Eg, A1u, A2u, and Eu. Now we have totally symmetric representation, so all ones A2g will be 1 1 -1 1 1 -1, Eg will be 2 -1 0 2 -1 0 and we have now, 1 1 1 -1 -1 -1, 1 1 -1 -1 1, 2 -1 0 -2 1 0. Now if you look at these two areas here, so you have the basis sets written here so my basis set here is Rz, Rx, Ry.

Then I have z over here x y, then I have x square plus y square, as well as z square, then I have joint representation for x square minus y square, xy as well as xz, yz so these are my basis sets. Now I know that my psi v 0 is, so I is equal to psi v 0 f psi v 1 d tau, now psi v 0 is A1g, it is given that it is totally symmetric representation, f now can belong to any of this combinations with x y z, x square y square z square.

So, it can be A1g, it can be Eg, it can be A2u now our job is to determine psi v1 now it is very simple so psi v1, whenever f is A1g it has to be A1g, whenever f is Eg it has to be Eg. Similarly, A2u and so why is that, because now if I take a direct product of these three this will be a totally symmetric representation if I take a direct product of Eg into Eg this will contain A1g. If I take a direct product of A2u into A2u this will be A1g.

Similarly, Eu into Eu would also give you totally symmetric representation. Remember this thing comes from that direct product of two same irreducible representations will always contain a totally symmetric representation. And we want totally symmetric representation at least one of the components has to be totally symmetric representation. So, the only combinations where I will contain totally symmetric representation will not go to 0, others will all go to 0.

So, combinations of psi v 1 as A1g, Eg, A2u, and Eu will only give A1g and that is how these will be your correct answers. So, psi v can belong to any of this and only then it will give you non-zero I and hence the vibrational spectra of staggered ethane will be visible.

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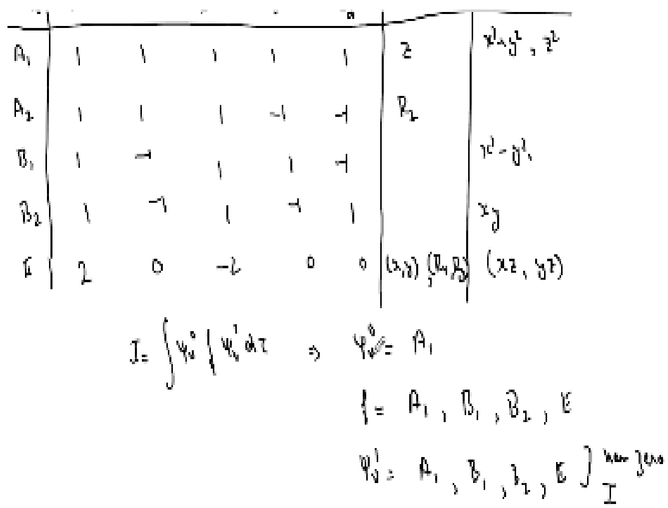

So, that is one now let us see the same case for square pyramidal molecule. so square pyramidal is C4v point group. So again, for C4v point group we need to first write down the character table. And then look at the basis sets. So, I suppose this should be easy but let us just do it for completeness E, 2C4, C2, 2 sigma v, 2 sigma d. And this side I have A1, A2, B1, B2, E and here I have all ones totally symmetric and here I have 1 1 1 -1 -1.

Now the most important part is to look at the basis set areas. So, this will be z, Rz and here it is x, y, Rx, Ry, x square plus y square, z square, x square minus y square, xy, xz, yz. Now here my integral is again of the same form psi v 0 f psi v 1 d tau. Now I know that psi v 0 is A1 totally symmetric representation, now what are my f’s what are the possibilities for f’s. So, f can take value as A1 because of this, then B1, then B 2, E.

And so that means my psi v 1 will also be of these forms that means the basis for psi v 1 can be A1, B1, B2 and E, depending on what is the actual function. Accordingly, this psi v 1 will have different basis, so these will have non-zero I. Because this direct product will contain totally symmetric representation. So, this should be very, very clear.

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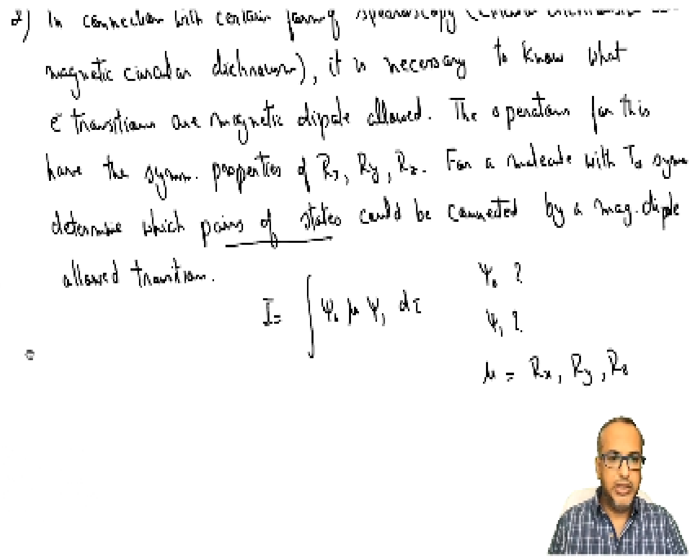

So, now let us look at one more example, one more question, one more application indirect product. So, the question reads like this, so in connection with certain form of spectroscopy again it is a spectroscopy related problem. So, in connection with certain form of spectroscopy which is a circular dichroism, if you have not learned about this you will learn it later and I mean not in this course though, magnetic circular dichroism.

So, it is necessary to know what electronic transitions are magnetic dipole allowed? So, we have already learned which transitions is electric dipole allowed. So, this one is about magnetic dipole allowed. So, in this case the transition dipole moment will be of different nature. Now the operators for this have the symmetric properties this is another way of saying that the basis of this operator symmetry properties of Rx, Ry, Rz.

So, now the question part is for a molecule with Tetrahedral Symmetry Td symmetry, Td point group, determine which pairs of states could be connected by a Magnetic Dipole allowed transition. So, now they are asking that if the operator for this have the symmetry properties as

Rx, Ry, Rz now for a molecule with Td symmetry, let us say methane determine which pair of states could be connected by a magnetic dipole allowed.

So, when they are asking which pair of states? That means they are asking that what will be the symmetry of those states which can be connected by a Magnetic Dipole Allowed Transition. So, the first thing first is to set up integral for this, so integral will be the same so you want to see under what conditions the integral will not go to 0, so psi 0 mu psi 1 d tau. Now, in this case we do not know what is psi 0 we do not know what is psi 1, because we want to calculate the pair of states these are the pair of states.

Remember that these are the functions which describe the states, psi 0 and psi 1. So, we do not know what is psi 0 and what is psi 1 or what is the symmetry of psi 0 and symmetry of psi 1? So, we want to calculate that and given is that mu has symmetry as Rx, Ry, Rz. Now we want to choose psi 0 and psi 1, so that the overall direct product of this does not go to zero, because it has to be connected by a dipole magnetic dipole allowed transition. So, that means I should not go to 0. Now let us look at the character table may be let us go to next page.

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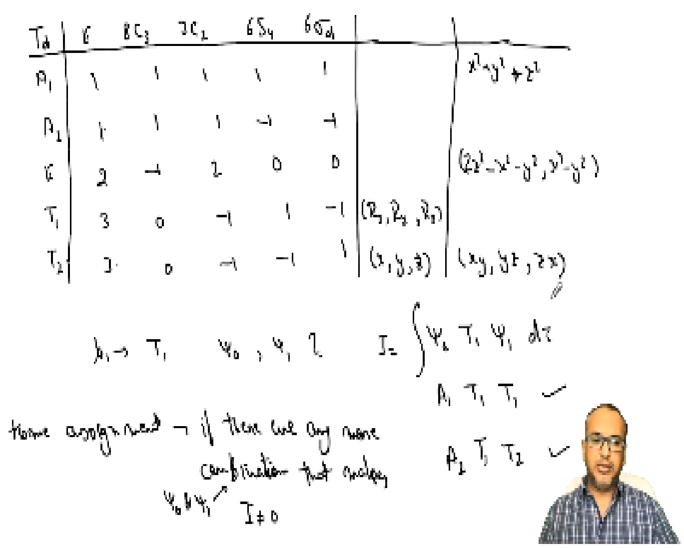

So, let us look at the character table of Td symmetry so tetrahedron point E, 8C 3, 7C2, 6S4, 6 sigma ds and you have A1, A2, E, T1, T2, ones, 3 ones and 2 minus ones, we have 2, minus 1, 2, 0, 0, 3, 3, 0, 0, - 1, - 1. Now is an interesting part which you want to focus on Rx, Ry, Rz, and this is my x, y, z, x square + y square, although it is not required to see this one now. E is 2 z square minus x square minus y square. So, now the question is saying that mu has the symmetry of T1, mu is symmetry of R x, R y, R z.

Now psi 0 and psi 1 we do not know. Now we have to take a direct product of psi 0 mu and psi 1, so that the overall thing contains totally symmetric representation. So, now what are the combinations which are possible so you have psi 0, T1, psi 1 this is my integration. Now we know mu so I have put T1 over here. Now what are the combinations for which psi 0 and psi 1 can be put over here so that the overall direct product triple product of this will not go to 0 that means it should contain totally symmetric representation.

So, I can choose this as A1, T1, T1 that is my first possibility because now I know that if this is A1, it will not matter the direct product of this will not change upon multiplication with A1 because A1 is all ones. So, T1 into T1 must contain A1. So, overall it will contain A1, so this will not go to zero then what else now the other possibility is T1 is constant, T1 I cannot change. Now the other possibility is if I create another T1 by multiplication of these two.

How can I create another T1 by multiplication of, so it has to be a one dimensional and another three dimensional representation so that means it has to be at T 2 now if I combine T 2 into A 2 what do I get. So,1 into 3 will give me 3 1 into 0 will give me 0 1 into - 1 will give me - 1 minus 1 into - 1 will give me + 1 - 1 into 1 will give me - 1. So, that means if I multiply A2, if I take a direct product of A2 into T2, I will get T1.

So, that means again I will have a situation where direct product T1 will come. So, this combination will also not go to zero, so that means there are two possibilities which will not go to zero at least, by just looking at it. Rest of the possibilities I would ask you to do a home assignment, you have got the concept, If there are any more combinations that makes I not equal to 0 combinations of psi 0 and psi 1.

So, these are the two possible combinations that I have just told you by just using the direct product rules but you can take different combinations, you can place different IR irreducible representations here and see the triple direct product whether it contains totally symmetric representation or not and accordingly tell what will be the answer. So, the idea is once you know how to deal with direct product you can solve a large number of Spectroscopy based problems.

So, that is all for today. So, let us look at symmetry adapted linear combinations, more problems into that next week all right, thank you.