Symmetry and Group Theory
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Lecture -38
Direct Product Applications

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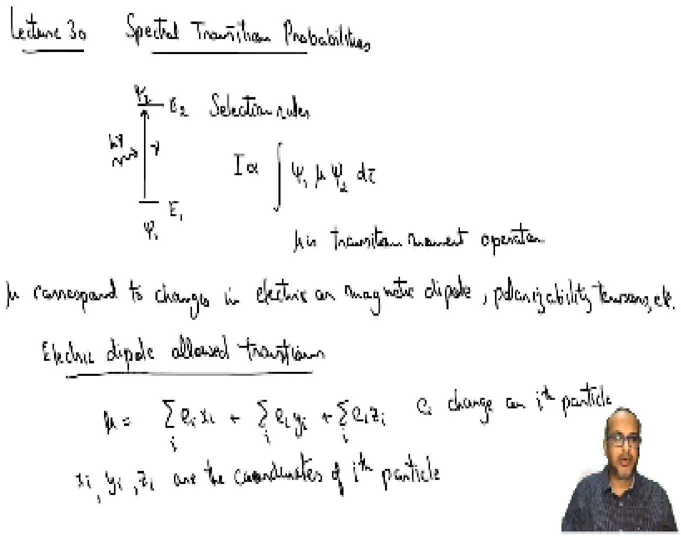

So, in the previous lecture we have discussed an example where we looked at the application of direct product in solving energy elements. So, in this one we will look at one more application of direct product where we will be looking at something called as Spectral Transition Probabilities. So, what is it? What is the meaning of this term? Let us first try to understand that.

So, if we have 2 energy levels, if you are trying to perform spectroscopy and we have 2 energy levels let us say, E 1 and E 2 and then there is energy difference between this which is defined by nu. So, the energy corresponding to h nu will be able to carry out the transition from E1 to E2. And whether this transition will take place or not will be defined by the selection rules.

So, selection rules will tell you, this you must have learnt in spectroscopy that whether the transition will be possible or not. So, let us say how does the selection rule come actually. So the intensity will of this transition will be directly proportional to psi 1 mu psi 2 d tau. So, where psi 1 defines the state for the state 1 and psi 2 defines this state the excited state. And mu, what is mu? So, mu is called as transition moment operator.

So, which can take different forms as in it can correspond to. So, mu can correspond to changes in electric or magnetic dipole, polarizability tensor etc. So, depending on what type of spectroscopy we are using. So, let us say in this case we are considering electric dipole allowed transitions. So, electric dipole allowed transitions. So, what is the meaning of this? That means the charge distribution in ground state and excited state corresponds to or differs in a manner which is similar to a electric dipole.

So, here charge distribution between the state 1 and state 2 are that is the ground state and excited state forms like a electric dipole over here. So, if this electric dipole can now interact with the oscillating electric field vector of the electromagnetic radiation. And then that interaction leads to either absorption of energy by the system or release of energy by the system, then we say that there is a transition which has been carried out.

There is a change in the dipole moment that has been carried out because of the applied frequency, right. So, now let us say that what is the form of mu, So, mu can be written as summation e i x i + summation e i y i + summation e i z i. And this will be summation over all i. Actually summation can be taken common here. So, what is ei? ei is charge on ith particle and x i, y i, z i are the coordinates of the particle.

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Electric dipole allowed transitions

$\mu = \sum_i e_i x_i + \sum_i e_i y_i + \sum_i e_i z_i$ e_i charge on i^{th} particle

x_i, y_i, z_i are the coordinates of i^{th} particle

$I_x \propto \int \psi_i\, x\, \psi_j\, d\tau$ $I \neq 0$ if $I_x, I_y, I_z \neq 0$

$I_x \neq 0$ if ψ_i, x, ψ_j correspond to IR rep^n^ whose direct product contains TSR.

$I_y \propto \int \psi_i\, y\, \psi_j\, d\tau$

ψ_i & ψ_j correspond to IR rep^n^ whose direct product contains an IR which has x on the basis

$I_z \propto \int \psi_i\, z\, \psi_j\, d\tau$

So, these are the coordinates and charge. So, now that means if I want to write the intensity factor again, so I can say that the intensity in x is proportional to integration of psi i x psi j or you can write 1 2 here d tau. Similarly, intensity along y will be proportional to psi i y psi j d tau and intensity along z will be similarly proportional to psi i z psi j d tau. Now, I will not be equal to 0 if any of this I x, I y, or I z is not equal to 0.

So, you can take if I x is not equal to 0 then also the total intensity will not be equal to 0 or if I y is not equal to 0, total intensity will not be equal to 0 and so on. So, what we need to calculate we need to calculate individual contribution of intensities and if anyone of them is not equal to 0 we will say that the spectral transition will happen otherwise the spectral transition will be forbidden.

And that is how you define the selection rules whether these 2 states will have transition from 1 state to another or not given the particular frequency the spectra will be transition will be allowed otherwise it will be disallowed. So, now let us say when this integration will be non-zero the integration will be non-zero when the direct product of the psi i x psi j, I mean the corresponding IR representations will contain totally symmetric representation.

So, I x will not be equal 0 if psi i x psi j corresponds to IR representation whose direct product contains TSR. And similarly, we can say for I y and I z. Now, there is interesting thing that we have x, one of the function we know that it is a unit vector along x, right, x can be treated as unit vector, y is unit vector along y, z is unit vector along z. So, we already know if we refer to any character table.

We already know the IR representation corresponding to x, right, and similarly corresponding to y. So, that that means we can reduce this condition to if psi i and psi j correspond to IR representations whose direct product contains an IR which has x as the basis because if it will have x as the basis that would mean that the direct triple direct product will contain A1, right, similarly for y and z will follow, right to see.

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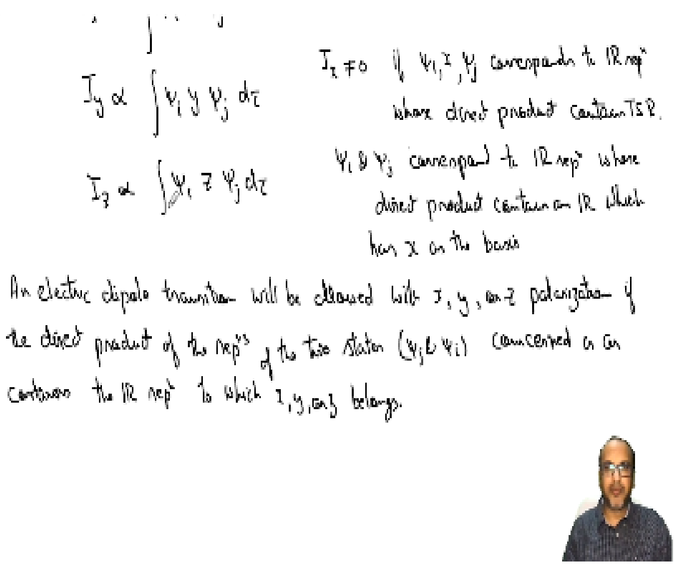

So, we can now write a statement that an electric dipole transition will be allowed with x, y or z polarization. So; why x, y, or z polarization? Because this is the polarity of the radiation which is applied, right, if the direct product of the representations of the 2 states which are psi i psi j and psi i, 2 states concerned is or contains it is the irreducible representation to which x, y, or z belongs.

So, if psi i and psi j together will form a direct product, which either corresponds to an IR representation containing x or contains an IR representation with bases x, y, or z then the direct this integration will survive and then we will say that the integration is not equal to 0 and then thus the spectral transition will happen otherwise the spectral transition will be forbidden.

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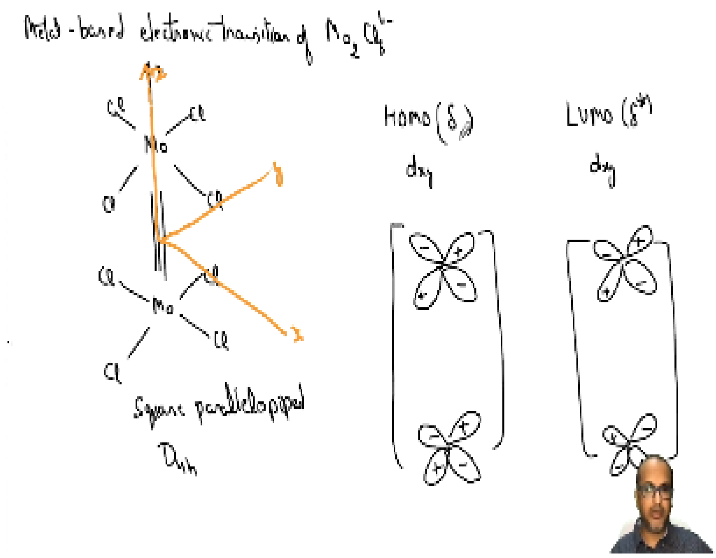

So, now let us look at an example. I will try to see if we can solve it. So, let me frame the question first. So, it is a solved example in Cotton, but let us see how to do this. So, let us say some metal we are talking about metal-based electronic transition of Mo2Cl8. So, first of all the structure of the molecule is given so which is Mo and this will be Cl, Cl, Cl. And then you have another one it is like a sandwich.

We have 2 planar molecules and then there is a metal-metal bond over here in between and the whole thing has 4 negative charges. So, let us say if you want to draw the x y coordinates, we can will be the z axis will be passing through this and we can say that our x will be passing through 1 of this. So, we can write draw x like this and y will be passing through 1 another Cl bond.

So, we can say our y will be like this. So, try to imagine this let me draw it like this in different colour. So, this is the molecule which is not square planar but you can say that it is a square parallelopiped or square prism also you can say, right, and we can also say that the point group will be like square planar. So, it will be D4h right because there is a symmetry sigma h over there passing through the metal-metal bond.

Now so now they say that this is the molecule and HOMO of this is HOMO is the highest or occupied molecular orbital is delta orbital which is basically composed of d xy orbital and it takes the shape like something like this. So, this is the delta orbital and this is given in the question and the lowest unoccupied molecular orbital which is delta star it is also composed of d xy, but now there is a change in symmetry.

So, we have this one is same whereas here there is a change of negative and positives. So, you have plus and minus. So, you can see that these 2 are different so this whole thing constitutes delta and this whole thing constitutes delta star. So, these are 2 d xy orbitals which are kept on top of each other and in this one there is a phase difference between the 2 and that is how there is a this is called as delta star and this is with same phase so this is delta.

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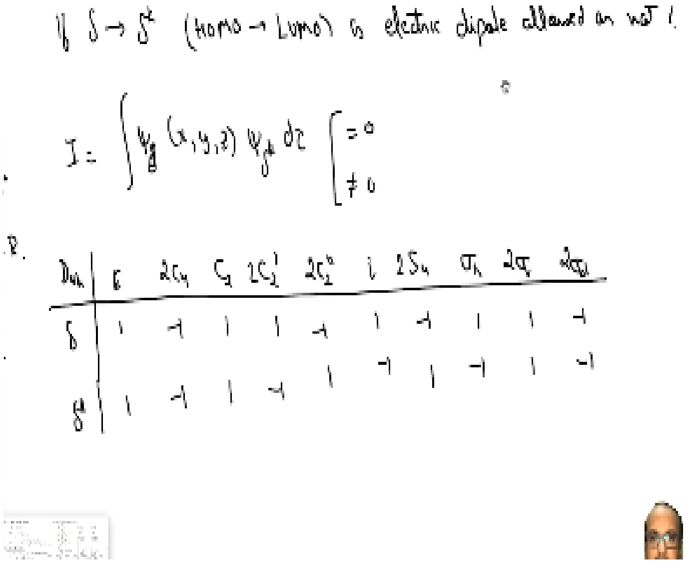

Now I will write down the question which this is asking. So, we need to see whether if delta to delta star that is HOMO to LUMO transition. So, HOMO to LUMO is electric dipole allowed or not. This is the question they are asking. So, that means what we need to do is we need to set up a integration where we need to see whether psi d psi delta x, y, z and psi delta star d tau. Now this integration whether this is equal to 0 or is not equal to 0. We have to identify this. So, what do you do in such a case? What you have to do is,

You have to first identify what is the basis for these orbitals under D4h point group? So, D4h point group let me write down the symmetry elements so this will be 2C4, C2, 2C2 prime, 2C2 double prime, i, S4^2, sigma h, 2 sigma v, 2 sigma d. Now for delta and for delta star what we need to do is we need to carry out these operations these operations and see what is the fate of this delta orbital and delta star orbital?

And depending on that will need to give the characters over here. So I would suggest you to do it I am not going to show it how to do it here, So, E will be 1 for both. So, if you do a C4 operation so if I do a C4 operation plus goes to minus the negative lobe goes towards the positive lobe and positive lobe goes to the negative lobe and this happens for all of them. So, that means all the positive signs go to negative all the negative signs becomes positive.

So, this would mean that you have the character under C4 as negative 1 for both orbitals. Similarly, if you do a C 2 the positive is exchanged with positive because opposite it is a 180 degree rotation now along z axis so positive goes to positive negative goes to negative and so on. So, C2 character is plus 1. So, in the same way you can carry out all these and find out the character.

So, I will just note down the characters from my notes and these are 1, -1, -1, 1, 1, -1, 1, 1, -1, -1. So, remember that you have to take both the orbitals together and orient it along the coordinate system as they are because it is you know it is a d xy orbital and once you do that you should be able to carry out all these operations. So try to do it yourself so that you know how to find this out.

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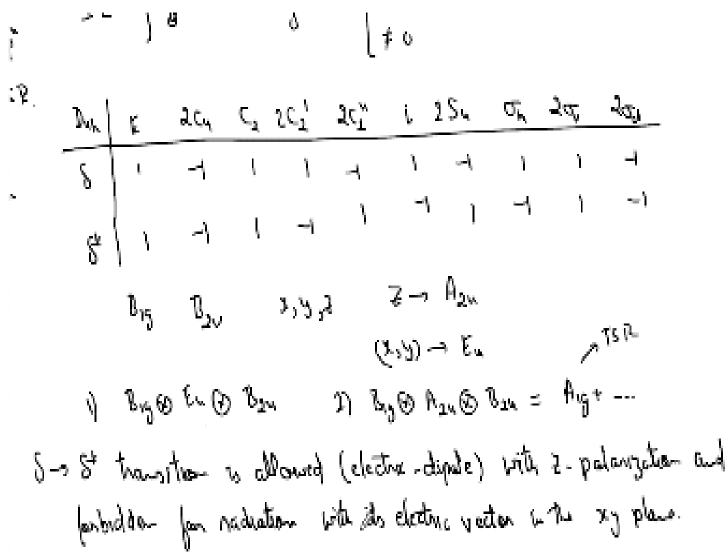

So, once you do that and you find out what is my representation corresponding to delta and delta star I can now compare it with the standard character table of D 4h and find out that my delta is actually so one of them is B1g and the other one is B2u. So, now I have found out the IR representation corresponding to the basis delta and delta star. Now for x, y and z, z corresponds as A2u.

So, this can be read from the character table, so you know the unit vector transformations are written in this area and then what is the IR representation corresponding to z you can find out and x, y is jointly forming the basis for Eu representation. So, now what you have to do is now the problem is simplified to finding the direct product between B1g, Eu and B2u that is 1 for x and y and for z you have to do that B1g, A2u and B2u.

So, as it turns out if you do this calculation all you have to do is you have to multiply the corresponding characters and traces and find out what is the IR representation here, whether it contains a totally symmetric representation or not. So, as a matter of fact this 1 contains A 1g plus something else it may contain but one of the representation is totally symmetric representation.

So, if it contains totally symmetric that means we can make a statement now that delta to delta star transition is allowed or you can say electric dipole allowed because that is the form of mu which we have taken here, electric dipole allowed with z polarization. Because we found TSR only in z integral, the other integral which was x, y integral we did not find A1g so then we can say that and forbidden for radiation with its electric vector in the xy plane.

So, look at the power of this method. So, you now know not only the selection rule whether the transition will be allowed or not but you also know with what polarization the particular transition will be allowed. So, you do not need to actually throw in the light with all polarization, so you if you just throw in the light with z polarization the electric dipole transition will be allowed because xy light is not being used here.

So, you not only come to know whether a transition is allowed or disallowed but you also get the details of which polarization that transition is allowed. So, with this we finish the direct product application and in next class we will be looking at symmetry adapted linear combination. So, we will be looking at the chemical bonding and all right that is all for today.