Chemical Applications of Symmetry and Group Theory
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Lecture – 24

Welcome to the day 4 of 5th week. Yesterday we learnt about the relation between the group theory and quantum (Refer Time: 00:22) little bit. Today will start with a concept, the concept of the direct product. We introduce that in I think couple of classes ago, but here we are going to have some detail about that.

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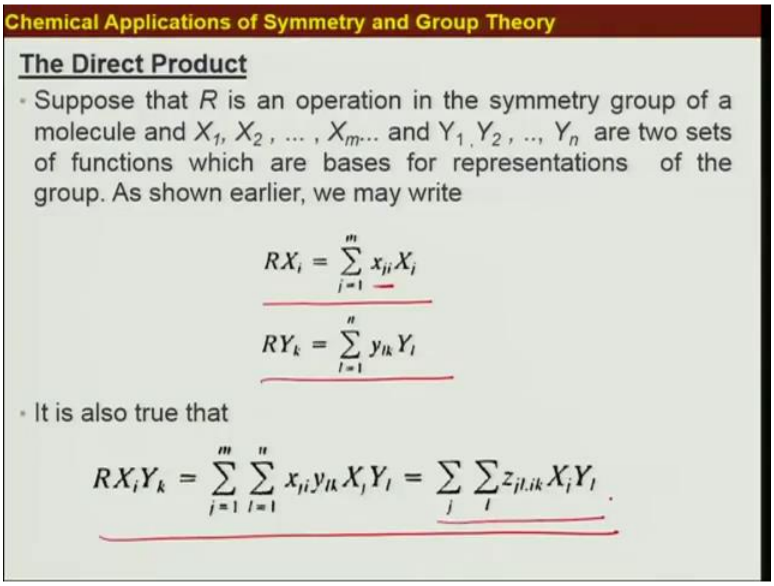

So, if we take R as an operation in the symmetry group of a molecule and X 1, X2 up to Xm and beyond and Y1, Y2 up to Yn are 2 sets of functions which are the basis for representation of the group. In that case what we can write is given here. So, I can express this operation R on Xi, as a sum of the continuations of each Xi's. So, in terms of this coefficient small xji or small ylk right; so I can write that. And also we can have this particular relation. So, which you know tells you when you combine this basis functions X's and Y's and then operate the symmetry operation R on that and you get that result as this one; which is really not much different from these individual ones, if you look at that.

So, this which are we are talking about is that combination of the basis functions, 2 different sets of basis functions, essentially 2 basis sets. And then combined them and then operate the symmetry operation on that and you get the result.

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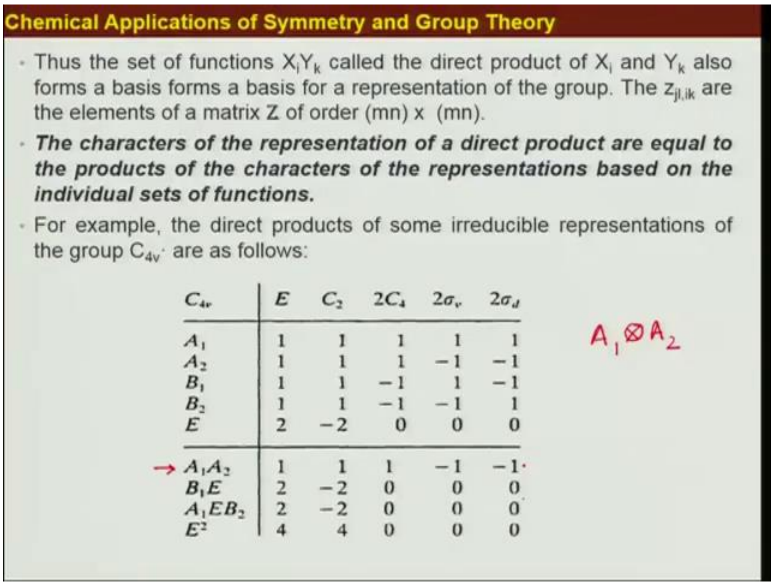

Therefore, the set of function is Xi, Yk they are called the direct product of X i and Yk. It also forms a basis for the representation of the group is very similar to you know the example that we gave in a last class, where you had this you know way function which acts as an Eigen function, now when you operate symmetry operations on that. So, you get r Xi that r Xi also acts as an Eigen function.

So, here this is just an analogy you have individual basis functions as Xi's and Yi's or by k,s when you multiply combine them 1 to 1, then they set that you get that also act as a basis set for the representation on the same point group. Now the characters of the representation of a direct product are equal to the products of the characters of the representations based on the individual sets of functions. So, the example is given here below. So, we have taken an example of point group C 4v and this is the character table for the (Refer Time: 03:52) C 4v. Now you have a direct product. So, generally direct product you can like you know a1 and A2. So, if you add have a direct product between this one. So, you normally make it like this or simply like this.

Now when you have the direct product here, what you have you have 1 to 1 you know product between the characters corresponding to the, you know 2 different irreducible representation and a particular ones which we operation. So, for example, if you want to have a direct product of a1 and A2, then I would have the you know the product of this character and this character both of which correspond to the same symmetry operation E, but we will not have any crossed of between these and these.

After having this 1 to 1 product, we get another representation. So, we get this here. So, this is very easily you can this see that 1 into minus 1 gives minus 1 again one minus 1 gave minus 1 and if you have any you know direct product combining you know one particular irreducible representation and the E representation then you get the corresponding direct product as it is given here like B1 and E the direct product gives you this representation. Now you can take any particular point typical find the character table and then you can combine any 2 irreducible representation by doing the direct product of them.

Now you may ask; why do I need this direct product. In the previous class we have seen one example of having the direct product. Now there are much more you know important role that direct product actually played. So, let see how this direct products are used actually.

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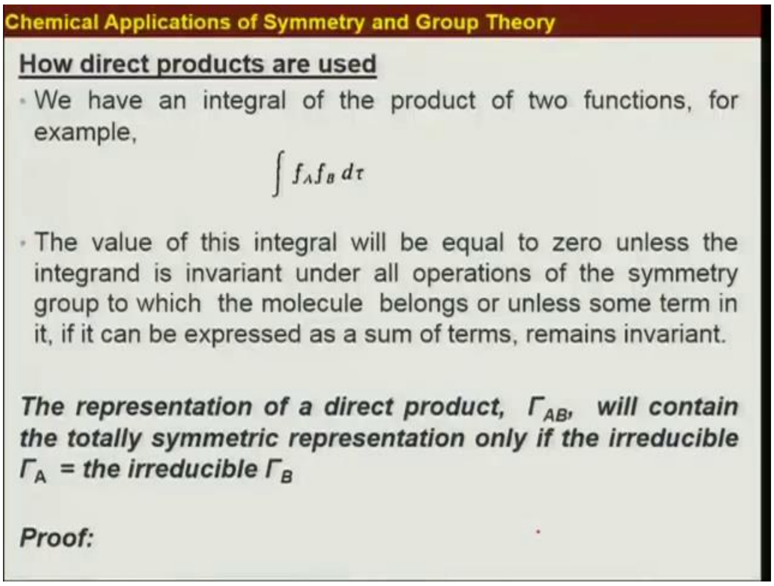

So, if we have an integral of the product of 2 functions for example, fA and fB and we integrate over all the coordinates denoted by tau. This integral will need 0, until or unless is you know integrand is invariant under all the symmetry operations of the point group to which the molecule belongs to. Also you know it will give 0 unless some term in this integral if it can be expressed as a sum of terms that remains invariant. So, in a nutshell if we have to talk in terms of group theory and symmetry what you can say is, following the representation of a direct product if we denote it as gamma AB and gamma AB will contain the totally symmetric representation only if the irreducible gamma A is equal to the irreducible representation gamma B.

So, you can proof that quite easily how you can proof that. So, let us do this.

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So, you know we are familiar with this particular equation, which gives you the number of times an irreducible representation will appear in a given representation that one can form. So, that is given by I reducible of any given r and the particular irreducible representation that we are concerned right, this far you know. Now we are what we have talking about here that is the, you know this irreducible representation, we are talking about that the representation that is formed by the direct product of 2 irreducible representation. Now we have been talking about this particular integral, that integral fA B over d tau that will vanish until and unless the total integrand is invariant. So, what do you mean by this invariant here; that means, it is you know whatever symmetry operation you operate its not going to change. So, all the time it will give you a plus 1 as character way.

Now these functions will be you know and way function right. And way functions they form the basis of irreducible representation. So, ultimately it boils down to the property of the irreducible representation. Therefore, I can think of this fA into fB to be the direct product of 2 irreducible representation rights.

So the result of the direct product if it gives you the total symmetric iR then only this integral will survive, of otherwise if it is not symmetric, then this integral over all the progress it will vanish right that is well understood. Now what will wanted to proof here that in a direct product the total symmetric representation will occur like if I have a 2 representation say A and B and the representation that we get after being the direct product that is gamma AB, it will contain total symmetric iR only if gamma A equals to gamma B, where gamma A and gamma B are 2 irreducible representation and that is what we are going to show here.

So, this i represents one of these gamma A on one of the iR's of the point group. Here particularly we are interested in a particular iR which is totally symmetric iR and total symmetric iR is always represented by a1. So, if I replace this i by pi 1 and here I write a1 meaning, that I want to find out whether this a1 that is the number of times the total symmetric iR who occur in this representation, which in our case say AB right that is direct product representation that you get. So, how many times this a1 symmetry there is a total symmetric iR will occur in this 1 correct. Now this is a 1 dimensional irreducible representation. So, I can write here clearly 1 fine.

So, once I am talking about the total symmetric iR for which all the characters are plus 1, when I can simply write this one as 1 upon h sum over all the R pi AB of R, now by definition of direct product pi AB is equal to the product of the characters of representation a and representation b correct. So, if iR replace that here then what I get is is this. Now if I look at this, from the greater product deployment, I can easily say that this will survive, this whole thing will be non 0 only when A equals to B correct. So, this means delta AB right. So, this is equals to 1 where A equals to B and that is what exactly the same.

If A and B are same; that means, if the direct product is done between the same irreducible representation, then only the total symmetric irreducible representation will occur will be contained within that direct product otherwise it will not and therefore, if I have a represent you know if I have an integrand where you know 2 functions, which transforms as 2 irreducible representation of the point group. They will survive only when those 2 functions correspond to the same irreducible representation. Otherwise they will not survive. What these properties used? This is used when you try to find out the energy elements of any a given molecule or you want to find out above the spectral transition probability and we will have a look at those things right now. So, you know what is energy integral? Energy integral we can easily find out because you know about sidereal equation.

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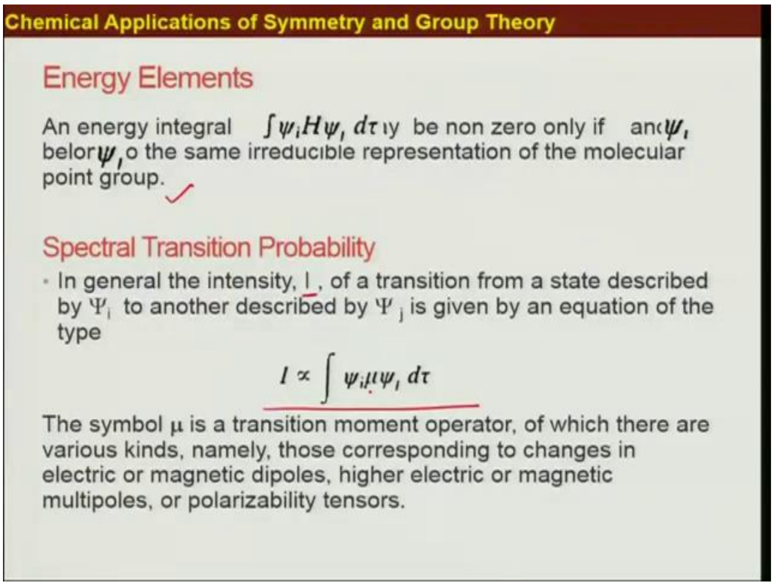

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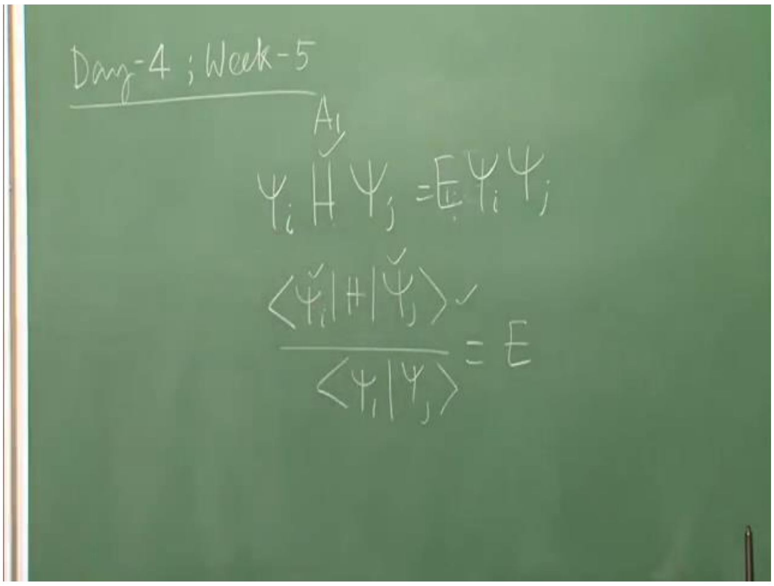

So, you have say H psi j equals to E j psi j right. Now if you multiply both sides by psi i and then you know integrate. So, E being a constraint I can easily shuffle this one. So, what I can do is I can write psi i j and b e here. Now if I integrate over all the phase. So, what I can have is psi i fine that is my energy.

So, this phase particular thing is called the energy element of a system. So, and in this is also known as energy integral. So, this will be non 0, if an only if this psi i and psi j they belong to the same irreducible representation. Why so, because I know that this Hamiltonian operator that does not change the symmetry properties of a molecule right, H converts with any symmetry operation, that we have all ready seen. What does that mean that H is invariant to any symmetry operation? Again what do I mean by that; that means, h which is in you know energy operator is you know is the basis for the total symmetric irreducible representation right. So, if this belongs to total symmetric irreducible representation then it must be A1 correct, now you multiply anything with a one will give you back the same irreducible representation because you are just multiply with plus one.

So, therefore, if this integral has to you know survive what I need to have is that this 2 product that is the direct product of psi i and psi j meaning the direct product of the irreducible representation to which psi i and psi j belongs to they should you know either yield total symmetric iR or should contain the total symmetric iR. So, just now we have seen here that the total symmetric iR will be contained within the direct product representation only if the 2 iR's that we are combining are equal fine. So that means, here that iR corresponds to which this psi i belongs to must be the same iR to which psi j belongs to you. So, that is what is stated here.

Now, the next important thing that we will be talking about is the Spectral Transition Probability and will see how this direct product you know helps us in getting this spectral transition probability. So, we are already in the application part and sum it. So, for any you know transition between 2 states, it can be an electronic state by Vibrational state or any other state. So, thus if the state ground state and the excited state if we are describing them by two way functions psi i and psi j, then the intensity of this transition which is denoted as this I is given by this integral. So, this is called transition moment integral.

Now the intensity of this transition is directly proportional to this integral and this mu here which is acting as operator this is a transition moment operator. So, this can be different way this operator convert for example, you know it can be you know electric dipole operator, it can be magnetic dipole operator, it can be a magnetic quadruplural higher other multiple it can be a polarizability tensor and. So, the nature of mu can vary, but the you know the most common form of mu in the spectroscopic that we often use is the electric dipole and will also restrict our self in our all the discussion even in the following weeks to this particularly electric dipole allowed transitions.

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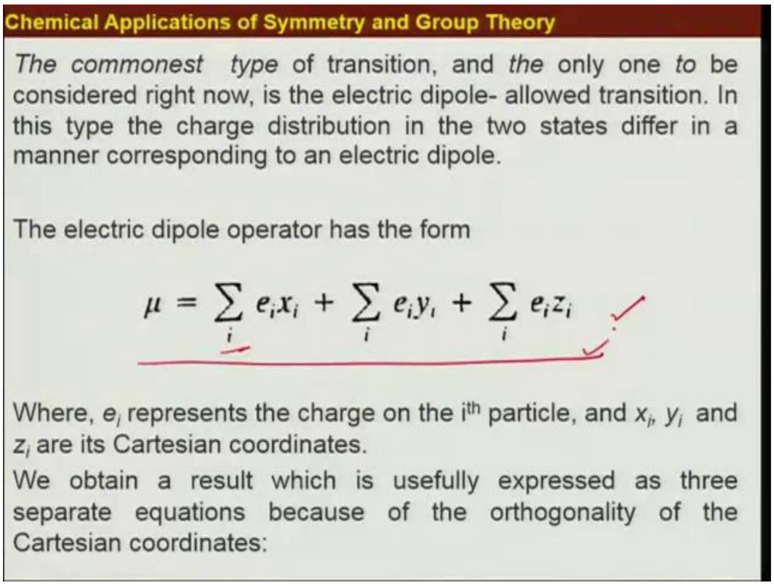

So, where you know mu will have the form as given here. So, mu will be a dipole moment operator and a dipole moment is given by the charge by deployed with the distance. So, for any given particle, the distance is quantified by 3 Cartesian coordinate coordinates. So, x, y and z, therefore, we can express mu as the sum of this choice dispensed product in 3 different directions x, y and z as given here and we can have many particles in the systems. So, for each particle I can have this you know charge dispensed product for each project and then we can sum it over all the particles, so that is given here.

So, this is you know beauty of this orthogonal you know coordinates system x, y, z. Why? Because I can you know separate the different continuations of you know mu along x and y and z directions and expressed then just by you know sum of the 3 coordinates and they are not depended on each other. So, I can separate them out very easily as shown here in this particular equation. So, when I can separate different continuations of mu that is mu x, mu y and mu z, I can overall, I can you know split the transition moment integral also into 3 different integral as shown here.

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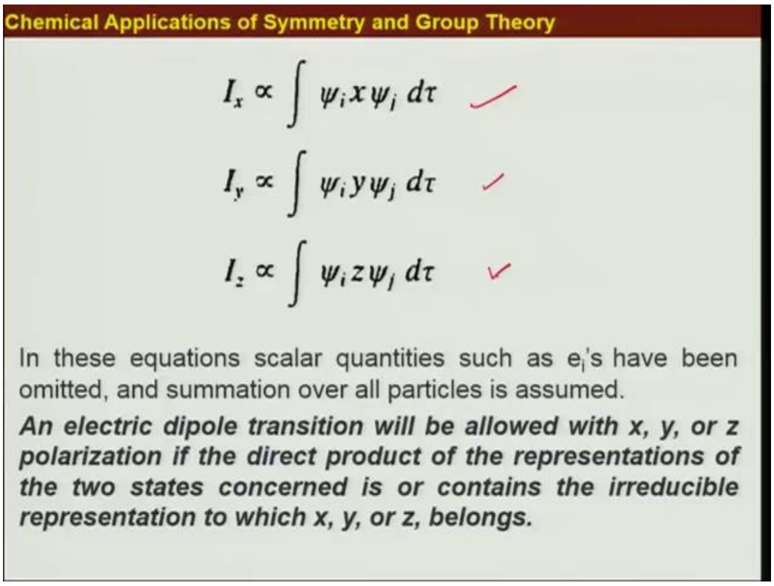

So, I can have you know an integral which is depending on the x coordinate then y coordinate and z coordinate fine. Now one thing you notice here that we are not using this charge values here because that is a constraint and we that does not change the value of integral right. So, that we just multiplication after you solve the integral. So now, if 1 or more integral survives then what you say, is that transition from psi i to psi j is allowed and is allowed in those particular direction meaning like suppose the integral involving x is non 0, but other two integrals are 0 then we say that the transition is x polarised or suppose if it is you know surviving for integral involving x and y, but the integral results 0 for you know the z axis then we say the transition is to polarized in the x, y plane.

So that means, if we come with light which will calls transition for one step to another if will have the electric field vectors of this light polarized in those directions then only will have the transition.

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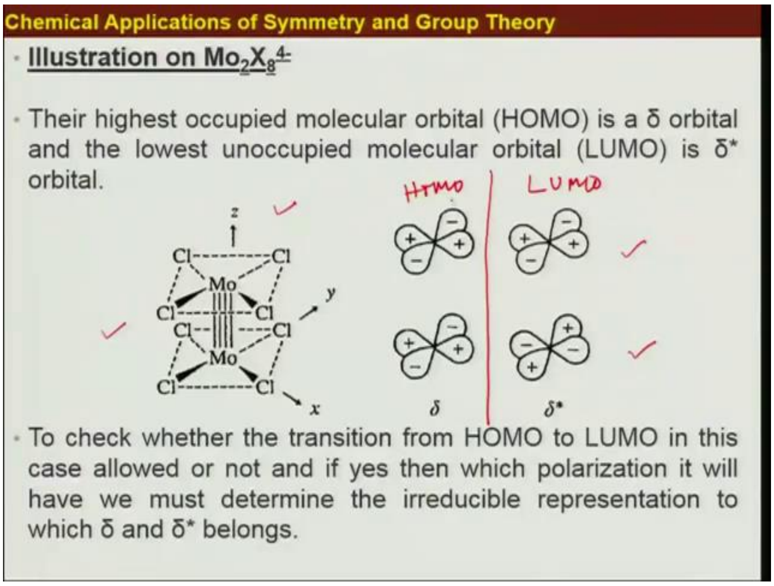

So, we can give you very quick example and then we can close this section move on to the next part of the symmetry (Refer Time: 24:40) linear combination. So, if we look at and the example of a particular molecule which is di molec denom complex of legen which is like simples chlorine provide, for this particular molecule was structure is shown here, they are you know highest occupied molecular orbital or HOMO is a delta type orbital and the lowest unoccupied molecular orbital or LUMO is the delta star type orbital you do not have to worry about what is you know delta star and delta because we are giving the detail picture of the orbital for this HOMO and LUMO explicitly here.

So, this is, this HOMO pad and this is the LUMO pad right. Now if you have to find out whether the transition from HOMO to LUMO is allowed in this particular case and if it is allowed then in which particular direction, then what we have to do? We have to determine the irreducible representation to which this 2 orbitals delta and delta star belong to now since we have the you know details picture of delta and delta star we can find out the irreducible representation to which this molecule belong to. So, what you have to do we have to operate all the symmetry operations for this particular point group to which this molecule belongs to operate on this HOMO and LUMO and delta representation. So, the molecule belongs to D 4h point group.

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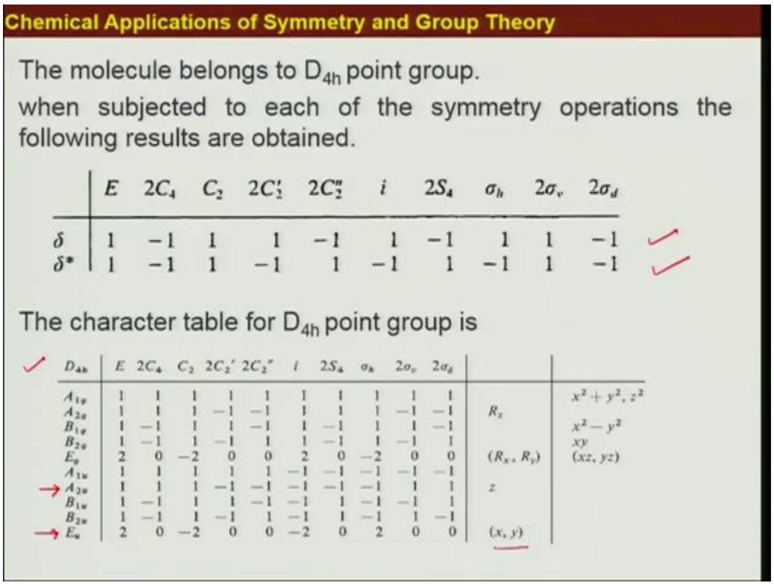

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The molecule belongs to D_{4h} point group.

when subjected to each of the symmetry operations the following results are obtained.

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
δ	1	−1	1	1	−1	1	−1	1	1	−1
δ^*	1	−1	1	−1	1	−1	1	−1	1	−1

The character table for D_{4h} point group is

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

So, if you are not convinced here then I will request you to go back to you know the second week of tutorial the second week of this lecture and learn little bit more about this point today analysis. So, this molecule is having D 4h symmetry. So, once we operate all the symmetry operations on this 2 orbitals delta and delta star we see that we get representation as this right. Now what you have to do you have to consult the character table of D 4h point group? So, any standard group will give you the character table of all the point groups. So, here we are giving you the character table of D 4h. So, now, if you compare this representation with this character table as a whole then you can find out which illusive representation delta belongs to and to which representation the delta star of that belongs. So, that is given here.

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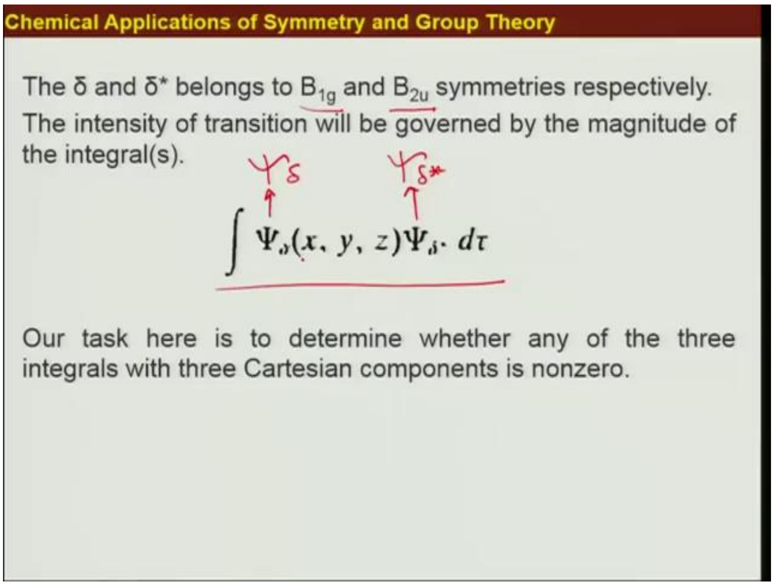

So, the delta belongs to B 1g and delta star belongs to B 2u symmetries. So, we have got the irreducible representations to which this two orbitals R A which form HOMO and LUMO they belong to. So, why what you have to do, why you have to look at the transition moment integral. So, that is given here and here again you notice that we are not bothered about the charge because that is not going to alter the fate of the transition correct. So, we will be operated you know. So, this one is this is essentially is psi delta and this one is psi delta star right. So, this integral we can split in 3 different integrals involving x, y and z separately. Now this is what to we have to do? We have to find out to which irreducible representation this integral x or y or z coordinates belong to or in other words for which iR this x or y or z form the base ok.

So, if you look at the character table we can easily locate that. So, you can see that z. So, z forms the basis for A 2u. So I can say z transforms as A 2u and you can see x, y they transforms together as the illusive representation E u. So, we got all the information that we need to solve the integral right.

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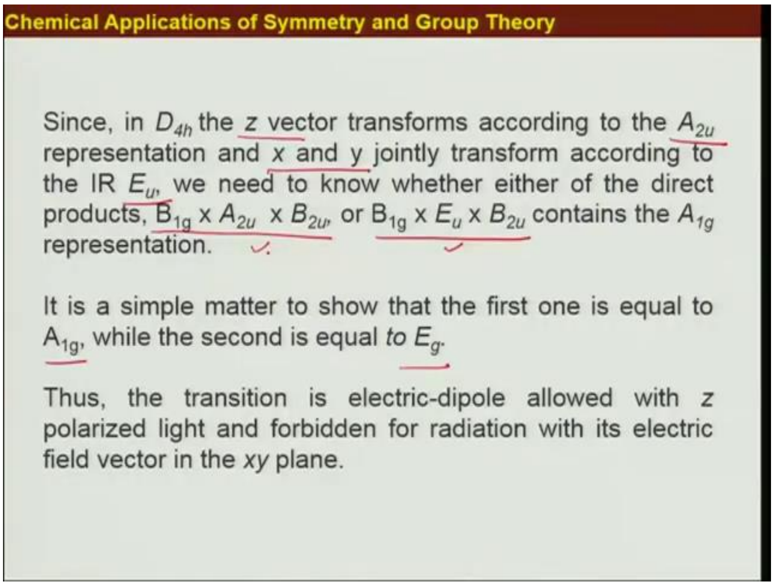

So, you have already find that you know z vector transforms as to A 2u and x and y together transform according to E u. So, what you have to do we have to replace this you know this delta and delta star by their respecting irreducible representation and also we have to replace the x, y and z by the respective irreducible representations. So, then we are left with this 2 different you know cases of direct products.

Now whichever direct product yields the total symmetric irreducible representation that will survive. Now here in this particular case this x and y forms together. So, this particular representation it gives with x and y together and while this one it deals with the z polarization and once you solve it which is very easy and you can figure out that first one it gives you A1g the total symmetric Ir. While other one is not the total symmetric iR. So, clearly the integral involving z will survive, while the other one will vanish. That means, our this HOMO to LUMO transition is allowed overall, but it is allowed in the z direction and it is forbidden in the x, y plane.

So, we also call that the transition is z polarized. So, here we showed that how this concept of direct product can be very much useful to have an idea about the transition probabilities and intensity of the of any given transition, knowing the you know properties of direct product involving the irreducible representation of any symmetry point group.

We will stop here today. And I thank you for your attention.