Chemical Applications of Symmetry and Group Theory
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Lecture – 25

Hello, and welcome to the 25th class of this course. In the last class we learnt about the relation between Group Theory and Quantum Mechanics, and there we saw that the brief functions which are ican functions of any given operator. For example, Hamiltonian operator which is an energy operator can act as the basis of for the illusive representations for any particular molecule belonging into a particular point group.

Also we learnt about the direct products of the illusive representations, which will be extremely useful in the coming weeks. And we also learnt how this direct product are used, they can be used. So, we took an example to show that direct product can be used to find out the energy elements, and also to find out the spectral intensity most precisely to probability of transition whether its allowed or disallowed and if it is allowed then, in which particular polarization it will be allowed.

Now one thing we did not talk about in the last class, that not only the wave function, which is an I can function of an operator, can found the basis for illusive representation, but also the linear combination of the wave function can also act as the basis for the same ire illusive representation. Which is quiet understood, because if I have an ican functions, psi i, I for an operator, say H, the Hamiltonian then I can express psi i as a linear combination of various phi's.

Therefore, its no wonder that proper linear combination, of the ican functions can also act as a basis of the ire illusive representation. And this property is of utmost importance when we try to find out which kind of say atomic orbitals will combine to give molecules orbitals, or which will contribute to the habituates orbitals. Also to find out like which particular born vectors will combine to keep an internal motion like vibration. So, in general the chemists they try to use the symmetry restrictions, and to facilitate themselves to understand chemical bonding and molecular dynamics. For example, as I said, constructing habit orbitals or molecular orbitals or finding proper orbitals sets under say Allegan field or also analyzing vibrations of molecules.

In order to do that, that is developing such understanding based on symmetric restrictions one faces a common problem. The problem is that one needs to take one or more sets of orthonormal functions as required by a both group theory, and quanta mechanics. And here this orthonormal functions in case of this chemistry problems, this functions are taken to be the atomic orbitals. Or, in case of vibrational motions, are there other internal motions, they are internal coordinates of a molecules. In order to make proper combination, which will keep in the resultant function orthonormal, and that will act as a basis of ire illusive representation one needs to be quiet careful in his formulation of the problem.

And as we learnt in the last class this kind of the relation between the quanta mechanical observables, the wave functions rather not the observables and the symmetrical strength, this really is important for solving this problem.

So, in case when one tries to find out which atomic orbitals will form the hybrid molecular orbitals or in general molecular orbitals, one needs to take care of the symmetry constraints.

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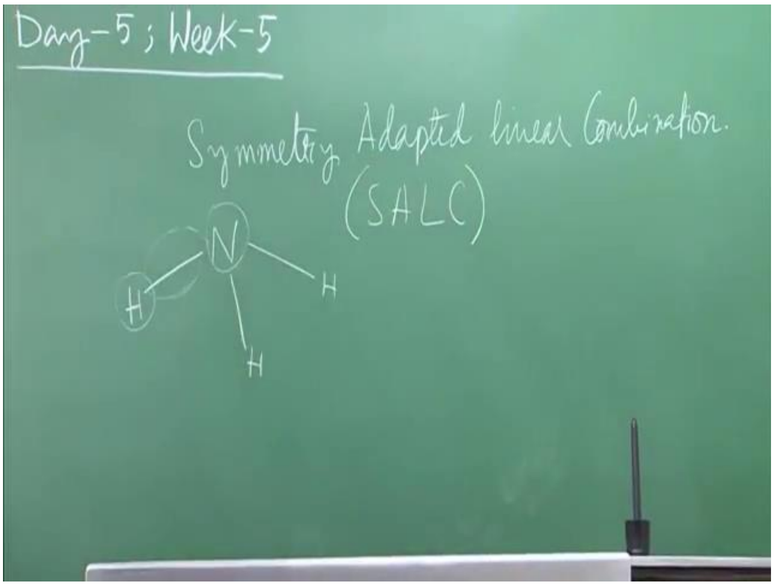

And then ultimately the linear combination that one gets, is known as Symmetry Adapted Linear Combination, or in short SALC. So, when SALC. So, how ne can find out, that which orbitals will be able to combine in a linear fashion, and keeping the symmetric constraints to give a proper basis for a particular ire illusive representation of particular point group to which our constraints molecules belongs to. Now you see, why the symmetric constraints needed? Because for example, you take an any molecules; for example, ammonia. So, in the case of ammonia what we have is this bond that we write.

Now, bond means what? This is the you know combination of the atomic orbitals. So, hydrogen has one s orbitals, and nitrogen has 1s, 2s, 2 p orbitals. So, which orbitals will combine to form this successful bond, is not only governed by the energetics, but also governed by the symmetry. So, until unless the orbitals of this atoms, have the same symmetry they cannot combine. So, there is a symmetry restriction and therefore the you know the combination that we form to facilitate the bond formation, will be symmetry adapted linear combination, combination of atomic orbitals. So, how do you do that? So, there is a fundamental tool which is universally accepted and this particular tool is known as projection operator.

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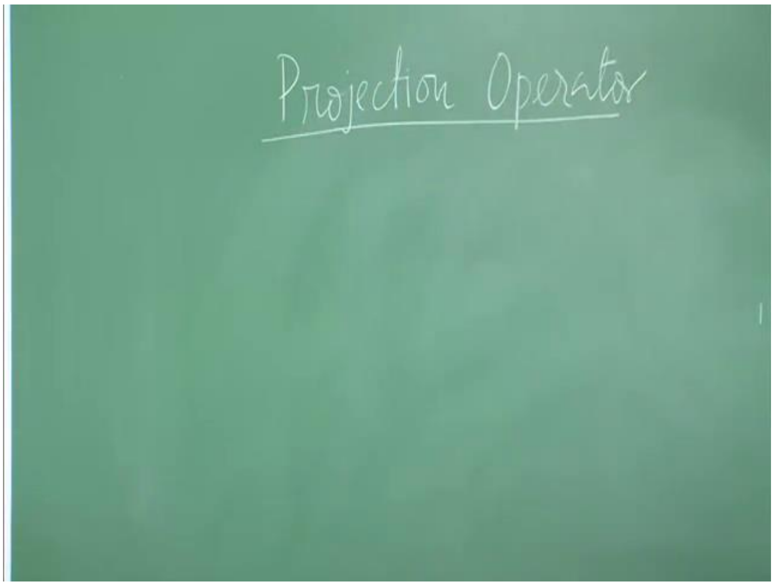

So, now we will learnt about this particular projection operator, which will help us in finding on the SALCs, for any given molecule. In order to understand the position of at as functionally we better learn how to get this position operator first, and then will go for the actual application of this projection operator, by showing some illustrative examples. So, let us start with.

Let us assume that we have a orthonormal set of li number of functions, such as phi 1 phi 2, up to phi Li.

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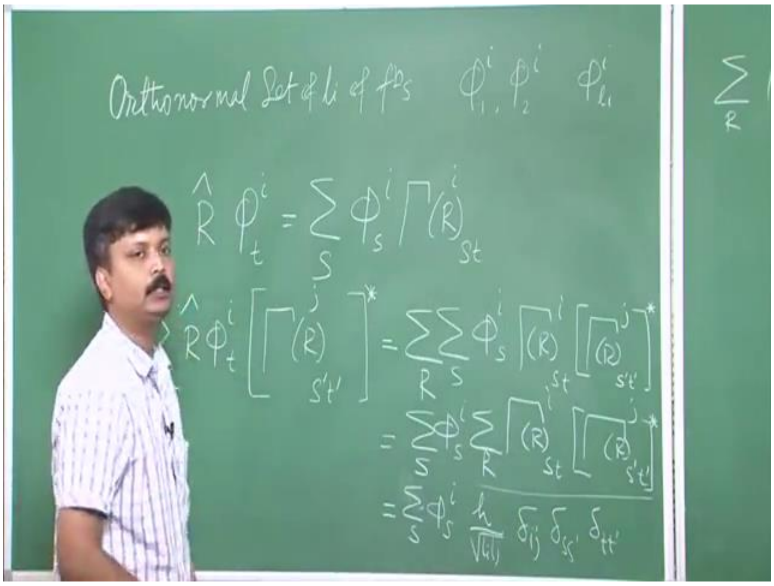

So, we have a li number of such functions, and we also assume that this functions form the basis of the ith ire illusive representation of a point group, to which our concerned molecules belongs to. So, if this forms a basis for an ith ire illusive representation, so were put a superscript as i, that will tell you that to which ire illusive representation, this functions act as basis form. And the order of the group, that will are concerned, let us take as h, as usual. Now if I consider any operator, any symmetry operator as R, and e i take anyone of this functions, and operate any symmetry operation, on that function, then what should I get? So, if I take any arbitrary function phi t, phi t is 1 of this you know, li number of this, which formed of basis for ith ire illusive representation.

So, that I can write as right? So, I can write this one, as I have taken this function to be the basis for ith ire illusive representation, and this gamma R having superscript i is a representation for this particular symmetry operation R, giving ith ire illusive representation and s t you can understand is a particular element. So, this gamma R is a matrix representation. So, s t gives me the particular element of that representation right? Now, what we have to do in order to, find out how to get the projection operator, what I will do I will multiply both the sides, with another representation for jth, I r.

So, I will multiply both the sides, by a quantity which is gamma of the same operation R, and belongs to jth ire illusive representation, and some element is s prime, t prime, and I we will take a complex conjugate of that particular element, and after that we will sum it over all the symmetry operations r. So, we have to do the same thing on the right hand side as well. So, in that case I have summation over R, summation over s, phi i s gamma of R, s t multiplied by gamma of R, for jth ire illusive representation having elements s prime, t prime ok?

So, now one thing you notice here, this phi I is an function. So, it is independent of the symmetry operation right? It, it does not clash with the symmetry operation. So, I can you know, very easily separate this phi part, and this representation part. So, what I can do, I can rewrite this one as, summation over s phi s i, and then summation over R and this part. That means, gamma R for ith ire illusive representation, and element s t multiplied by gamma of R, for jth ire illusive representation having element s prime, t prime, and take the complex conjugate of this one. So, this we can very easily do right.

Now, we have a situation, where this right hand side tells me that I can have such li number of such products, where you know, each one will be a function phi s that belongs that forms basis of (Refer Time: 25:05) ire illusive representation and that is multiplied by a co-efficient. So, this part is a co-efficient which is multiplied this phi s, and I can get such li number of products fine. Now, if I considered, this particular co-efficient, what does this co efficient tell me? So, this co efficient themselves R the summation of the products of 2 ire illusive representations, over all the symmetry operations, that is what it tells me.

Now, such sum of the products of ire illusive representation over all symmetry operations are governed by the great ortholonomatic theory. So, what does the great ortholonomatic theory tells me about such an such a co-efficient.

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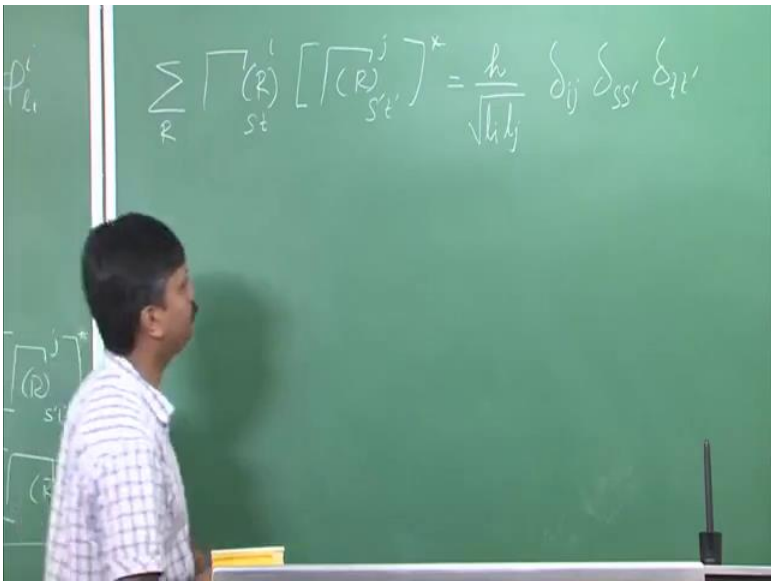

So, if I just take this one. So, it is sum over R, gamma of R, for ith ire illusive representation, and have been elements s and t, multiplied by gamma of R, for jth ire illusive representation, having elements s prime, t prime, is equal to, if you remember the great ortholonomatic theorem, that we discussed earlier. So, we have considered the order of the group to be h. So, here order of the group, and then I have 2 different ire illusive representation, ith and jth.

So their dimensions let us assume l I and l j, therefore, this will have l I and l j, right? and then I will have series of delta functions. So, here what we have? We have 2 ire illusive representation get (Refer Time: 17:31) theorem will you know, guide you, how you can write the delta functions here. So, for 2 different ire illusive representation, I will have the delta I j, and then, I have elements as s t for the ith, and s prime t prime for the jth ire illusive representation therefore, I will have 2 more delta functions, one will be delta s s prime, and other 1 we will delta t, t prime alright? So, now what does that tell me? It tells me that I can replace this one over here.

So, this part will remain as it is, and I can write here, as h sorry, summation over s, phi s, for ith ire illusive representation, and h by route over, l I, l j and then 3 delta functions, right? And then whatever I have on the other side that remains. So, here this right hand side immediately tells me that phi s, this side actually will give non 0 value, only when this is equals to s prime right? I am summing it over s. So, if I operate this operator on this particular function phi t, form ith representation, then I will have this right hand side having 1 0 value only when s is equals to s prime.

So, I will get phi s prime here, with 2 more delta function, delta I j ,delta t t prime. So, which means that not only that it has to be a particular function phi s prime. In other to have non 0 value for this part, but also the 2 ire illusive representation that we are considering here must be identical meaning I equal to j and other element also should be the same that is t equals to t prime. Therefore, if consider all this what do I have is following.

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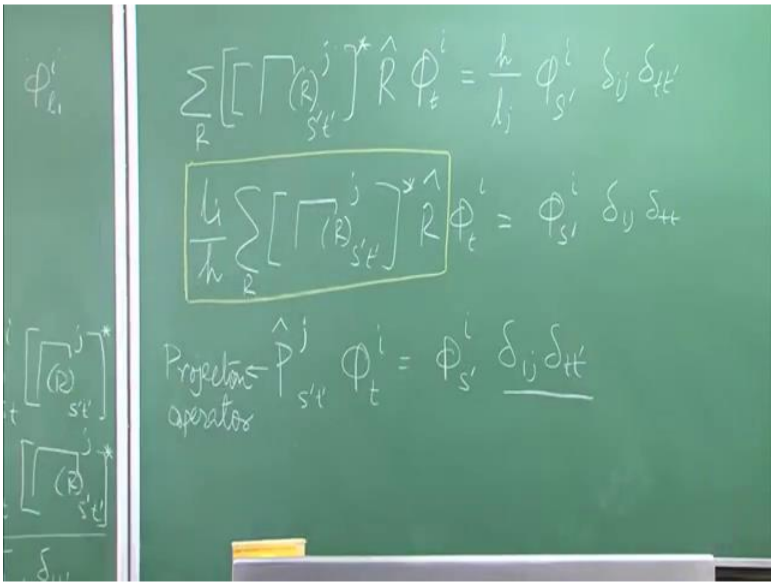

So, what we have here, the left side, sum over R, I can just slightly rearrange, because this 2 are not interfering each other. So, I will write this term first. So, I have gamma of R, for jth ire illusive representation, having elements s prime t prime, multiplied by the operation R and optimum phi t, forming basis for I, ith represent ire illusive representation. So, this is equals from here whatever I said if I can write that h by l j, because when li, I equals to j, then only this right side I can write with survive. So, therefore, for I equals to j, I have li equals to l j. So, l j square and take a route, I get l j. And I have phi, now s prime because for s equals to s prime, this will survive and for at this is representation. And if I still keep the deltas, took it the generality still, I will have this part.

Now, by rearranging, I can have l i by h, whatever we had, phi of s prime, I, delta I j, delta t t, all right? So, this, this part of the left hand side, is known as the projection operator, and this is abbreviated as p of s prime, t prime, for jth ire illusive representation. So, this is equals to the projection operators, and then you have this right? So, this is my projection operator. So, now, you can see here, that this particular operator when it is operated on any arbitrary function phi t, it projects out another function phi s prime.

So, this projection will takes place, only when, this you know function phi t, contains or it, it itself is phi t prime. So, then it will give you know, that you know, survive, because I have this delta function delta t t prime. Moreover it has to you know, phi, you know belong to the same particular ire illusive representation. So, then I can have this phi s prime, being projected out from an arbitrary function, or the combination of the function, which is given by phi t.

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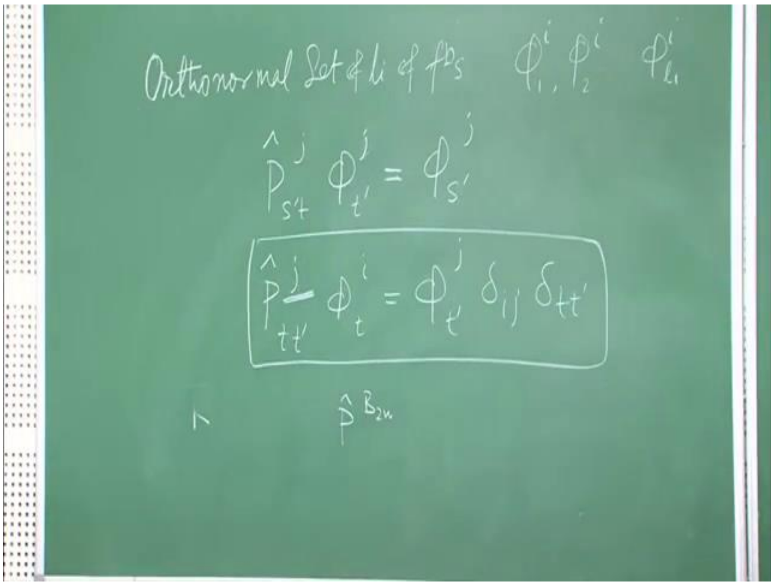

So, ultimately by taking care of this delta functions, what I can right is this, making. So, I will rub this part. So, therefore, what I can write is, p of acting on general function, any arbitrary function t, which will give me ultimately phi t prime, if I take care of this delta t t prime.

So, essentially it means that this phi t must contain some component of phi t prime, in that case, I will have when phi t prime, and for any arbitrary any ire illusive representation j, I can write this general form of this. Now this is the most general form, but I can have the special case. So, the special case is as follows. So, if I take this; so this is a particular special case, that we can considered. So, what does this special case tells me? So, it tells me that this p j t t prime, that is the projection operator, which will project out phi t prime, out of an arbitrary function which is phi t that we started with right? So, by using li such projection operators, based on li diagonal matrixes.

So, that is element rather we need generate from some arbitrary function, which is phi t that we discussed, as you know a set of functions, which will form the basis of the jth ire illusive representation. So, this is what we have as projection operator. Now this projection operator will be used in specific cases when we consider in the following class, taking a particular example of an molecule there we will consider the atomic orbitals there were functions and we will operate this projection operators here. So, here like, we say that this is particular ire illusive representation j.

Now, what we can do we can you know take the real ire illusive representation. So, you have to look at the character table find out the ire illusive representation that you want to work with. So, for example, some ire illusive representation b to u. So, can have that projection operated written as p b to u. So, in the following class we also see that there is, there are 2 type of projection operator one is like complete projection operator, another is incomplete projection operator.

So, most of our purpose we are pretty good with the incomplete projection operator itself which deals with not the matrix elements as such, but only with the characters. So, we can use the characters from character table belong to particular ire illusive representation, to form the projection operator. And, thereby we can work on the particular orbitals of any you know atom within a molecule to project out which are the orbitals that can combine a linearly to form the you know say orbit orbitals.

In the following class we will learn more about this and try to form differently SALC’s is from for different molecules; till then have a nice week.

Thank you very much.