Symmetry and Group Theory
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Lecture -39
Symmetry Adapted Linear Combinations

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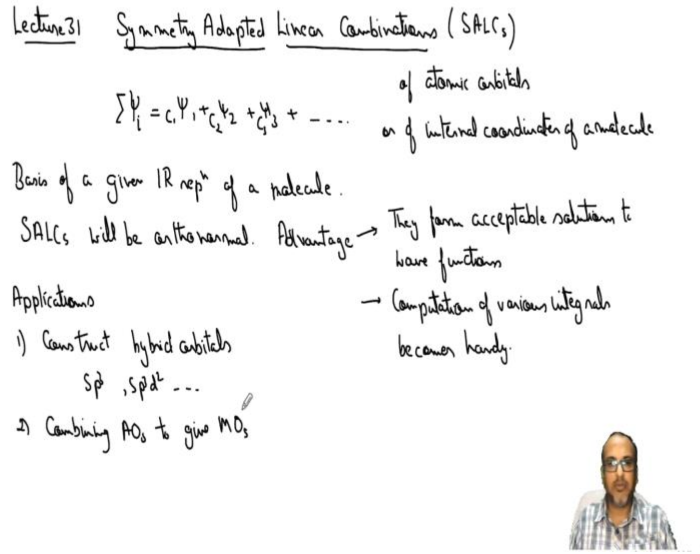

Welcome back, in this lecture we will be discussing something called as Symmetry Adapted Linear Combinations. So, let us first try to understand the term, what is symmetry adapted linear combinations. So, linear combinations, we know that they are sum of various things linear can be, combinations can be sum of different functions. For example, if we are talking about let us say a wave function psi i.

Where i can vary, so we can have it like this psi 1 + psi 2 + psi 3 and so on and then of course there can be some coefficients around. So, this is called as linear combinations and linear combinations can be of different functions. In this particular case we will be discussing of linear combinations of atomic orbitals. That is the wave function of atomic orbitals or also of something called as internal coordinates.

We will see what that is later, not in today's lecture, but later in this course. Internal coordinates of a molecule. But today we will see what is the linear combination of any given function and what do you mean by symmetry adapted. So, symmetry adapted means taken any linear combination such that we know it is symmetry and how do we know it is symmetry. So, we know it is symmetric because we will be taking such linear comments so that it forms basis of given irreducible representation of a molecule.

So, what is advantage if we do that, so if we take let us say we have a set of atomic orbitals or set of wave functions of atomic orbitals, and if we try to combine those wave functions, so that the resultant combinations, there can be different combinations like if we have n such orbitals there can be n number of linear combinations.

Now all such linear combinations, each individual linear combination can form basis of an individual IR representation and in such cases those linear combinations, we will know the symmetry. So, that is why they are called as symmetry adapted linear combinations and they will also be orthonormal to each other. So, in short, we can say SALCs will be orthonormal. That is how we will construct them.

We will choose the orthonormal combinations. What is the advantage of this? So, advantage of choosing orthonormal sets is, we will see that they form acceptable solutions to wave functions. Well, we will not see in this course, but this is generally accepted that if the wave functions, if the combinations are linear or linear combinations are orthonormal, they will form acceptable solutions to wave functions.

And the second is that if we know the symmetry, computation of various integrals becomes easy, becomes handy. Because of various group theory rules can be then implemented on to those integrals, like we have seen in the case of direct product that how to compute the integration given that we know the irreducible representations corresponding to which wave function is forming a basis.

So, the goal here is to obtain linear combinations which are symmetry adapted and obtain the orthonormal sets. We will see how to generate them and what are the applications of such

SALCs? So, let us call them as SALCs, symmetry adapted linear combinations. So, the applications of SALCs, that also we will cover later in this course are, we will see when we are going to construct hybrid orbitals, when we will study chemical bonding.

Hybrid orbitals; so, for example, sp3, sp3d2 and so on. So, we know what the hybrid orbitals are so while constructing hybrid orbitals, SALCs come become very handy. When we are combining atomic orbitals to give molecular orbitals. In that case, also SALCs will become very handy.

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sp, spd ...

2) Combining AOs to give MOs

3) What AOs are to be chosen in the presence of a ligand

4) Analyzing/Visualizing vibrations of the molecule

<u>To generate SALCs from a set of function</u>

Projection Operator → Complete projection operator (matrix elements of sym operation)

→ Incomplete " " (works with traces of matrices)

1D IR rep^n → matrix = trace, Incomplete PO = Complete PO

2D, 3D ... IR rep^n → matrix ≠ trace explicitly calculate SALCs using Complete PO

And we will also see SALCs will help us find out what atomic orbitals are to be chosen in the presence of a ligand. So, when ligand is coming to form a bond with a central metal atom, what kind of atomic orbitals are to be chosen, to make or facilitate these bonds. So, all these combinations are decided by the symmetric criteria and we will see how then SALCs are helpful for allow this.

Similarly, when we are analyzing or visualizing vibrations of the molecules. In that case also SALC's will be highly useful. So, we have seen that now, what are SALCs, we will see, the linear combinations of different wave functions or internal coordinates of the molecule as the case may be, given that they have a given symmetry. That is, they will form the linear combinations, will form basis of IR representation such that all the linear combinations are actually orthonormal to each other.

So now, how do you generate such linear combinations. To generate SALCs from set of functions which are wave functions in this case, but you can generate SALCs from any given function. We will use something called as Projection Operator. We will see what a projection operator is, in detail. So, projection operator helps generate SALCs from a set of functions, so all you need to know set of functions and how to apply projection operator.

So, you should also have the knowledge of the character table of a given molecule, and the matrices also. So, projection operator can be of two different types, you can have complete projection operator and if you are saying complete, the other one has to be incomplete. So, this one actually relies on the full matrix elements of symmetry operations. You know how symmetry operations can be written into matrix form.

So, you need to know all the matrix elements of all the symmetry operations and incomplete projection operator actually works with trace. Simply the traces of above matrices. Matrix representation of symmetry operations. So, what is the difference between complete, why do we use matrix elements. So, if we do this complete calculation, the calculation is tedious and all, but this gives you complete details of SALCs without any human intervention.

That is you can write a program and do this complete calculation by itself. In case of incomplete projection operator, it will give you partial combinations and then you will have to, but the workload is less. But to obtain complete set of SALCs here human intervention would be required. So, for example, if you are talking about functions that are basis for 1D IR representations.

In this particular case matrix is equal to trace, matrix representation of a given symmetry operation is equal is same as the trace. So, in this case incomplete projection operation is equal to complete projection operation. So, basically it will give you the same result. But in case of 2D, 3D or higher IR representations, we cannot say this. So, matrix is not equal to trace. And thus we need to explicitly calculate SALCs using complete projection operation or using incomplete also we can do but we will see how to actually do it.

We will discuss the case with one 1D IR representation and 2D and 3D IR representation separately. Let us first see what do we mean by projection operation and let us derive an expression for the same.

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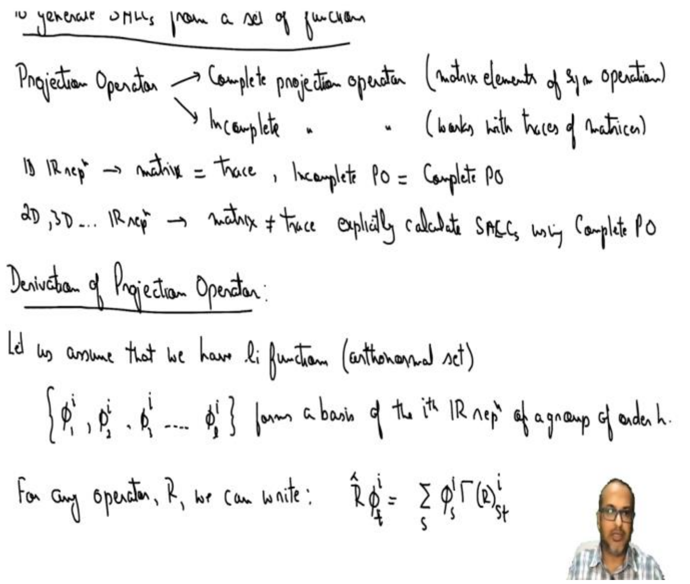

So, let us assume first that we have an orthonormal set of Li functions. Let us say that the set is something like phi 1 i, phi 2 i, phi 3 i. So, i is the index which I am giving here just to show that this is forming basis for ith irreducible representation and Li this does becomes the dimension of that representation, so you have phi li. This is the set of functions and each of these functions is orthonormal to each other.

Orthogonal to each other and these individually there are normalized so that is why orthonormal. So, now this set forms a basis of ith IR representation of a group of order h. Now for any operator R in this group, as per definition, we can write, for any operator R, let us say so if we operate R on to any given function phi t, phi t i, we can say that what we have is summation over s phi s i and tau R st i. So, what do I mean by this let us see in more details.

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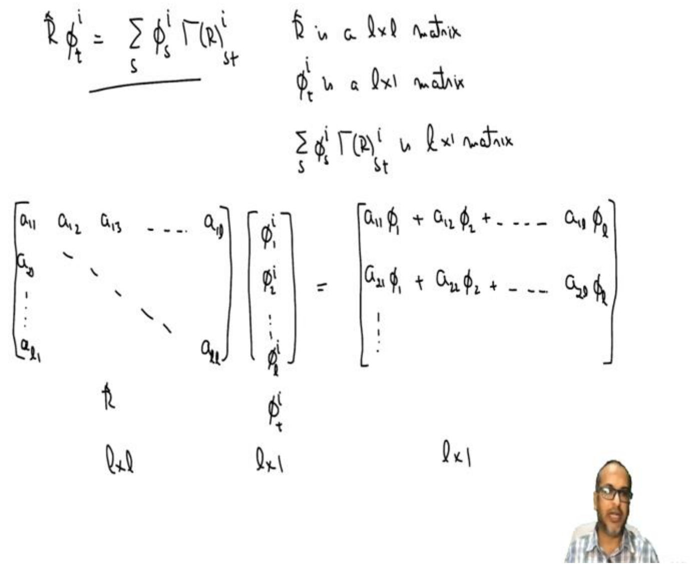

So, when I am saying, R let me write the expression again is operating on phi t i to give me summation over s, phi s i tau of R st i, so in this case R is a L cross L matrix. Then phi t i, if I am writing this in matrix form. Then phi t is L cross 1 matrix. Will see these matrices, what are these matrices and if I am saying that then, these two are matrices and this whole thing becomes L cross 1 matrix. Then summation s phi s i tau R st i is L cross 1 matrix.

Let us see what do I mean by that, so let us say if I write the above equation in terms of matrix presentation, I can say that this is a 11, a 12, a 13 going up to all the way a1L. So, here a 21, aL1. And if I go like this, this will be aLL. So, this is, l cross l matrix, so this is R matrix. So, now for phi t. So, phi t is any general function from that set of orthonormal functions. So, that means I can write this matrix as phi 1, phi 2, all the way to phi L.

So, this is my phi t i. I can write the i index over here. So, now if I do this multiplication, what do I get? I get the following, so I will get a11 phi 1 + a12 phi 2, this is L cross 1, I should get L cross 1 on the multiplication, this is not the direct product, this is the regular matrix multiplication. So, similarly if I do, if I keep on doing this, I will get a21 phi1 + a22 phi2, a2L phiL and so on. So, now you can see that how do when I write this equation basically what I am doing is I am operating R to any given symmetry operator on to a set of functions.

And each of these function then gets transformed into the final form. So, this we have done it many times so I am just writing it in general form.

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$$\begin{array}{cccc} & 3\times 3 & 3\times 1 & 3\times 1 \end{array}$$

$$C_3 x = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y + 0z$$

$$\begin{array}{ccc} a_{11} & a_{12} & a_{13} \end{array}$$

Multiply with $\left[\Gamma(R)^j_{s't'}\right]^*$ and taking sum over all R

$$\sum_R \underline{\left[\Gamma(R)_{s't'}\right]^*} \hat{R}\phi^i_t = \sum_R \sum_{s=1}^{l} \phi^i_s \underline{\left[\Gamma(R)^j_{s't'}\right]^*} \left[\Gamma(R)^i_{st}\right]$$

$$= \sum_{s=1}^{l} \phi^i_s \underline{\sum_R \left[\Gamma(R)^i_{st}\right] \left[\Gamma(R)^j_{s't'}\right]^*}$$

$$= \sum_{s=1}^{l} \phi^i_s \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{ss'} \delta_{tt'}$$

So, for example when I do a C3 operation on to x, y, z, we have seen what does it mean? So, matrix representation for a C3 operation is we have seen how to write this minus half, minus root 3 by 2, 0. This is plus root 3 by 2, minus half, 0, 0, 0, 1. And we apply it on x, y, z. This is my 3 cross 3 matrix, this is my 3 cross 1 matrix, which is phi t and what I get here is minus half x, minus root 3 by 2 y. Then root 3 by 2 x, minus half y, and z.

And this is my 3 cross 1 matrix, so when I say that C3 operated on x, it gives me minus half x minus root 3 by 2 y plus 0 set. So, I can say this that, this is my a11, this is my a12 and this is my a13. So, I can say, so this is just to show you that we have already done this, we are now just writing it in mathematical form, you already know this, so now if to the original equation which we are written earlier if we multiply with tau R s prime t prime j and star.

And taking sum over all R. So, now I am trying to make an expression which is similar to what we have learnt in our great orthogonality theorem, so that is why multiplying this and taking sum over all R, so what do I get? So, I get tau R s prime t prime star, and I had operator R, phi t i and what do I have here. And I also take summation R for this. Because I say that taking some over of all R, so, I also do summation over all R here.

There was another summation S equal to 1 to L, and I had phi s i, and now I have tau R s prime t prime j star. And I had initially tau R st i. So, this is simple, all I have done is, I have multiplied this factor with this factor over here this particular factor on both sides and I have taken the summation overall R. So, now if we carefully see that this particular term over here does not include any of this R, so it is independent of summation R.

So, this can be taken out, so I can rewrite this equation as s equal to 1 to L phi s i. So, now I can just have summation on to these two terms. Summation R I just write this one first just to because it is familiar in this order s prime t prime j star. Now I know what this is? This is using our great orthogonality theorem. I can rewrite this again. What is this? This actually becomes summation s equal to 1 to L phi s i. h upon square root of L i L j delta ij delta ss prime delta tt prime, so this is easy to see.

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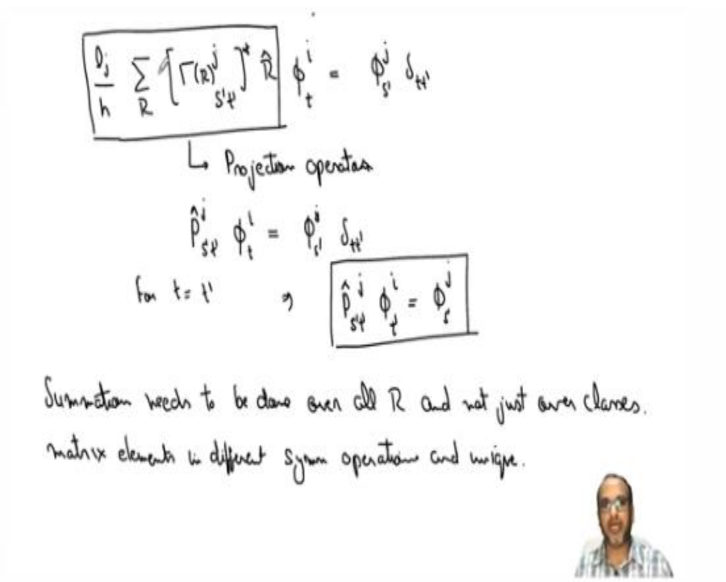

So, now let us go to next page, so now this whole thing will survive so let me just write this complete expression again now. Summation over all R tau R conjugate, R phi t i is equal to summation over all s phi i and h over square root of Li Lj delta i j delta ss prime delta tt prime. Now we have a summation over s where s goes from one to L. So, that means we can simplify the summation.

So, all the values of s where which are not equal to s prime will go to 0 so that means only s equal to s prime will survive over here. So, out of this whole summation I can just write the one of the terms. So instead of this what I will write here is phi, now my s becomes s prime because that is the only value which will survive rest all the other values of s will go to 0, i h over Li Lj delta ij and delta tt prime.

Now similarly I can say that i equal to j only those values will survive where i will be equal to j all rest of the values will go to 0. So, then now I can convert all of this into j so now this is summation over all R tau R s prime t prime j star R phi t j, because my i is equal to j now, and i can say phi is prime j h over or you can write in terms of i, so Lj we need to convert i equal to j only on the right hand side left hand side is still the same because that is still i.

Let us keep that i because the delta is only on the right-hand side. So, then I can say that this is my Lj. And what else I have got here so delta tt prime. Let us now write the expression would take everything else on this side, so now what i do is Lj write the expression for the projection operator, so if i do take all of this on this side Lj over h. Summation over all R tau R s prime t prime j star operator R phi t i gives you phi s prime j delta tt prime.

Now this whole expression is called as projection operator. See, what this operator is doing it is operating on to a function, which is the basis of ith representation is actually giving you a function which is basis for jth representation here. So, what I can say here is, so I can write this as operator p, short form for projection operator and I can say that this is my j index and s prime t prime operated on phi t i gives me phi s j, and say i equal to s prime j and delta tt prime.

Again, so if I say if I need to equate this to tt prime t equal to t prime, so that the right-hand side does not go to 0. So, for t equal to t prime can now write the projection operator as s prime t prime j phi t prime i is equal to phi s prime j, so this is my projection operator. So, the formula how to calculate the projection comes from here, but combining this becomes the complete definition.

So, we will see an example we will see an illustrative example, but I hope this derivation part is clear and now there is some sense of how to derive the projection operator but now various elements in this are; this is the, dimension of the representation then this is the order of the group summation over all R, this is the corresponding matrix element which we are going to use so different matrix elements have to be used at a given point of time.

And now because here we are using different matrix elements that would mean that we need the complete matrix details of all the symmetry operations. So, also understand that here the summation needs to be done over all R and not just the different classes because symmetry operations of different classes will be having different matrices, this is very very important. So, summation needs to be done over all R and not just over classes.

That is because matrix elements because we are using matrix elements in this, so matrix elements in different symmetry operations are unique. Matrix elements are not common so that is why we need to carry out the complete summation over all R. So, I think that is all for this lecture, so please go through it in more details and see if you have any difficulty understanding the derivation part and we will do a lot of examples so that it becomes very very clear.

How to use projection operator in different problems, so we will be taking different examples and will be trying out, trying to obtain different linear combinations which are symmetry adapted. So, we will try to calculate the SALC's using different combinations so that this is very very clear. I think that is all for today, so we will discuss some examples in the next class.