Mathematics for Chemistry
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Lecture - 36

So, today we are going to see some very interesting applications of symmetry in quantum mechanics. This is something you might have seen before in a different form. But, the advantage here is that we use the character tables to predict which matrix elements that appear in various quantum mechanical calculations are 0 and which are not 0. This will also help us identifying which are the spectral lines that will be observed. In order to do this, I am going to introduce something called the direct products. This is something we touched upon when we were doing products of vectors.

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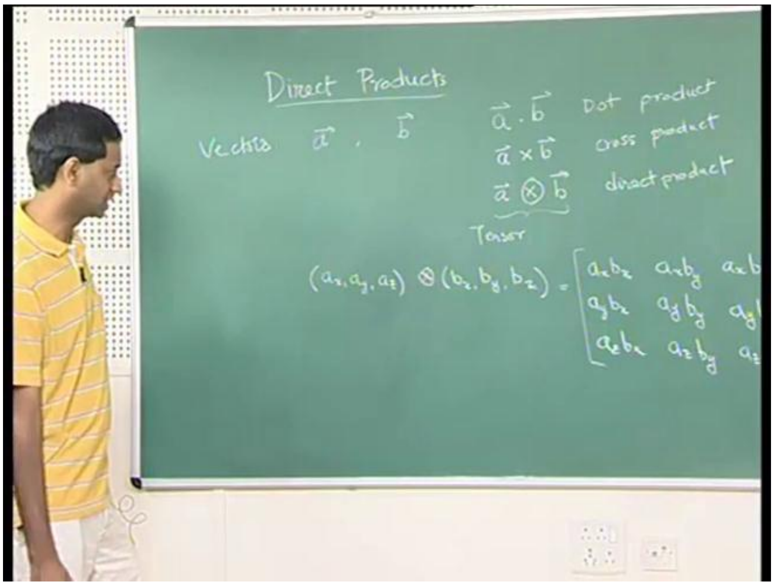

If you remember when you were doing vector products, we had a vector. You have two vectors a and b. We said that there are different ways to take products of vectors. You can take a product, where a dot b is called a dot product. The result is the scalar. Then, you have a cross b, where the result is a vector. Then there is something called a this, a direct product. This is called a direct product. This a direct product with b gives you a tensor. So, the easy way to visualize this is if a had components a x, a y, a z, and b had components b x, b y, b z, then this tensor product is can be thought of as a matrix a x b x a x b y a x b z a y b x a y by a y b z a z and b x a z b y and a z and b z. So, you can see that this is a very natural way to take the product. So, you take the products one by one. You take all possible products and you are ends them in the form of a matrix. So, this is called the direct product. This is something that we will use very shortly. Before we do that, I want to say that this can also be used.

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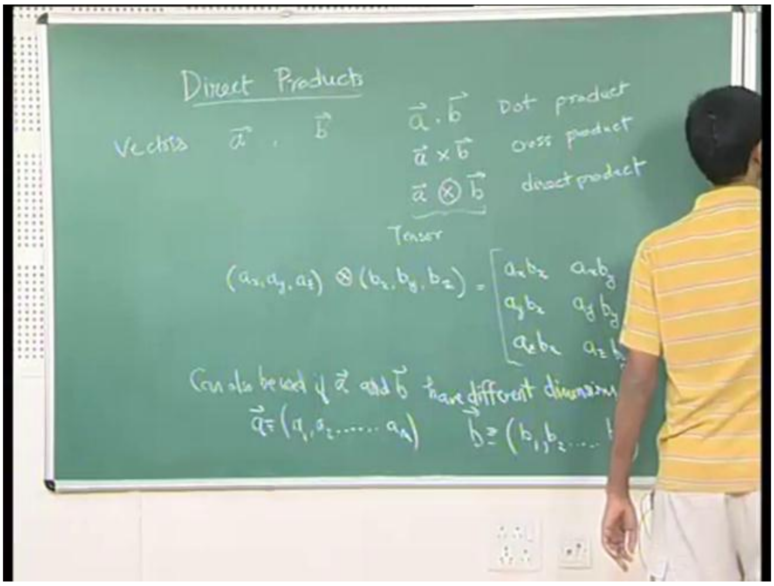

Also, be used if a and b and b have different dimensions. So, for example, if a is an m dimensional vector if a 2 up to am and b is a n dimensional vector up to b n. So, this is m dimensional. This is n dimensional.

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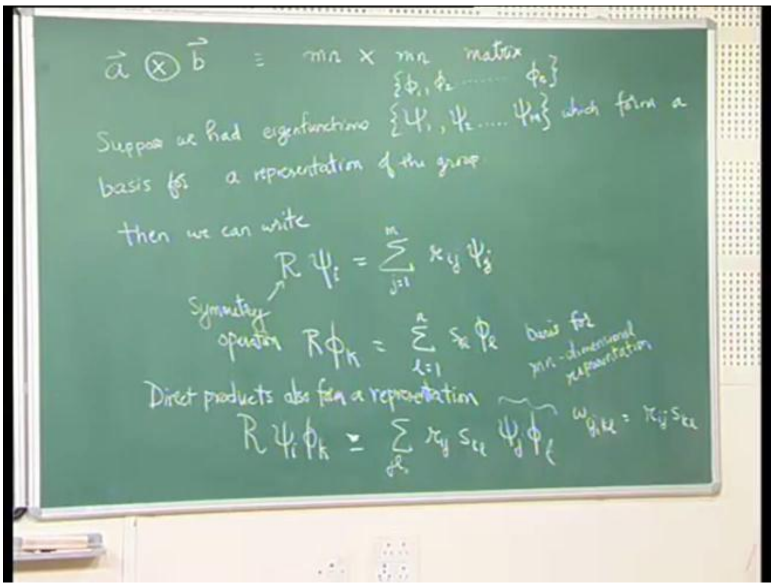

Then, a cross b is also a direct product with b. This is a mn by mn matrix. So, you represented by mn by mn matrix because there are mn times mn components. So, there are mn different products. You can take them in any order. So, you have m n times m n components. So, this notion of direct products is something that we will use very shortly. Now, suppose, we had Eigen functions psi 1, psi 2 up to psi m, which form a bases for a representation. So, suppose, to form a bases for the representation some it could be or it could be some irreducible representation some representation of the group.

Then, we can write. So, we can write the following expression; suppose, you operate r. This is the symmetry operation. So, suppose you operate r on any of the psi. Then, you will get a linear combination of all the psi sum over 1 to m. I am using r i j psi j. So, I can write it in this form. Now suppose, you had another representation; see suppose, you had yet another representation. Let us say Eigen functions this set. You had another set phi 1, phi 2 up to phi n. So suppose, you had a different representation; a different basis for another representation.

Then, you would write r times phi k is equal to sum over l equal to 1, 2. When now you might have some other matrix elements, I will just call it s l, k l, psi l. So, you would have some other matrix elements. So, these are the matrix elements corresponding to this operation in the representation. How do you think of that direct product? A direct product is most phi. So, the most natural way to think of the direct product is if you just you just take phi j.

So, we say that the psi j, they form a representation for this group. So, they form a basis for this representation. Similarly, phi l forms the basis. So then, you can ask, you can show that the quantity. So, that direct products also form a representation. So, what this means is suppose, I take a direct product like psi i, phi k. Suppose, I take psi s, psi i, phi k; i operated by r. So, if i operated by r then, it is not hard to show that. So, what you will get is the following. You will get sum over l jl. So then, what you will get is r i j s kl psi j phi k.

So, you can see this has very much structure of something like this. So, what you see is that after this symmetry operation, this product looks like this. So, this quantity is like quan matrix element of that mn by mn matrix. So, this quantity r i j w j k is equal to something wrong, w j l phi f. So, w i k; there should be w i k. So, on the left, you have i and k. Here, you have i j kl. You have to sum over j and l. So, the right hand side also depends only on i and k. So, w i k is r i j s k l. Sorry, you write this slightly different. You write it as w i j, k l. This is a quantity with four and dc i j and k l. So, we call quantity i j, k l.

This corresponds to this; is an element of that mn cross mn matrix. This is 1 of the matrix elements of another representation. So, this is a mn dimensional representation. So, in fact, this particular thing is the base for mn dimensional representation. So, you can see this expression very easily. You just take a product of these two. Then, you will end up with that expression. So, what this means is that this direct product; this is one to one element of this direct product. This direct product serves as a basis for the mn dimensional representation.

Now, what we are going to is we are going to show that that this direct product has some more properties that we are interested. So, we said that this direct product of psi and phi that also forms that the direct product of these two basis functions. That also forms basis function for another representation. Now, the question that you will ask, the two questions that you will come up with are if it is a representation; is it irreducible or is it reducible. The second question is if it is a representation, what are its characters?

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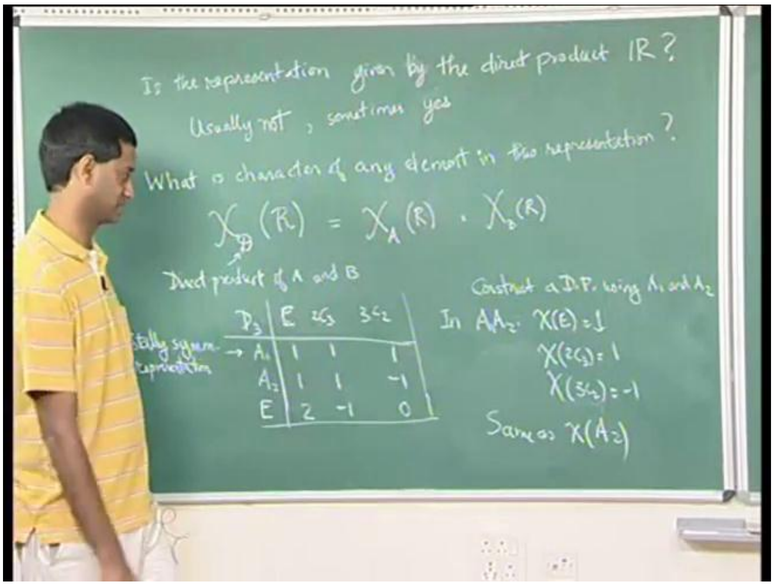

So, this is the representation given by the direct product. Is it a irreducible representation? The answer is usually yes. You will see shortly that in some cases, it is not sometimes. Next is what is the character of any element in this representation? Now, no usually, it is not an irreducible representation. Sometimes, it is. So, usually it is not a reducible representation. Sometimes, it is an irreducible representation. So, the question is direct is a representation by a direct product and irreducible representation. The answer is no. But sometimes it is a representation. It is an irreducible representation.

Next is what is a character or trace of any element in this representation? So, I will write it this way. So, the kye in this is the direct product,; product of A and B. So, you have two representations a. This is the direct product representation. So, if you look at the character of any element in this direct product representation. It is nothing but the character of the same element in A multiplied by the character of the same element in B. So, this is the character of R in representation A. This is the character of R in representation B.

If you in case did notice, these are the things that appear in the character tables; suppose, you had a character table. Let us say you have D 3. So, D 3 has A has E 3 classes. It has E C 3, 2 C 3 and 3 C 2. The three irreducible representations will be A 1, which is a totally symmetric. Then, there has to be A 2, which is 1, 1, 1 minus 1. The two dimensional representation E has characters 2 minus 1, 0. So, these are the characters of these operations in A 1, A 2 and E. So, notice that this is a totally symmetric representation. So, in this totally symmetric representation, the trace of each of the character of each of the operations is 1. Now, you can see suppose, I construct a direct product, suppose you construct a direct product, a direct product using A 1 and A 2.

So, you can construct a direct product representation, A 1, A 2. Then, you can see the trace of the various characters. So, in A 1 A 2 phi of identity E equal to 1 kye of 2 C 3 is equal to 1 kye of 3 C 2 is equal to minus 1. So, this is same as phi n A 2. It is clear. So, suppose you construct a direct product representation. Now, this will be since this is one dimensional, this is also one-dimensional. So, the direct product will also be one dimensional. In fact, the direct product is nothing but A 2. That is because this is a totally symmetric representation, okay?

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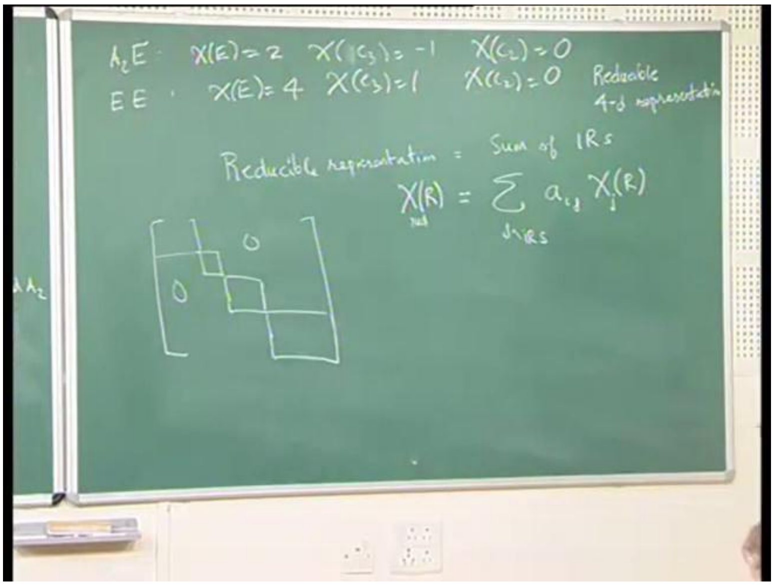

Now, consider A 2 times E; so, A 2 times E. Now, the character of identity is 2. Character of 2 C 3 of C 3; I should not write 2 C 3. I should write character of C 3 is minus 1 character of C 2 is equal to 0. This is A 2 E. The characters are identical to E. That is because this is a one-dimensional representation. This is a two dimensional representation. Their direct product will be a two dimensional representation and 2 dimensional representation is identical to this E. Now, we can construct other representation. For example, you can say, you can look at E times E. Now, in this case, kye of e is equal to 4 kye of C 3 is equal to 1 kye of C 2 equal to 0.

So, 2 into 2 is to four. You can get 1 and 0. So, in this way, you can go and construct many such direct products. The dimensionality of E is a four dimensional representation. It is a four dimensionality representation. The character of identity will be 4, character of C 3 turns out to be 1, character of C 2 turns out to be 0. So, using direct products and clearly since, it is a four dimension representation, it cannot be an irreducible representation. It has to be a reducible representation. So, this is a reducible representation, reducible 4 D representation

So now, there is something that you might have noticed. When you construct direct products, you sometimes end up with these reducible representations. In some cases, in these cases, it turned out to be the same as existing representation. So, they turned to be irreducible. But in general, you end up with reducible representations. Now, reducible representation; we said that if you have a representation that is reducible, you can sort, break it into block diagonal forms.

You can write as a sum of irreducible representations. So, reducible representations can be written as sum of irreducible representations. This is what we had seen. If you had a reducible representation then, you could make it block diagonal. Then, you would say it is sum of these four representations and also these 0 everywhere else. Also, we looked at cases where one representation; one irreducible representation might appear many times in a reducible representation. So now, this leads us to something interesting because you have this reducible representation. On the one hand, they are written as sums of irreducible representations.

So, this looks like sum over j a i j kye. So, you say, you had the expression, the character in the reducible representation is the sum over all irreducible representations of kye of r over all irreducible representations. So, we had an expression like this. So, on the 1 hand, you can take this reducible representation. Write it as a sum of irreducible representations. On the other hand, you would have this reducible representation, which you can sort of factor out into these into product as irreducible representations. So, the direct product is like you make irreducible representations by taking products of irreducible representations.

The other way you can do is that take the reducible representation and writes it as a sum of irreducible representations and both these. So, what we want to do is we want to look at how these two things are related the point. I want to make here is that there are only some representations that can be written as direct products. Only a certain number of representations can be written as direct products though all representations can be written as irreducible representations or can be written as sums of irreducible representations.

So, this is generally true for any representation. This direct product is only true, when you construct your reducible representation using direct products. So, what we want to do is to look at the relationship between these. See how we can exploit the fact that you can write a reducible representation as a sum of irreducible representations. If our reducible representation had a form a direct product, how we exploit that? So, to see an application, a very simple application of these direct products.

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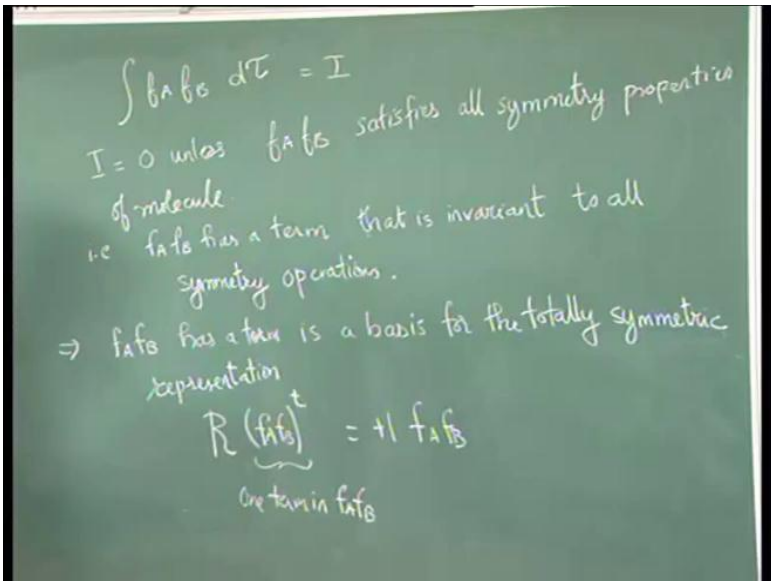

Let us consider this quantity. Let us consider an integral f of A, f of B d tau. What we want to think about is these are related to bases functions from 1 to representations. So, we want to think of these as bases. We will eventually think of these as bases functions from two representations. Now, this will be 0. So, an integral like this; so, we call this i. So, i equal to 0 unless f A, f B satisfies or all symmetry properties of molecule; in other words, f A, f B. So, in other words f A, f B has a term that is invariant to all symmetry operations.

So, the idea is following is you are looking at any integral. Then, this will be, this can be written as the sum of many terms. So, your f A, f B will look like a sum of many different terms. Now, each term will be 0 unless it is invariant to all the symmetry operations. So, unless your when you operate the by the symmetry operation, this term is not changed. Then, it will be 0. So, the point is that f A, f B should have a term. It could be a sum of terms. If it had only one term, then, f A f B would be 0 unless that term is invariant to all the symmetry operations. So, this is fairly obvious to see. I mean you can think of it as, you know when you take a one dimensional integral.

If you have an odd function then; an integral from minus infinity to infinity of an odd function will be 0. Then, you say that the function does not have the symmetry of the space that we are looking at. So, same way in this, if your integrant does not have appropriate symmetry properties, this integral will be 0. So, that means, this implies f A, f B has a term. So, this term, f A, f B is a basis for the totally symmetric representation. So, in other words, you operate by R on this. I will call this f A, f B. I will put a t here. So, if you take this term so, this particular term and you operated by R. So, this is one term and f A, f B.

So, you operated by R. Then, you get back so, you get plus 1 times f A, f B. So then, f A, f B is a totally f A, f B is bases for this totally symmetric representation. So, for any operation, you get plus 1. So, the character for every operation is 1. So then, f A, f B base is the bases for this totally symmetric representation. So, what we have is that if this integrant is not 0, if it is not 0 then, it has to be a bases for the totally symmetric representation. This is the property that we will exploit a lot. So, unless f A, f B is a base for this totally symmetric representation, this integral f A, f B d tau will be 0. Now, the question is this is something about the product.

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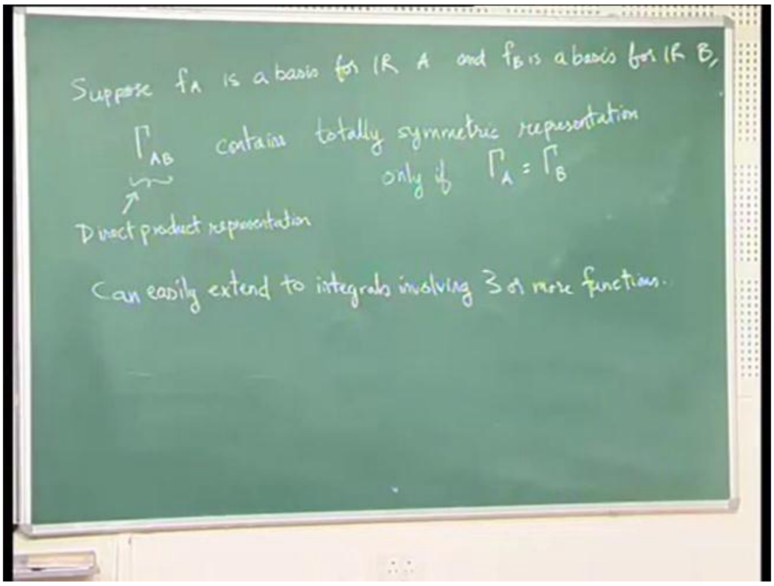

Now, suppose, f A is a basis for irreducible representation A. f B is a basis for I R B, irreducible representation B. Suppose, f A is a basis for irreducible representation A and f B is the basis for irreducible representation B. Then, what can you say about this representation A B, versus A and B. So, this representation is direct product representation. So, this is the direct product representation. Now, the question is unless this is a basis for the totally symmetric representation, this integral is 0. Now, what we want to find out is when will this be a basis for the totally symmetric representation.

So, if f A is the basis for irreducible representation A and f B is the basis for irreducible representation B. Then, this direct product representation contains totally symmetric representation. So, when does it contain the totally symmetric representation? This contains the totally symmetric representation. It is not hard to show this. That means the way you think about this is direct product representation is written as a sum of various representations, various irreducible representation. This contains a totally symmetric representation only if the irreducible representation A is the same as irreducible representation B.

So, in other words, this integral is this; is a round. This is a way of saying that this integral is non zero only if f A and f B are the same. So, if A and B are irreducible representations then, this integral is 0 only if f A and f B are the same. So, f A and f B belong to the same representation. So, only f A and f B are basis functions of the same representation. So, if these two are basis functions of the same representation then, this integral will have one term that is non zero. In other words, that term, that product will be a basis for the totally symmetric representation. So, this is the basis for the irreducible representation. f A is basis for irreducible representation A. f B is basis for irreducible representation B.

Gamma A B, this direct product representation contains a totally symmetric representation only if gamma A equal to gamma B. This is very easy to show this is just based on the expansion of reducible representation; in terms of irreducible representations. What is important is that. So, you can just look at the symmetries of these basis functions. You can conclude on the non zero properties of the representations. So, similarly, you can easily extend two integrals involving three or more functions. So, I did this for two functions. But, it is fairly straight forward to do it for three or more functions. I would not bother doing that. Now, let us look very popular application of these principles.

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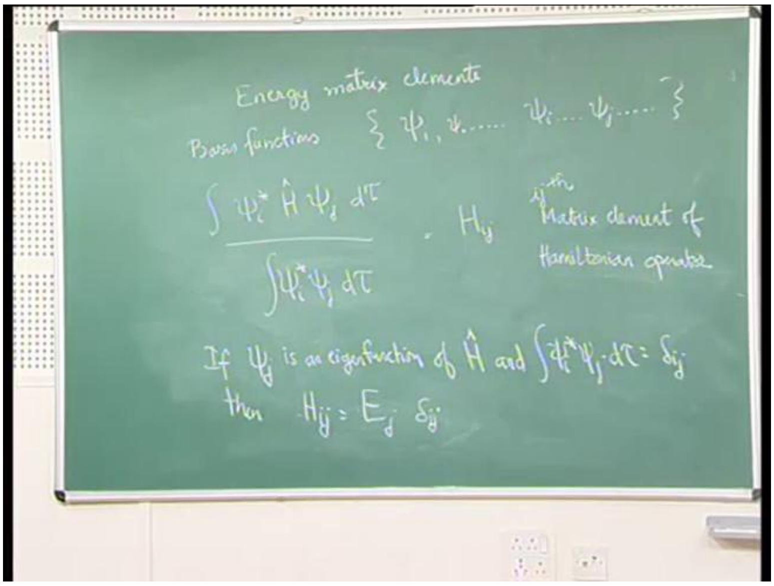

So, the first we will talk about is energy matrix elements. These are extremely useful when we are doing calculations of the electronic structure of various large systems. Then, you have then, calculate lot of these energy matrix elements. Any input you can take from symmetry that will help simplify the calculations is extremely useful. So, let us look at an application here. See, suppose, you have your basis functions psi 1, psi 2, phi I, phi j and so on. Suppose, these are your basis functions. Now, what do you mean by energy matrix elements?

You consider integrals of the form integral psi i star Hamiltonian operator psi j d tau divided by integral psi i star psi j d tau. So, you look at expression like this. This is referred to as h i j. This is matrix element of Hamiltonian. I will say i j th matrix element of Hamiltonian operator. So, it is a i j th element of the Hamiltonian operator. Now, if your psi j th and the Eigen functions of the Hamiltonian, if your psi j th and Eigen functions of the Hamiltonian. Then, you can easily show that if psi j is an Eigen function of H and psi i star psi j d tau is equal to delta ij. That means it is orthogonal. I mean these vectors form an orthogonal basis. Then, H ij is equal to E. So, H times psi j will be E j times psi j. So, it will be E j.

Then, you have psi i star psi j d tau divided by psi i star psi j. So, H i j is nothing but E j times delta i j. So, if i is not equal to j then, the integral will be 0. So, you can work it out. You can use such a relation. Now, if in general, this might not be Eigen function of the Hamiltonian. So, you do not know the sometimes it is a challenge. In the challenge is to find out which is the appropriate Eigen function. So, you want to find an appropriate eigen function. So, if you try some function, it will typically not be an Eigen function of the Hamiltonian. When such terms appear in variation theory and all methods of approximate methods of calculating structure, now, you want to know when H i j equal to 0.

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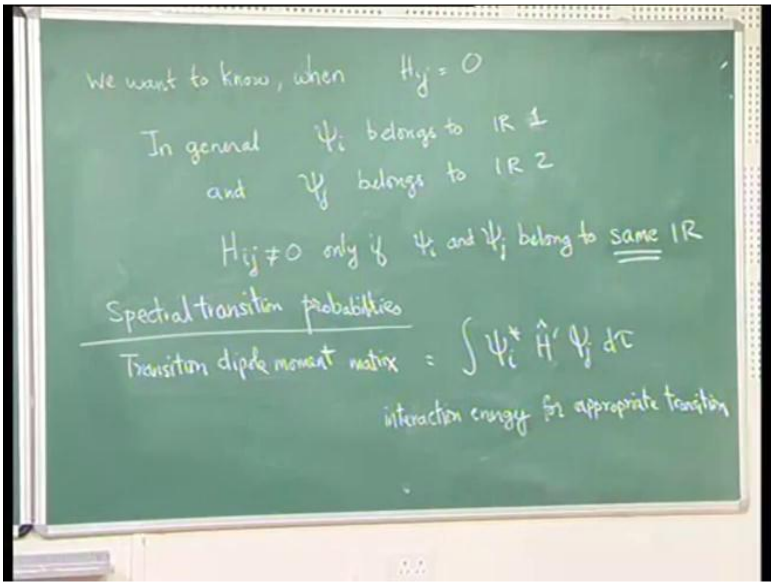

So, we want to know when H i j equal to 0. So, when is H i j equal to 0? So, that is a question that we want to answer. Now, so, we have two functions psi i. In general, psi i belongs to irreducible representation 1. Psi j belongs to irreducible representation 2. So, what I mean by psi? Psi i belongs to irreducible representation 1. Psi i is one of the basic functions for an irreducible representation. Similarly, psi j is one of the basic functions for another irreducible representation.

So, psi j they belong to irreducible representations. Now, H i j not equal to 0 only if psi i and phi j belong to same irreducible representation. So, that means, if these two basis functions in this of the same irreducible representation, only in that case, will this integral be non zero. This is an extremely powerful theorem and a very useful result. We look at some applications of this.

So, the other very common application is in spectral transition probability. So, this is one application we saw was energy matrix elements. In that, you can use some ideas of symmetry to find out which of these energy matrix elements will be 0 and which will not be 0. The other application is in spectral transition probabilities. Again, the idea is very similar. So, here typically spectral the transition probabilities are there is a quantity that appears we call the transition dipole moment matrix.

This is given by integral psi i star mu psi j d tau. So, the i j th matrix element of this transition dipole moment matrix is given by psi i star mu psi j. Mu is transition dipole for appropriate transition. What I mean by appropriate transition is that if you are looking at a transition caused by the electric field then, this will be the electric dipole.

If you are looking the transition caused by the magnetic field, it will be the magnetic dipole. So, which ever, whatever quantity couples to the external field is what will appear here. Now, this is more. This is, I will write it as x prime. This is interaction. This is interaction energy for appropriate transition. This is related to the interaction that couples that interaction with the external field. That allows this transition to take place. It is related to the interaction energy. Further so, if you are looking at so as an example.

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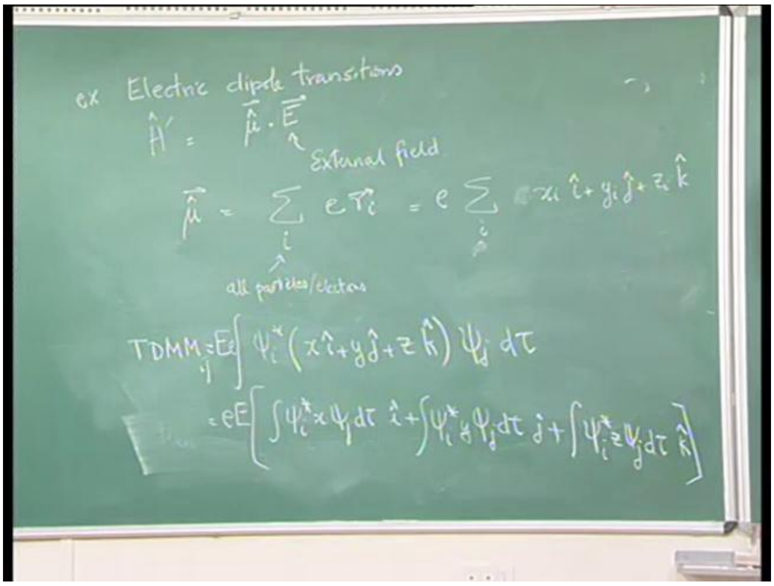

Let us look at electric dipole transitions. Then, in this case, x prime is equal to the dipole moment operator times E. So, dipole moment operator dot to E. Now, the dipole moment operator; this is the external field. Mu, this operator can be written as sum over all particles. In this case, we will be looking at electrons. What you can write it? You can write it as e, which is the charge on the electron times r i. It is the position of the particular electron. This can be written as sum over all particles e x i. So, I will take the e outside x i i hat plus y i j hat plus z i k hat. So, this integral involves H prime.

So, transition dipole moment matrix looks like i j th element integral psi i star. Now, you have E, e and what you have is x i hat plus y j hat plus z k hat psi j d tau. So then, you can write it as three integrals E t times e. The first integral will look like psi i star x psi j d tau and this thing multiplied by i plus integral psi i star y psi j d tau. This thing will be multiplied by j plus integral psi i star z psi j d tau. This will be multiplied by k. So, this is i j th matrix element of the transitional dipole moment matrix.

This tells you the probability of transition from i to j or from j to i. This tells you the probability of transition from i to j or j to i. Now, you can immediately see this will be 0. Unless one of these integrals is non zero, this will be 0; unless one of these integrals is non 0. So, equal to 0 unless one of three integral above not equal to 0. So, can we say something about which of these integrals will be non zero just based on the symmetry properties of psi j and psi i.

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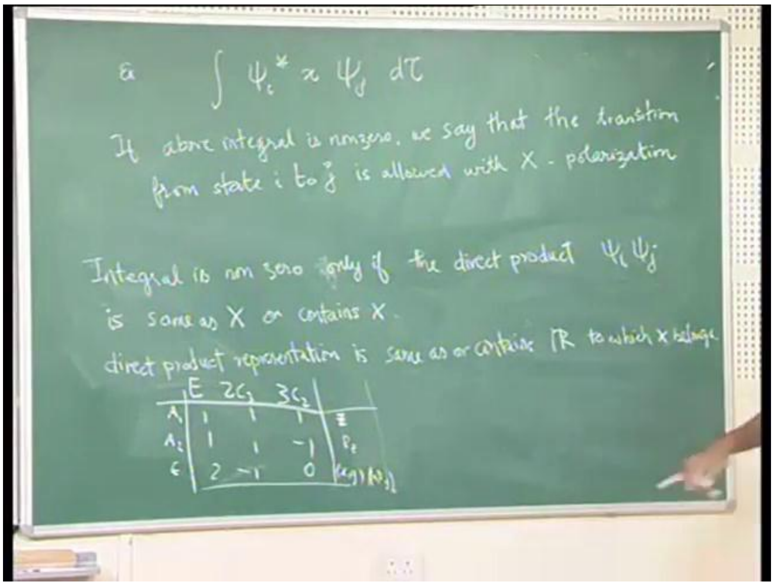

So, let us take example. Again, let us take integral psi i star x psi j d tau. So, the question is when this integral equal to 0 and when is it not equal to 0. Now, if this transition dipole is non zero, if this is not equal to 0 then we say that the i to j transition is allowed with x polarization. So, i to j transition x polarization is allowed. So, that is what you say in this case. So, the question is when is this i to j transition with x polarization allowed?

So, of above integral is non zero, we say that the transition from state i to j is allowed with x polarization. So, the question is when is this allowed? The answer is actually very, it looks very simple. But it should be fairly obvious, when you it should be fairly obvious to see so.

So, integral is non zero if or only if the direct product psi i psi j. So, the direct product representation psi i psi j is same as x or contains x. So, what I mean by is same as x contains is that same as this means. In other words, the direct product representation is same as or contains I R, the irreducible representation to which x belongs. If you recall you have E 2 C 3 3 C 2 and you have typically A 1, A to E, you have all these characters 1, 1, 1, 1, 1, 1 minus 1, 2 minus 1, 0. On this side, what you have here is x y, x y z, r z, r y, r z.

Suppose, let us say y. Let us say you have x y, r x, r y. Let us say this is z r z. So, if you had something like this then, what you see is that x x and y appear in this representation, in this irreducible representation. So, this integral will be non zero only if direct product psi i star psi j b belongs to this irreducible representation. So, only this direct product belongs to this irreducible representation.

That again, it should, it is something that can be shown fairly easily. So, what this helps you is that. So, now you realize the significant of writing all this x y z here. So, you can immediately see which transitions will be allowed with z polarization, which transitions will be allowed with x y polarization. So, next we will look at some more applications of this in the next class.