Symmetry and Group Theory

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Lecture - 02
Symmetry and Parity Operator

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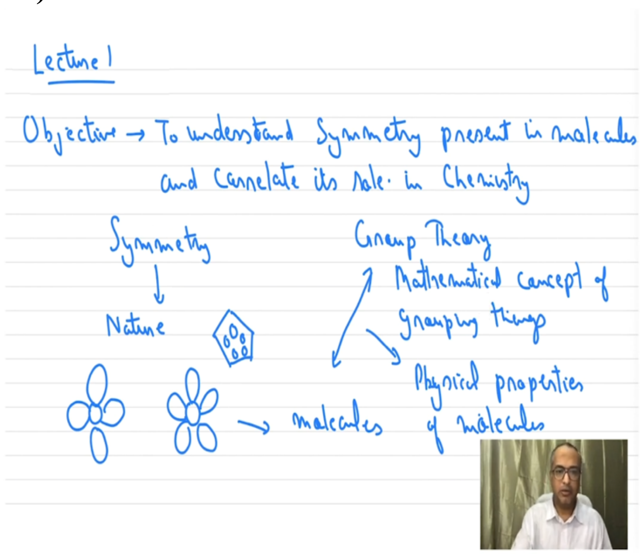

Welcome back everyone let us start with lecture 1, let us first look at the objective of this course. So the objective is to understand symmetry present in molecules and correlate its role in chemistry. So let us see how to do that. So the course has 2 aspects 1 is symmetry, another is group theory, right? Now symmetry as we know it is present everywhere around us it is present in nature it is created by nature.

So for example let us look at the cross section of okra, the vegetable, or it is also called as lady finger you must have seen that it is pentagon in shape and then nice 5 circles or 5 small pentagons arranging center. So there is a lot of symmetry going on in there. Then you can also see the differences in flowers with 4 petals versus flowers with 5 petals, right? So our brain immediately tells us that this flower is different from the other.

So we have been coded with the information that symmetry is present out there. Now what we are going to do in this course is we are going to tap that information and we will try to visualize symmetry in molecules. And then we will try to group molecules based on symmetry. Once we do that, we will try to combine the rules of group theory with the symmetry and then we will try to predict physical properties or explain physical properties of molecules.

Now what is this group theory? Group theory is a mathematical concept of grouping things. This is based on certain set of rules and we will all see what the rules are to group things based on certain properties. So let us look at let us move forward.

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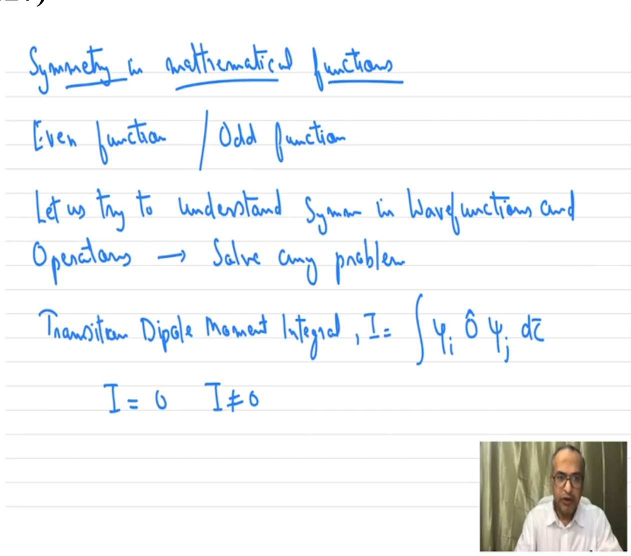

And let us actually start with what we know. So let us try to see the symmetry in mathematical functions. So we are well aware of what is an even function and what is an odd function. So we will be using this concept of even function and odd function to be able to say or comment about symmetry in wave functions and operators which are mathematical functions. So let us try to understand symmetry in wave functions and operators and see if we can solve any problem using that. So in certain areas of chemistry you will be encountered with, specifically spectroscopy, so you will be encountered with something called as transition dipole, do not worry about it as of now but this will explain later, so transition dipole moment integral which is denoted by I which is equal to integral of psi i operator psi j d tau. Now a lot let's say a lot depends on whether I goes to 0 or I does not go to 0. And let us say if we can apply symmetry rules or symmetry in mathematical functions to be able to say whether I is going to be 0 or not for a particular set of operators and their functions. Can we do that? So let us look at how to do that?

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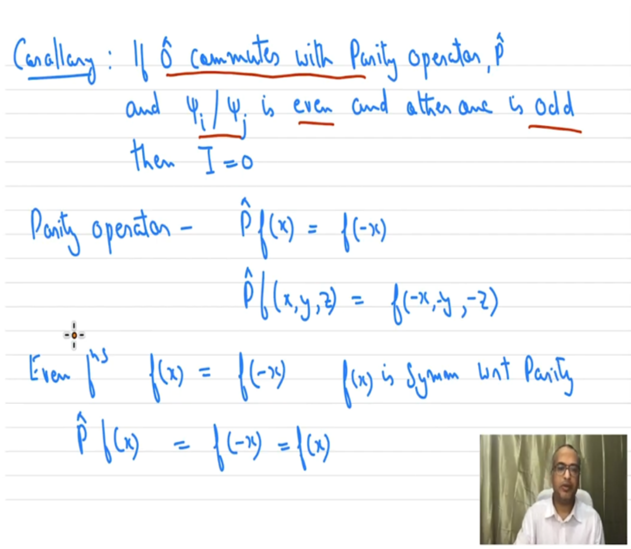

So let us say if I have a corollary based on rules of symmetry which says that if operator commutes with parity operator p. So what is parity operator? We will come to that. And psi i / psi j is even and other one is odd, then I goes to 0. So basically, it is dealing with 2 conditions one is if O commutes with parity operator, second condition is one of these functions has to be even and the other one is odd, then I go to 0.

If both are even or both are odd then we can say that I do not go to 0 but first it has to fulfill the condition that O has to commute with parity operator. So now let us look at first what is a parity operator. So parity operator, is denoted by p, on any function inverts the sign of the variable. So if it is a function in one variable it will be p on f(x) will give you p of minus f(x). If it is a function in that say P variables all P variables will have inverted sign -x, –y, -z.

So it is like flipping a function through a origin. So it is very clear thing. Now let us say if we apply parity on different types of functions like even functions. So even function f(x) = f(-x). So if we apply parity on even function it will be f(-x) which will be f(x) because for even function these 2 terms are equal. So we can say here that f(x) is symmetric with respect to parity. Now let us see what happens if we apply parity on odd function.

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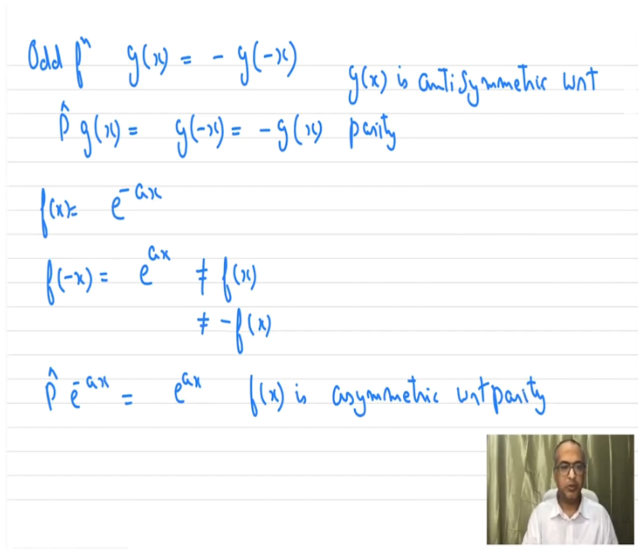

So, let us say that is considered an odd function g(x). So definition of odd function tells you that g(x) is equal to negative of g(-x), right. Now let us say we apply parity on g(x) what we will get is g(-x) and in term we get minus of g(x). If we get this kind of situation, we say that g(x) is antisymmetric with respect to parity. Now in certain conditions it is the function can be neither even or odd, right, is not necessary.

So, for example let us say if we take an example of f(x) is equal to e(-ax). Now what happens if you apply f(-x)? You get e(ax) which is not equal to f(x) which is not equal to -f(x). So, in this case if we apply parity on e(-ax) we will get e(ax) which is neither f(x) nor -f(x). So, we can say that this particular function is asymmetric with respect to parity. This should be clear, right. It should be easy to grasp.

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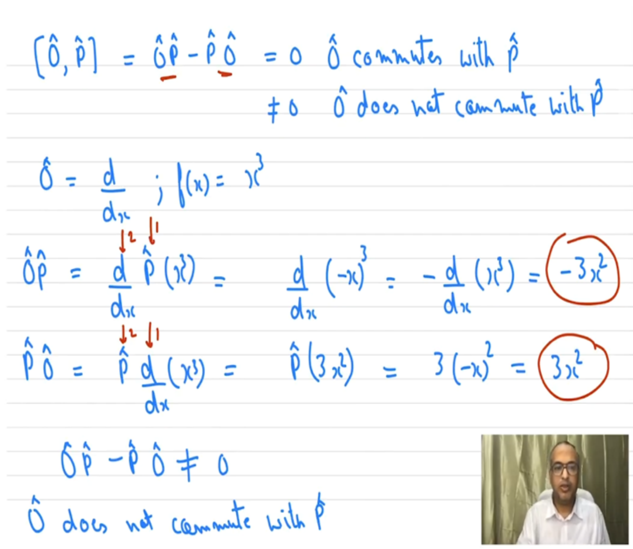

So now let us come back to the first condition. So, the first condition in the corollary says if operator commutes with parity, so what do you mean by commutation? So commutation is written in mathematics as O P comma with square brackets it means mathematically O P minus P O. So, we have to calculate this and if this thing goes to 0 we say O commutes with P parity if this thing does not go to 0 we say O does not commute with parity.

So, to be able to calculate this we need to assume certain operator. So, let us assume d/dx. And we also have to have some sort of a function. So, let us assume a function is x cube. Now let us calculate the first part this part and then we will calculate this part. So, OP will be equal to d/dx let us write the parity and operator and the function x cube. Now whatever function comes at the right side will operate first.

So, in this case though or whatever operator comes in the right side will operate first. So, in this case the first will be this will be the first and this will be the second operation. So, parity we all know by definition x cube x has to be replaced with minus x which will give you minus x cube. So d/dx[(– x)^3] this will be minus can come out d/dx(x^3) and first derivative of x cube will be 3x^2, we have negative sign out.

So now let us calculate PO, so in this case P d/dx(x^3). So now let us see this will be your first operation and this will be your second operation. So first operation derivative of x^3 which will be 3(x^2) and we have parity on this. Now if you replace x with -x to apply parity, so we will get -x^2 which is equal to 3x^2. So, notice that these 2 terms are not same right. So that means OP-PO is not equal to 0. So, O does not commute with P. So, our first condition of corollary is not fulfilled here. So, let us now look at another example.

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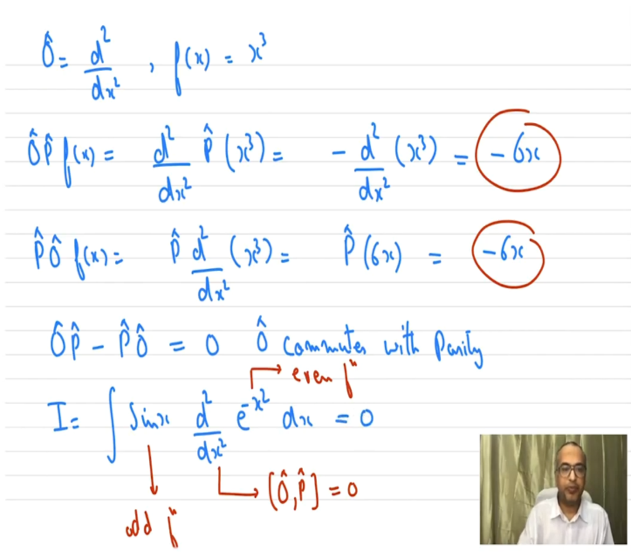

Let us take O as second derivative d^2/dx^2. Let us keep the function as x^3. You can choose different functions or combination of different functions and operators to visualize yourself. So now let us calculate again OP f(x). This will be d^2/dx^2 parity x^3. Parity of x^3 we have all seen is -x^3. So, minus comes out d^2/dx^2 (x^3).

Now first derivative will be 3x^2, secondary derivative will be 6x. So, we have -6x. Now let us calculate PO f(x). We have parity on d^2/dx^2 (x^3). Now second derivative will be 6x (within parity). x is replaced by -x because of parity so what you will get is -6x. So, notice now that these 2 terms are same. So, we can safely say that OP - PO will be equal to 0.

So, we can see now O commutes with parity. So, first condition is fulfilled now. Let us look at let us now set up an integral to see if we get a combination of even and odd function in psi i and psi j. So, let us have our transition dipole moment integral as let us say you have sin(x). We know that d^2/dx^2 operator commutes with parity, we have just proved that. Now let us say we have a function e(-x^2), dx.

Now we know that this thing so by looking at it if we can solve it will be really cool it looks a dreadful integral to solve but let us see what are the symmetry rules which says, so OP commutation is 0. So that means O commutes with P. Now this is an even function or odd function? This is an odd function, and this is an even function. So all the conditions of the corollary are fulfilled that means we can safely say that this particular integral goes to 0.

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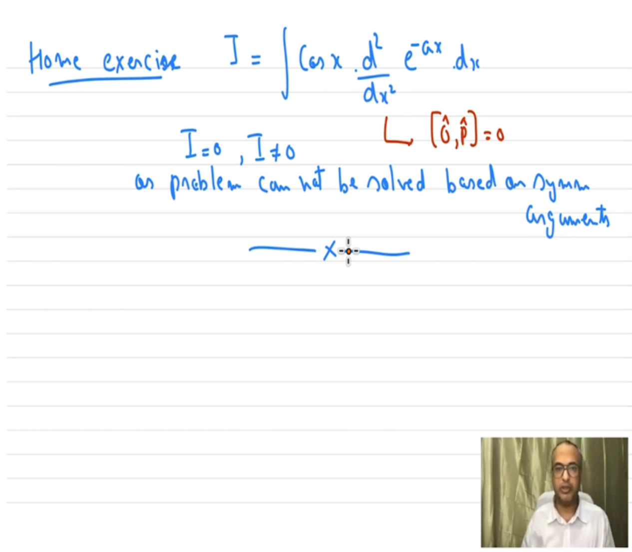

So very easy. Now do it as a home exercise, let us set up an integral with I = cosine(x) d^2/dx^2 e(-ax) dx. Now we all know already that this thing d^2/dx^2 operator commutes so this thing is already clear that operator commutes with parity, now try to identify whether this is an even function or odd function, do a little exercise. Try to identify this is an even function and odd function and now based on symmetry rules can we say if I = 0, I is not equal to 0, or problem cannot be solved based on symmetry or symmetry arguments.

So, try to do it and come back with answers or contact me for answers if you have any difficulties. Okay that is all for today. In the next video we will look at symmetry elements and symmetry operations. Thank you.