Introductory Quantum Chemistry
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Lecture - 31
Generalized Uncertainty Principle

So, we were looking at the properties of Hermitian operators. We saw one property; the property is that any Eigen value of a Hermitian operator has to be a real number. Now we want to look at one more property. This is regarding orthogonality of the Eigen functions.

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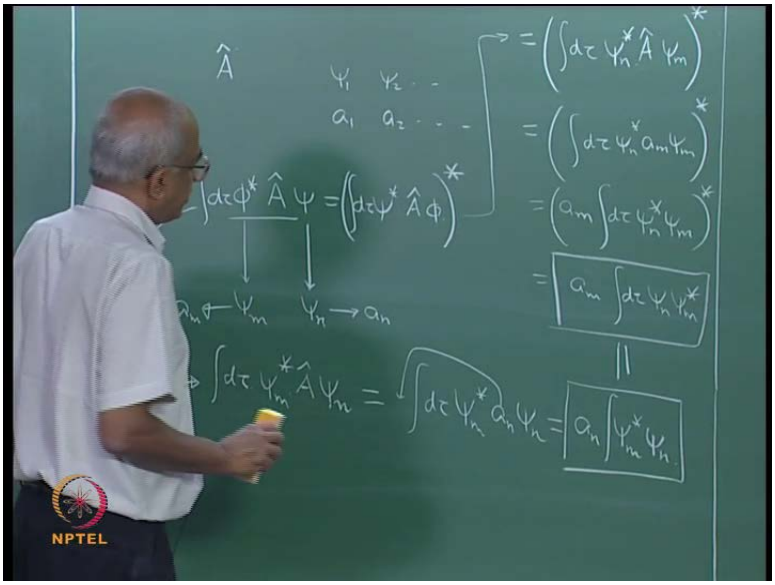

So, we imagine that we have this operator A. It has the Eigen functions which we denote as psi 1, psi 2, psi 3, etcetera, and the corresponding Eigen values are a 1, a 2, a 3, etcetera, and what we will prove is that any one of these Eigen functions belonging to different Eigen values will be orthogonal. This is what we will prove? And the way the proof goes is like this, because A is Hermitian I know that A operating up on any acceptable function psi multiplied by phi star integrated over the whole space must be equal to A operating up on phi multiplied by psi star volume element d tau integrated over the entire space star.

So, these two numbers must be complex conjugates of each other, for any two acceptable state functions psi and phi. So, now what we will do is, we will imagine that the psi is

one of these Eigen functions or let us say it is the nth Eigen function having an Eigen value which is A n, correct, and phi I will choose it to be the m th Eigen function, okay, psi m having an Eigen value which we will denote as m, and further I will also assume that a m and a n are different. So, they do not have the same Eigen value, but they have different Eigen values. So, a m is not equal to a n. So, let me evaluate the left hand side of this equation. The left hand side is going to be integral d tau psi m star. I am just evaluating this part A operating upon psi n; that is the left hand side this part, and if you look at this expression, what is going to happen? A is operating up on psi n; psi n is an Eigen function of this operator.

So, what is going to happen? The result will be psi n multiplied by the Eigen value A n. So, therefore, this will become integral d tau psi m star a n psi n, but a n is just a number. So, it is not necessary for me to keep it here. I can take it from there and move it to this place. So, therefore, this will become integral a n multiplied by psi m star psi n, okay. So, that is the left hand side. Now you have to evaluate the right hand side; may be I will start from here. The right hand side is actually integral d tau; psi is identified with psi n. This psi instead of psi I am going to put psi n. So, I will have psi n inside. Then I will have a. Well, the psi n should be having a star. Then I will have a operating upon; the phi is identified with psi m. So, I will have psi m, and then of course, the whole thing after evaluation I have to take the complex conjugate, correct, and now what is A operating up on psi m? Psi m is an Eigen function of A.

So, therefore, this is going to be equal to integral d tau psi n star a m psi m, but this a m I can move out. So, I will have a m integral d tau psi n star psi m, the whole thing star, correct, and this star suppose I perform the star operation I am going to get a m star, but a m is an Eigen value of the Hermitian operator. So, a m is assured to be real. So, the star operation taking the complex conjugation does not affect a m. So, what will happen this actually I could say a m star, but a m star is the same as a m, because a m is real, multiplied by the star of this, and what is going to happen? You are going to get psi n. This star you take inside psi n star star that is nothing but psi n, and psi m you have to take the complex conjugate. So, we evaluated the left hand side, left hand side is equal to that. We evaluated the right hand side; the right hand side is equal to that. So, therefore, that implies that these two have to be equal, correct. For a Hermitian operator this has to be equal to that and that let us write that equation.

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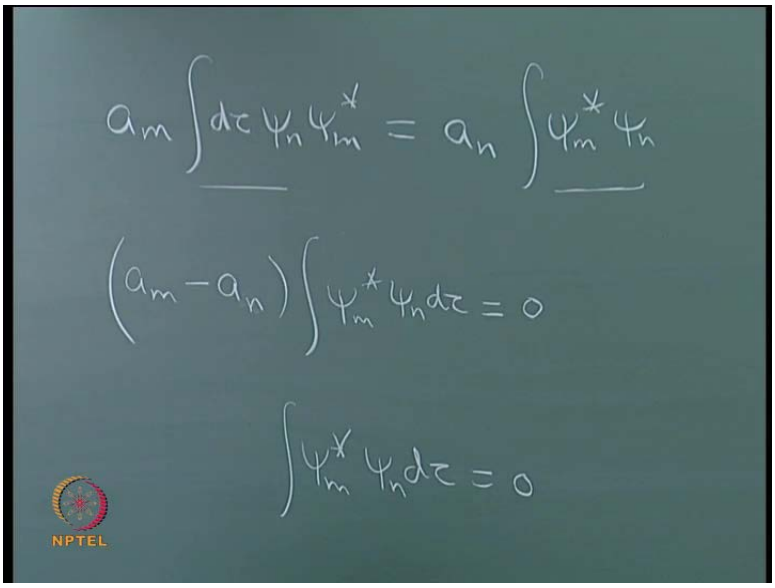

What it says is that a m into integral d tau psi n psi m star is equal to a n into integral psi m star psi n. This is what happens, and so if you took the right hand side to the left hand side, what are you going to get? You are going to get a m; you see that this and that are the same. So, therefore, what you are going to get is a m minus a n into integral psi m star psi n d tau must be equal to 0. This is the result that you are getting, but then we have already said that we are interested only in the cases where a m is not equal to a n. So, therefore, a m minus a n cannot be 0 and therefore, I am perfectly justified in dividing throughout by this expression. If this was 0 then I i cannot divide by that, but by definition a m minus a n is not 0, because the two Eigen values are not the same.

So, you divide throughout by this, and what do you find? You find that the m th Eigen function must be orthogonal to the nth Eigen function. We have seen examples of this. For example, in the case of particle in a one dimensional box or harmonic oscillator; even in the case of the hydrogen atom you can show that this is valid, but you may ask what will happen if the Eigen functions have the same Eigen value? Then the proof is not valid, and they need not be orthogonal, okay. They need not be orthogonal, but normally because we want everything to be orthogonal once we get the Eigen functions we make sure that they are orthogonal, and that is always possible, okay. Having seen this I now want to again go back to the postulate three and discuss that a little bit.

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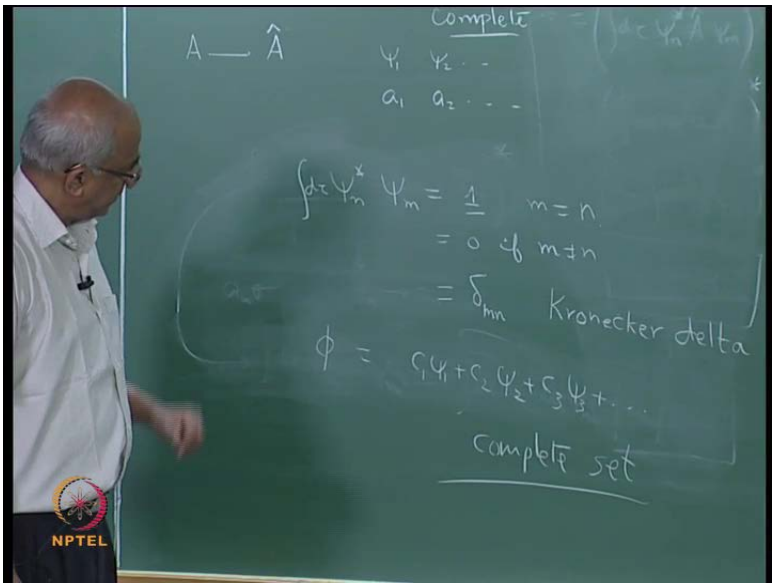

Now let us imagine that I have an operator A corresponding to some observable some observable which I may have to denote by this symbol A. For example, it could be momentum or it could be energy; it could be anyone of the may be angular momentum or some such observable is there, and I have an operator corresponding to that. And that operator will have Eigen functions which we have denoted by the symbols i 1s, i 2s, i 3s, i 4, etcetera, and the corresponding Eigen values are a 1, a 2, a 3, a 4, etcetera. And further I will assume that if I took any Eigen function may be the m th Eigen function and multiplied it by the n th Eigen function and integrated over the entire space, okay. I am going to now say that okay, this is such that the answer is equal to 1, when? When m is equal to n. If they are the same the answer is 1, and this is equal to 0 if m is not equal to n. So, I will assume that; I have already performed this normalization business.

So, each function is normalized, and each function I will assume is orthogonal to the remaining functions. So, this object you see this is an object which is if m is equal to n I have 1, and if m is not equal to n I have 0. This usually is written as delta m n. The definition of delta m n is this. If m is equal to n it is equal to 1, and if m is not equal to n it is equal to 0; that is the definition of this symbol, and it is referred to as the Kronecker delta; Kronecker is the name of a person. We have already seen another delta not delta, but a delta function. This was introduced by Dirac that we discussed earlier. Now in addition to this you see every operator that occurs in quantum mechanics has a very

interesting property. The Eigen functions always form a complete set. I suspect I have discussed this a little bit in connection with particle in a one dimension box.

What it means is that if you give me any arbitrary function which is an acceptable wave function then I can expand it in terms of these Eigen functions. You give me any arbitrary function, it is possible for me to write it as a linear combination of psi 1, psi 2, psi 3, psi 4, etcetera; that means suppose you give me a function anyone of you gives me a function phi which is an acceptable function. Then this phi may be expressed in terms of psi 1, psi 2, psi 3, etcetera, how? You can say c 1 psi 1 plus c 2 psi 2 plus c 3 psi 3 plus etcetera. So, if that is possible then you say that the functions form a complete set, and actually all the Eigen functions of the Hamiltonian operator they do form a complete set. This is something that is rather difficult to prove mathematically. So, we will leave this to the mathematicians; we would just use this information, okay.

So, suppose I have let us say a state function which I will temporarily normally we denote it by the symbol capital psi, but temporarily let me say I denote it by the symbol phi suppose; this is my function, and suppose I make a measurement of what? Of the observable which I have denoted by the symbol A and postulate three will tell you that the answer has to be an Eigen value of this operator that is associated with the observable.

So, therefore, if the operator A has the Eigen values a 1, a 2, a 3, a 4, etcetera. If you make a single measurement the answer will be one of these Eigen values, and I keep on making measurement again and again and again and again large number of times. It is not necessary that I should get the same answer. I may get answer a 1, then a 2, then may be a 3. So, finally, if I have made a large number of measurements then what will I do? I will calculate the average of all these measurements.

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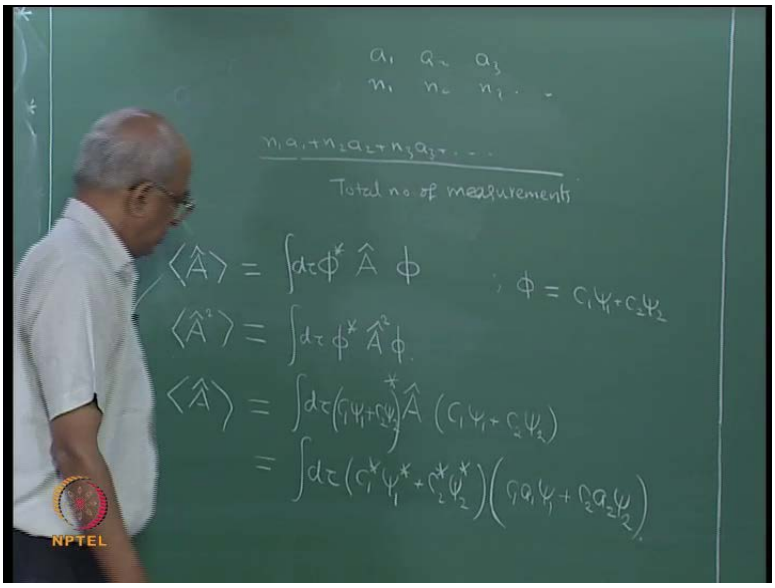

So, this is something that I have already discussed. I get a 1 n 1 times, a 2 n 2 times, a 3 n 3 times, etcetera. Then I can calculate the average; how would I calculate the average? n 1 a 1 plus n 2 a 2 plus n 3 a 3 plus etcetera divided by total number of measurements which is nothing but n 1 plus n 2 plus n 3 plus etcetera, and quantum mechanics actually gives you a definite procedure for calculating this average. What is the procedure it says that okay, what you have to do is you will take the state function which temporarily I have to decide to denote by the symbol phi. This is my state function allow it to be operated up on by the operator corresponding to the observable A. Then multiply the result by the complex conjugate of phi and integrate over the entire space, and if your function is not normalized you will have to divide this by phi star phi d tau, and this is referred to as the expectation value of A, and this average this experimentally measured average is actually equal to this expectation value.

So, therefore, if you know the state function it is not necessary to do the measurements actually. You can use the state function and calculate the average, and that is the use of quantum mechanics. You do not have to do the experiment; if you do not want to do it you can get the same result by doing this calculation. Now I will also assume might at least for this lecture that phi is normalized, right. So, that means this is equal to 1. So, therefore, if I wanted to calculate the expectation value of A; this is the formula that I have to use. I mean strictly speaking I should have this other term also which divides it,

but we will assume that the function normally; normally we always normalize the function. So, therefore, the integral will be 1.

Now what I am going to do is I am going to suppose I mean I wanted to calculate the average of a large number of measurements of the square of the observable A. Well, if you are doing the experiment, what you will do is you will have you would have measured the value of a 1. Then here in this expression you will put a; instead of a 1 you will put a 1 square. There you will put a 2 square, here you will put a 3 square and so on, right, and so the same thing. I mean if you wanted to calculate all that you need to do is instead of putting A you just have to put A square, and what will that be? It will be integral d 2 phi star A phi; oh sorry minor mistake it is not A but A square. Now just to illustrate the points what I am going to do is I am going to say I have a phi. Suppose phi is actually of the form may be c 1 psi 1 plus c 2 psi 2, okay. To work things out I will take such a simple example, and then see what will happen even if I had a general function which may be written as a combination of c 1 psi 1 plus c 2 psi 2 plus c 3 psi 3 c 4 psi 4, etcetera.

But to do the calculations may be it is simpler just to assume that phi is given by c 1 psi 1 plus c 2 psi 2. So, this obviously is not an Eigen function. You see psi 1 is an Eigen function of A; psi 2 also is an Eigen function of A, but this combination is not an Eigen function of A, right. So, I am imagining that I have such a situation that my state function is not an Eigen function of the operator whose observable I am measuring, correct. So, if you did this, if I now calculate the value of expectation value of A; this incidentally is referred to as the expectation value of A. This is equal to integral d tau, what is going to happen? I would have A operating upon c 1 psi 1 plus c 2 psi 2, and that is to be multiplied by what object? C 1 psi 1 plus c 2 psi 2 but with a complex conjugate, fine, and now you can look at this expression. A is operating up on c 1 psi 1; c 1 is just a number. It is a constant and c 2 also is a constant.

So, what will happen? A will simply operate upon psi 1 or A will operate up on psi 2; A can be taken inside the bracket and allowed to operate up on these two things. So, what is going to happen is I will get integral d tau c 1 may be the star operation can be taken inside, c 1 star psi 1 star plus c 2 star psi 2 star multiplied by this A I am going to take it inside, allow it to operate up on these things. So, the answer will be c 1 a 1 psi 1 plus c 2 a 2 psi 2. Now you see when you have such a product; well, here I have already used the

fact that psi 1 is an Eigen function of the operator. Now when you have such a product, obviously, you are going to get four terms, right, as a result of multiplying it out.

Let me just write the first term. The first term is going to be integral d tau; first term will be obtained by combining these two, okay. Well, I know that I am going to have an integral, but then of course, c 1 is a constant. So, it is not affected by the integration; a 1 also is unaffected by the integration.

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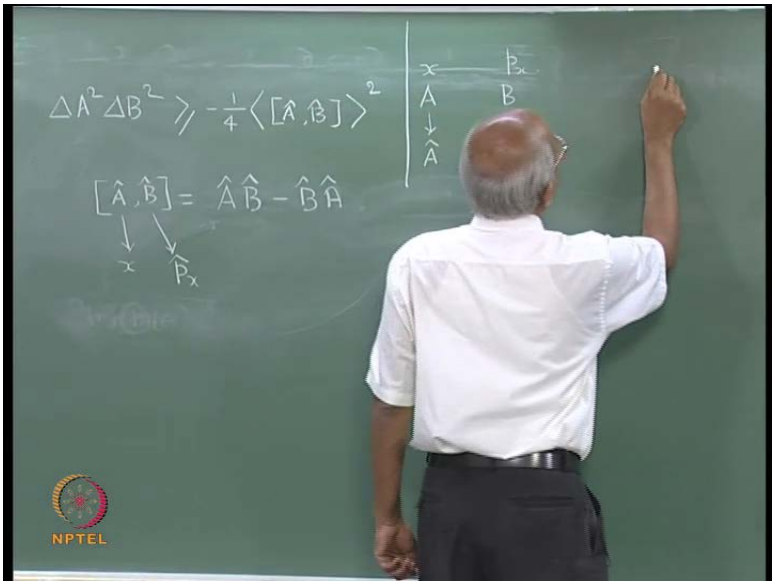

So, let me write those things outside. Imagine that I have an observable A associated with I have the operator which we normally denote by A with a hat on top of it, and I have an another observable B associated with which we have the operator B. And for example, A could be the x coordinate of the particle and B could be the corresponding momentum, and the generalized answer to the principle which we will prove, states that delta A square into delta B square; these are the uncertainties in A and B. It states that it has to be greater than or equal to minus 1 by 4 expectation value of the commutator of A and B the whole square. Now this of course requires explanation. What do I mean by the commutator of A and B? Let me first define the commutator.

When I write two operators A and B within such a square bracket this means that I am taking off AB minus BA, okay. So, this is the meaning of writing A comma B within this kind of square brackets, and just to illustrate let me imagine that A is actually x, okay, the operator corresponding to position, and B is the operator corresponding to

momentum which we normally write as p x. So, therefore, let me say I want to calculate the commutator of x with p x.

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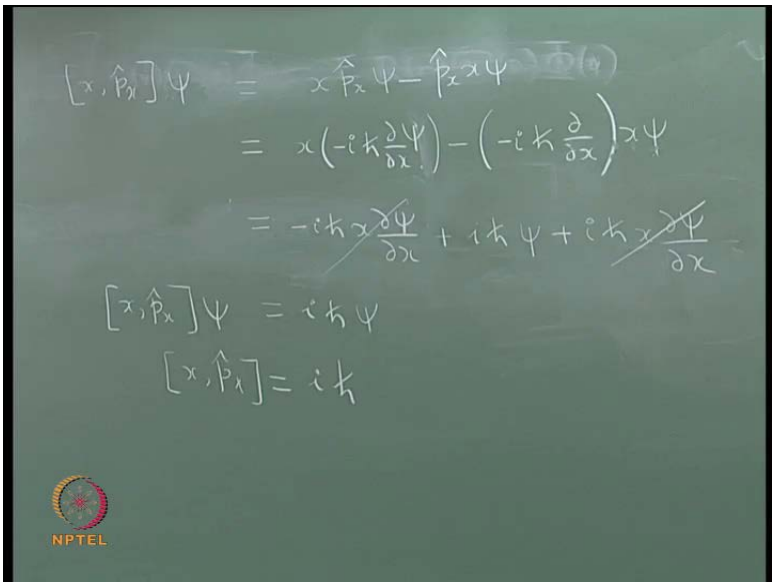

So, by definition it is actually going to be, well, these are operators. So, therefore, what I will have is I will have also have a psi on which the operators will operate, psi could be any function. So, the definition of that is actually x p x operating upon psi minus p x x operating upon psi, and the question is what is this? Well, let me calculate this. How do I calculate that? The answer is I can say okay, this is equal to x. P x is actually minus i h cross dou by dou x. So, this has to operate up on psi, and if it operates up on psi what happens? You will get the derivative of psi with respect to x multiplied by x and of course, multiplied by minus i h cross, and from there you have to subtract what? Minus i h cross dou by dou x operating upon x into psi, and let me try to calculate this, okay. The first term is actually x into, well, may be I will expand this and remove the bracket.

So, minus i h cross x into dou psi by dou x is the first term, and what happens to the second term? Well, obviously, this minus and that minus will make it a plus and i h cross dou by dou x operates upon a product, the product of two terms and so you have taken the derivative of two; derivative of a product of two terms naturally you are going to get the following. You are going to get plus i h cross; dou by dou x will operate upon x. So, the answer will be just psi, and you will have plus i h cross; dou by dou x will operate up

on psi, and the answer will be x into dou psi by dou x, and you can see that the first and the last term.

These two terms cancel nicely, and hence the result is just i h cross into psi. So, the commutator of x and p x operating up on any arbitrary function psi is just the same as multiplying that psi by i h cross. What does this mean? This means that the commutator of these two operators is actually equivalently multiplication by i h cross, okay; having calculated the commutator let me use it in this inequality. So, what will I do? I will identify a with x, right, a with x and b with p x.

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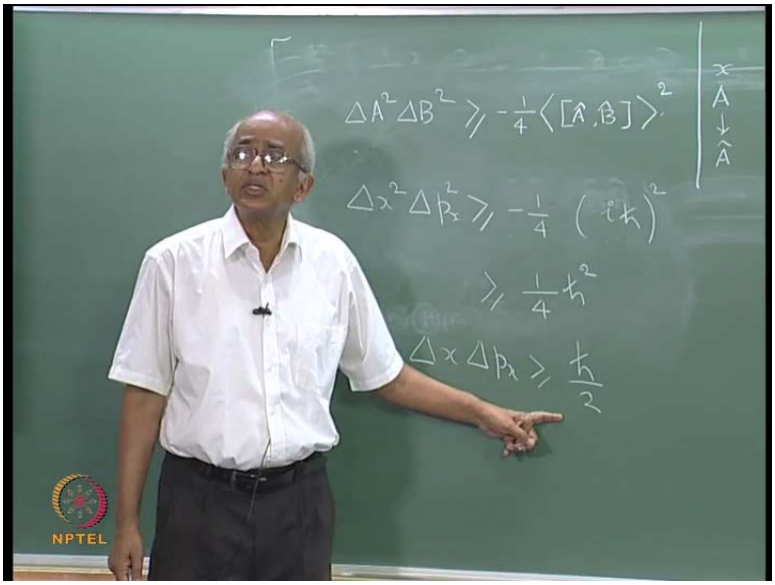

So, here I am going to have the square of the uncertainty in x, and this is going to be the square of the uncertainty in b x, and that would be greater than or equal to minus 1 by 4 expectation value of the commutator, but the commutator is just i h cross, right. So, you will have i h cross expectation value, but then it is just the expectation value of a constant and the expectation value of a constant is just that constant itself. So, therefore, it is not necessary for me to put this expectation value there. The answer is just the constant and then you have to take the square. So, therefore, you will have the whole thing square, and if you took the square what does it mean? I square is obviously minus 1. So, that will cancel this minus sign.

So, you are going to get 1 by 4 h cross square and this obviously may examine; sorry, there is a square that I should have put here which I forgot. So, now, I take the square

root of this, and what happens? I shall get the relationship delta x into delta p x must be greater than or equal to h cross divided by 2 which actually is the Heisenberg's uncertainty principle. So, using this generalized uncertainty relationship you can actually arrive at the Heisenberg's uncertainty principle which is the delta x into delta p x must be greater than or equal to h cross divided by 2. To make the ideas clear let me take an actual example.

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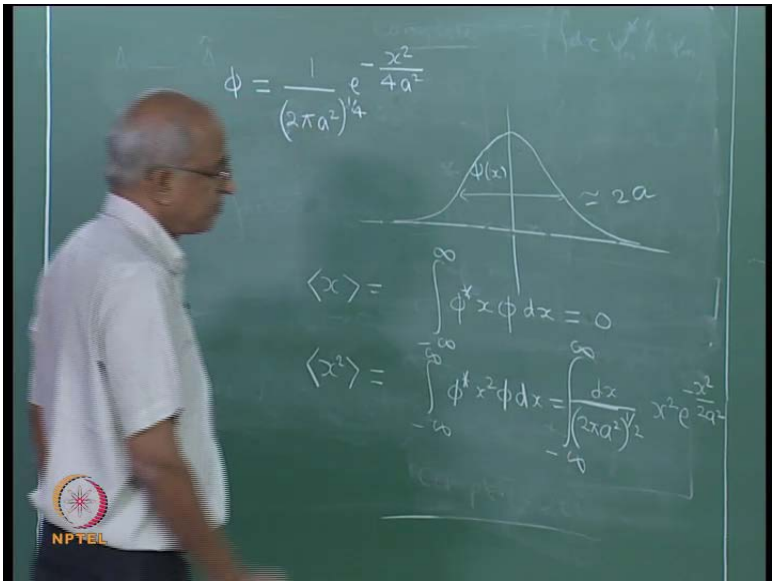

I am going to say that I have a state function phi which is equal to e to the power of minus x square divided by 4a square. I hope the notation is clear, e to the power of minus x square by 4 a square divided by 1 by 2 pi a square to the power of 1 by 4. You may wonder why this 1 by four answer is extremely simple. This function is normalized, and this is the normalization factor; that is all nothing more to it. If you look at this function, what will be the appearance of the function? Answer again is extremely simple. If you made a plot of this function against x you will get what is referred to as a Gaussian, okay. In fact, this wave function is just the wave function for the harmonic oscillator if you had chosen a to be equal to some constant, I do not remember what that constant is, but if you choose a to be that particular constant then this is just the Eigen function for the harmonic oscillator.

Now the width of this function, this is actually what is referred to as a Gaussian; the width of this actually is roughly I mean I would say it is proportional to a, roughly

speaking it is two times a roughly I mean the width of the function. So, if I had a very small what will happen is that the function is very narrow; while if I had a large what will happen the function is very broad, okay. If it is very narrow it will be highly peaked, right, because the function is normalized, right. So, now, if you had such a function, and suppose you make a measurement of position such a wave function implies that the particle will be found in this region with fairly large probability.

But if you were somewhere here the probability of finding it is very small; that is what such a wave function means and therefore, I can ask what will be the average value of its position? If I make a large number of measurements sometimes I may find the particle here or sometimes there or sometimes there. I make large number of measurements. I do the averaging, and the average value of the position of the particle will be obtained by a quantum mechanical calculation as expectation value of x; what will it be? It is going to be integral phi star. Well, star has no effect on this function. So, phi star x phi d tau or d x because it is a one dimensional problem, and that means of integration are from minus infinity to plus infinity. I do not have to do this calculation, because I suspect that you would be able to tell me what this is actually, what the answer will be if you did the calculation. Because this function is symmetric about the origin about this point it is an even function.

So, therefore, what will happen? The probability that the particle will be found on this side will be the same as the probability that would be found on the other side, and therefore, this when you calculate the average has to be 0. But then suppose I wanted to calculate x square, what will be the expression? It is going to be minus infinity to plus infinity phi star x square phi d x. I do not have any choice other than to calculate this, right. So, how will I calculate this? I will just substitute for phi 1 by 2 pi a square to the power of 1 by 2, right; that is coming from phi star phi. Then I will have x square e to the power of minus x square divided by 2 a square, and well, I do not have space. So, maybe I will put a d x here and integrate from minus infinity to plus infinity. So, this integral it is necessary to evaluate it.

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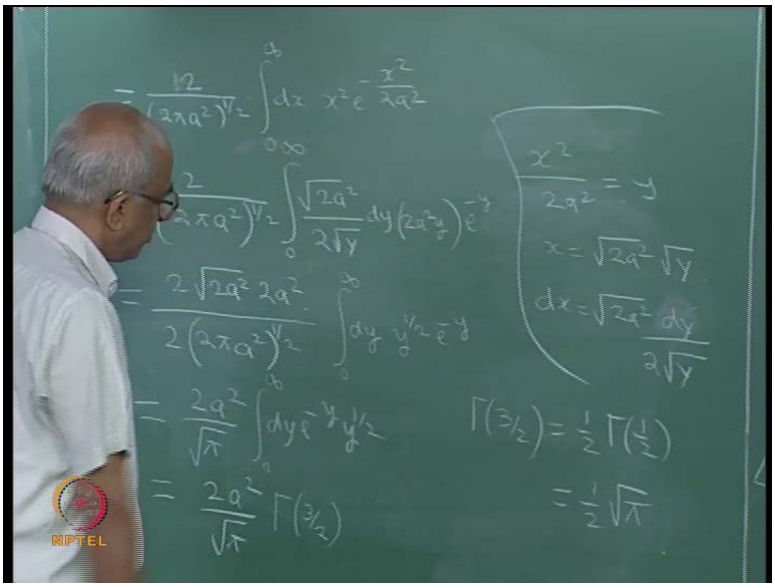

Let me go ahead and evaluate it. I shall get 1 by 2 pi a square to the power of half integral minus infinity to plus infinity dx x square e to the power of minus x square by 2 a square. I have just rewritten the integral, because you see your integrand is an even function. What I can do is I can I do not have to integrate from minus infinity to plus infinity. It is enough if I integrated from 0 to infinity provided I multiply the result by a factor of 2, and the next thing that I will do is I will make a substitution; what is a substitution that I will do? X square by 2 a square I am going to say it is equal to y, because I have e to the power of minus x square by 2 a square; I want to simplify the appearance of this. So, x square by 2 a square is equal to y or maybe what I can do is instead of saying that I could say x divided by square root of 2 a square is equal to y.

That is my substitution; that is that, x divided by square root of 2 a square. Oh no no, sorry, sorry, that is a mistake, x square divided by 2 a square is equal to y; this is my substitution. So, that actually means x is equal to square root of 2 a square into square root of y, okay, which obviously implies that d x is equal to square root of 2 a square into square root of y. Another mistake always I seem to make two mistakes successively. So, dx will be equal to that much. So, let me do this integral 2 divided by 2 pi a square to the power of 1 by 2 integral 0 to, well, when x is 0 y has to be 0; when x is infinity y has to be infinity. So, therefore, the limits are still from 0 to infinity, dx is equal to so much. So, you will get square root of 2 a square divided by 2 root y into dy; x square where is it? X square is equal to x square by 2 a square is y.

So, therefore, x square may be written as 2 a square y and e to the power of minus y. So, if I took this square root of 2 a square out, there is another 2 a square. This two also I mean please watch carefully; I would not want to miss any two or anything. So, this two also I have to take out, and then what will happen? I will have integral 0 to infinity dy. There is a y here; there is a square root of y in the denominator, so therefore, y to the power of half e to the power of minus y. So, let me cancel out the two's, a square also goes. Suppose this is correct; correct me if there is a factor of something missing, right. Now this is an integral that hopefully will be familiar to you. This is known as a gamma integral or a gamma function. The definition of a gamma function I should write it somewhere, maybe I can write it here.

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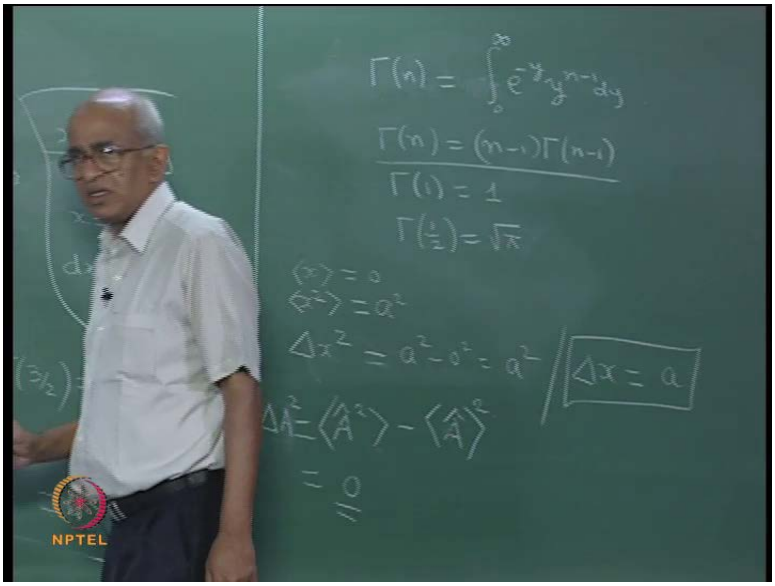

This is the definition of a gamma function. It is a function of n, okay, and you can say it is defined as this integral. Now this is actually very nice function, because you can easily show that gamma n is equal to n minus 1 gamma n minus 1. I am only writing the properties that I myself shall made which can be of course proved, but this is not a class in mathematics. So, we will not prove any of these things. So, you can easily show that gamma n is actually equal to n minus 1 into gamma n minus 1. In fact, you can further show that gamma 1 is something that you can easily evaluate. You will find it is 1, and gamma half again something that can be evaluated; the answer is square root of pi. This is all that we will need. So, therefore, if you look at this expression, what is the answer that I am getting? 2 a square divided by square root of pi.

You can identify that this is a gamma integral, and in fact it is actually equal to gamma of 3 by 2; that is all, because if you put a n is equal to 3 by 2 in this definition you are going to get that exactly the same integral, okay, and further gamma of 3 by 2 I can make use of this relationship gamma of 3 by 2. Let me write it here gamma of 3 by 2 will be if I made use of that this is actually recursion relation will be equal to half of gamma half using that relationship, and gamma half you know it is equal to root pi. So, therefore, using the information from mathematics we have been able to get the value of the integral, and it is just square root of pi divided by 2 which means that this is equal to 2 a square divided by root pi into the gamma of 3 by 2 is nothing but root pi divided by 2 and therefore, what is the answer that you get? Nicely this root pi and that root pi this 2 and that 2 cancel. So, you get the answer a square.

So, summarizing all these things what has happened? We found that x average is equal to 0, x square average you have just now evaluated; x square average actually equal to this is what we have evaluated x square average it started here, it ended only there that is actually equal to a square, okay. So, this actually means if I go on measuring the value of x I will get several different values; they do not have to be the same. I will go on getting different values, but the average of all this will be equal to 0. Then if you took the square and averaged then obviously, that will not be equal to 0, and that average also I have calculated that is equal to a square. So, therefore, I can define a kind of uncertainty in the measured values of the position of the particle. What is that uncertainty? I mean the way I would define it is I would say delta x square is equal to x square average minus x average square.

So, therefore, this is going to be equal to a square minus 0 square which is just a square, right and therefore, as far as this particular wave function is concerned or particular this state function is concerned I say that there is some uncertainty in the position of the particle, and how much is that? It is equal to a, agreed, and that is not surprising, because I told you roughly the width is dependant upon the value of a. If you increase the width of the function, if you wanted to increase the width of this function you just have to increase the value of a. This is something that I have mentioned at the beginning. You can make this function narrower and narrower by decreasing the value of a, and when you decrease the value of a, what will happen? You are actually decreasing the

uncertainty in position, because you saw that the uncertainty in position is actually equal to a according to this calculation.

So, you can choose your value of uncertainty; there is no problem, by just adjusting the width of this a, right, and now I ask the question suppose I make a measurement of momentum. Now we were talking about measuring the momentum, sorry talking about measuring the position; now suppose I am going to measure the momentum of the particle. This function is not an Eigen function of the momentum operator, right. So, therefore, I am going to get different values, and therefore, there should be a measured value of the uncertainty in the momentum of the particle that experimentally determines the uncertain in momentum; how much is that? We will calculate it in the next lecture, and then finally, we will find that the uncertainty principle according to the Heisenberg actually follows, when we calculate that and multiply the delta x with the delta p; you will find that the uncertainty principle results.

Thank you for listening.