# Chemistry I
# Introduction to Quantum Chemistry and Molecular Spectroscopy

## Lecture 26
## Heisenberg's Uncertainty Relation

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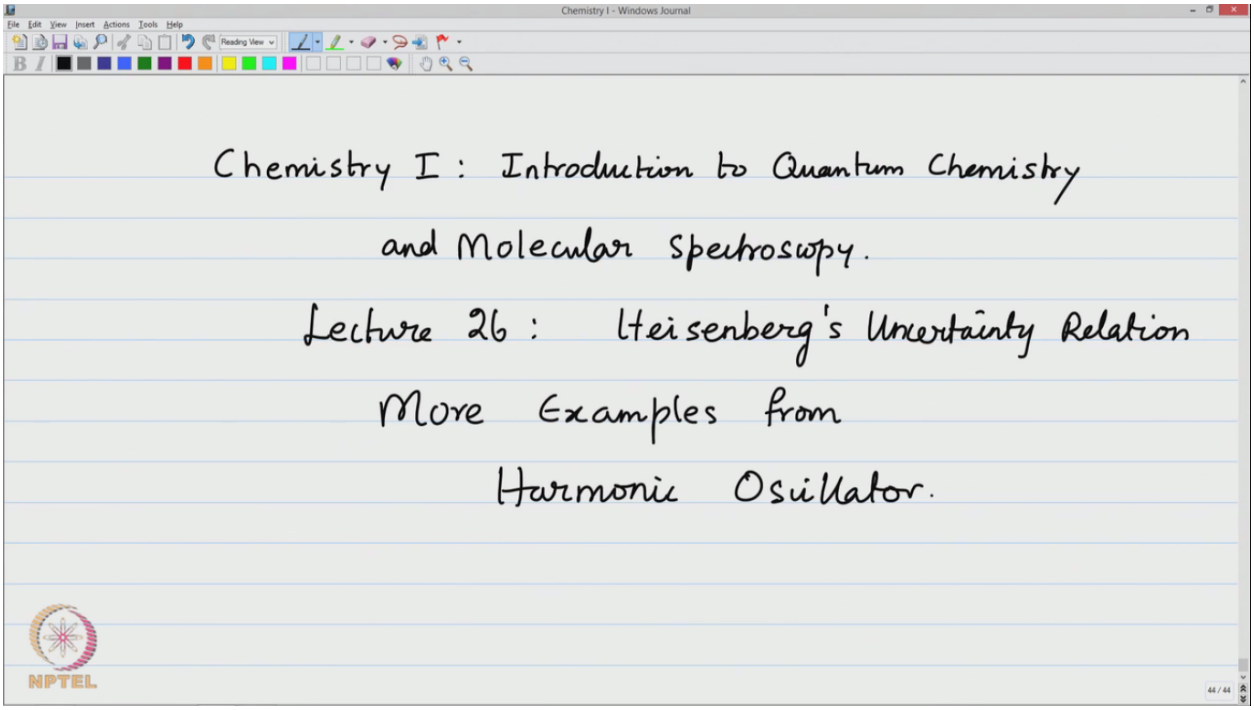
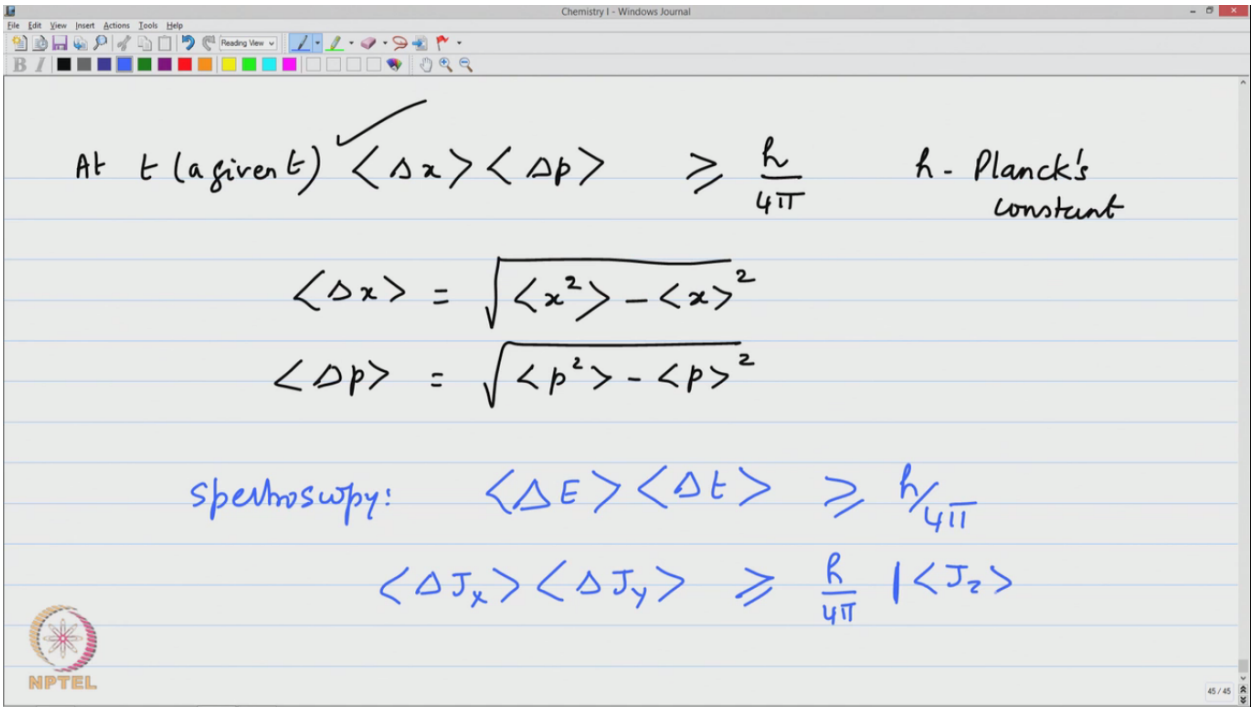


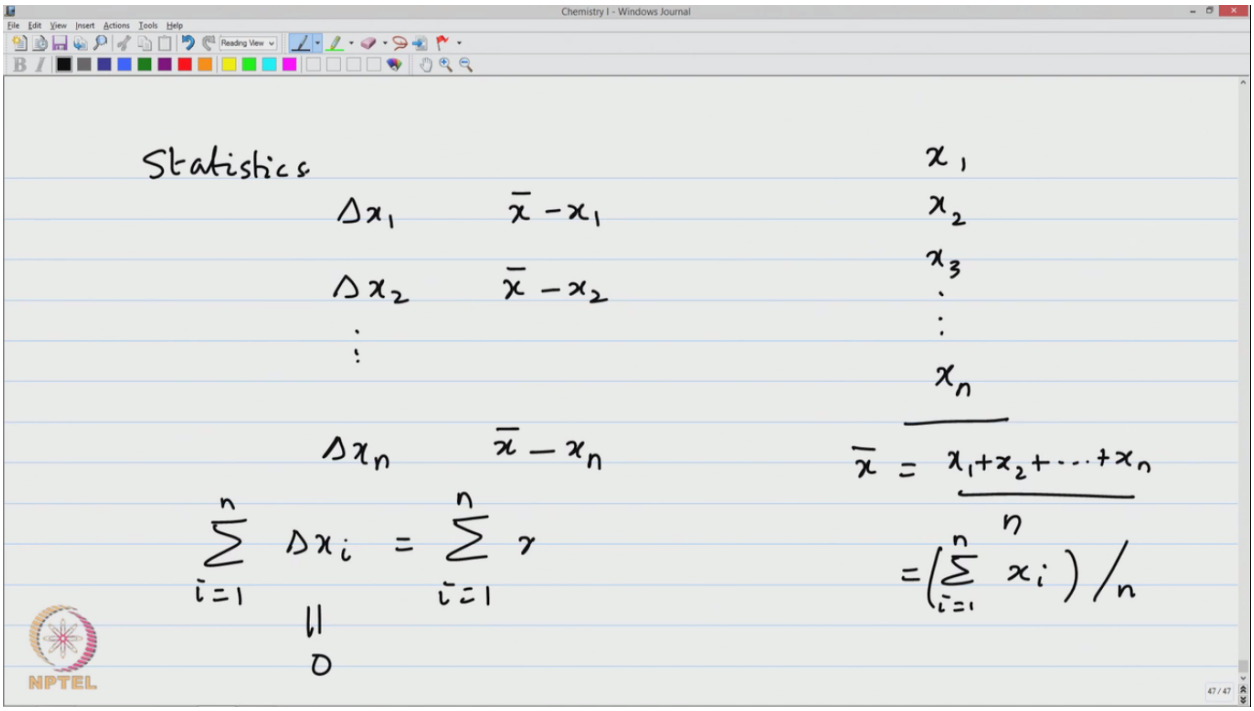
Welcome back to the lectures on quantum chemistry and molecular spectroscopy at the introductory level. Let me now continue with one important result in quantum chemistry and in all of quantum phenomena namely the Heisenberg uncertainty relation but with a specific example of how we understand this from the Harmonic oscillator model in this lecture. There are other examples that I have already discussed with the particle in a box and in the assignment problems before I have also mentioned how to calculate uncertainty through a molecular formula 3F formula. So let me start with the basic statements namely the uncertainty in the position of a particle at a given time and its momentum at the same time, at a given t the uncertainties are related by this inequality h by 4 $\pi$ $\Delta$ x which is the uncertainty in the position of the particle and the $\Delta$ p which is the uncertainty in the momentum is greater than or equal to h by 4 $\pi$ and h is Planck's constant.

It's one of the cornerstones of quantum mechanics and if you recall from the earlier statements in this course $\Delta$ x was written as the average of the squares of the position measurement minus the square of the average of the position measurement. So the average of the squares minus the square of the average the difference between the two is the square of the uncertainty. Therefore, the square root of the same is given as the uncertainty and likewise $\Delta$ p was written as square root of p square minus p whole square. So this is one type uncertainty. What is another type of uncertainty relation in spectroscopy when one studies molecular systems and excited states the molecular excited states do not have a infinite lifetime they have a finite lifetime and the excited state energies are also not very precise. There is a very small spread in the energies of the particles in the excited states and therefore one relates to an uncertainty there with the spread in the energy of the excited state, the uncertainty $\Delta$ e in the energy measurement of the excited state times the lifetime of the excited state the uncertainty in the measurement of the lifetime. If the lifetime is say for example 5 picoseconds what is the uncertainty in that 5 picoseconds plus or minus 0.05,0 .01 that $\Delta$ t and if the energy of the excited state is something like say 5 electron volts is it exactly 5 electron volts or is it 5 electron volts plus or minus some small amount that plus or minus small amount is what is called the uncertainty in the $\Delta$ e and this product is also greater than or equal to h by 4 $\pi$. Now this is for the spectroscopy and in scattering chemical reactions and in general in angular momentum we also have the uncertainty of the x component of the angular momentum $\Delta$ Jx and the y component of the angular momentum $\Delta$ Jy being greater than or equal to the absolute value of the commutator there is a formal relation but for our discussion it's h by 4 $\pi$ the absolute value of Jz the expectation value or the other way around sorry.



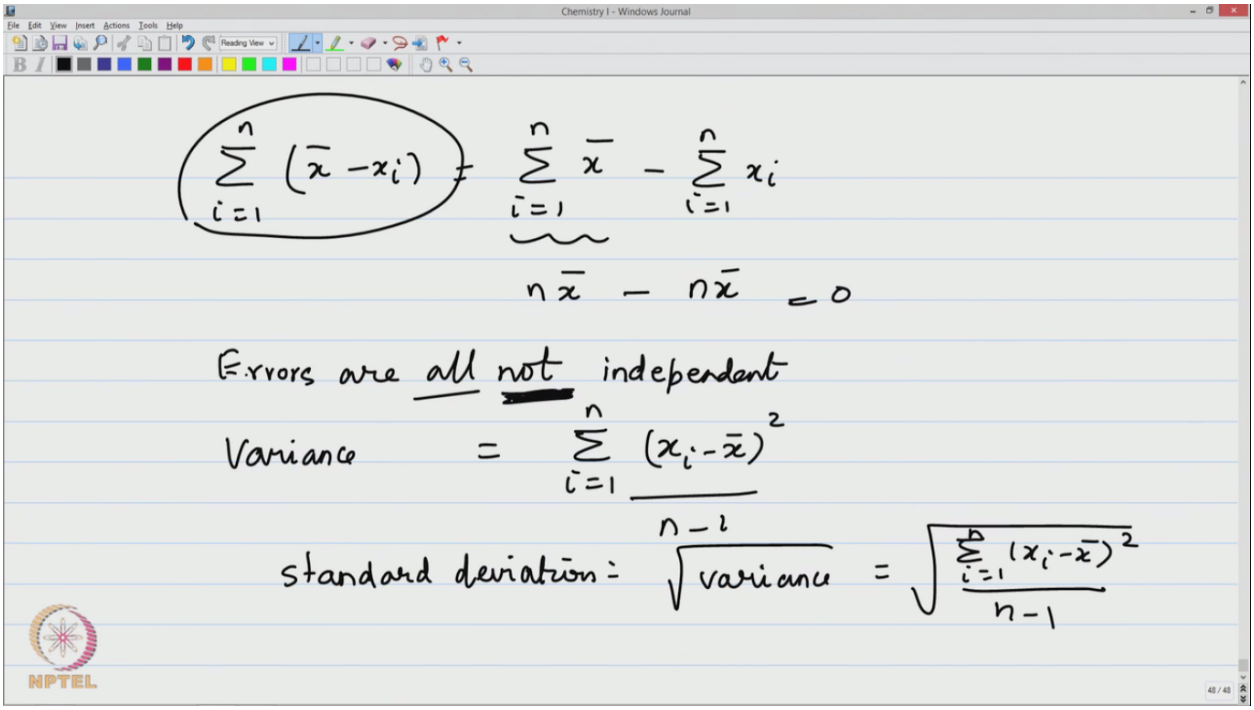

The absolute value of the expectation value. So this is another uncertainty relation for a particle on a ring remember that the position of the ring is given by a φ coordinate with reference to an axis. So the φ equal to 0 or π by 2, I mean 2 π, 3 π by 2 2 π and then the particle on a ring has this circular boundary conditions that anything greater than 2 π is in terms of the same position below 2 π. You remember the ψ of φ for a particle in a ring should satisfy the cyclic boundary condition φ plus or minus 2 n π so here this is the coordinate and the angular momentum there which is in I mean denoted in the Z component is minus ih bar dou by dou φ and so there is an uncertainty there with the coordinate uncertainty Δ φ and the uncertainty in the angular momentum Δ J which are complementary variables J and φ are related to each other the same way p is related to the position minus dou by dou x. So you have this is another uncertainty relation h by 4 π and so on.

Now the first of two parts to this lecture is why this formula x square minus x square square root as Δ x expectation value. Let's go back to our elementary statistics. Let's mix n number of measurements of some quantity say and we get different values x something that we measure say the temperature of a certain system and we take identical systems and we measure the temperature we do not necessarily get the same value. That's a slight variation. Therefore we make finite number of measurements and then we take the average. What is the average? The average x bar is x1 + x2 + xn by n which we can write in the summation notation i is equal to 1 to n Xi divided by n. That's the average.




Now the averages do not tell you how far the different values are different from the average obviously if all the values are identical then the average is also one of them, there's no question. And second if we did this experiment sufficiently large number of times infinitely many times that's the theoretical limit then the average that we get is a true experimental average but in the absence of doing an infinite number of measurements we do a finite number and we compute the average from the experimental measures. Therefore the definition of the average deprives the system of the n independent measurements by 1; why? for the following reason. If you take the errors Δ X1 the error is X bar minus x1 you take the error Δ X2 of the second measurement it is X bar minus x2 and likewise if you calculate Δ Xn it is X bar minus Xn. Now what is the sum of all of these errors? Δ Xi if you look at that then the errors are not independent of each other because the sum of all these errors by the way first result is it will become 0. Let's see that now. X bar Xi if we have to evaluate that sum over i is equal to 1 to n X bar minus Xi is sum over i is equal to 1 to n, X bar minus sum over i is equal to 1 to n Xi remember X bar doesn't change therefore this is the n times the X bar and this is already n times X bar that's how we got the X bar. Therefore, errors are all not independent. Most important they are not independent in this scheme of things and second the errors may be very large. One error may be so much on one side of the measurement and the other error may be so much on the other side of the measurement that the errors will cancel with respect to each other. That doesn't tell how accurate our experiment is. Therefore we have a second parameter we call as variance and the variance is the sum of the squares of all the errors Xi minus X bar square. So the moment you take the square of the errors this sums cannot cancel each other. There's no positive error. There's no negative error. There's only one positive error whether it's on this side or that side the square of it is positive. Therefore, that tells you how far your measurement spreads out from what is called the median or the average. So we introduce a variance as something that is divided by n minus 1 Yn minus 1 precisely because of the fact that your average deprives the system of that one degree of freedom that of the n minus one of the n errors that you notice only n minus 1 are independent because the

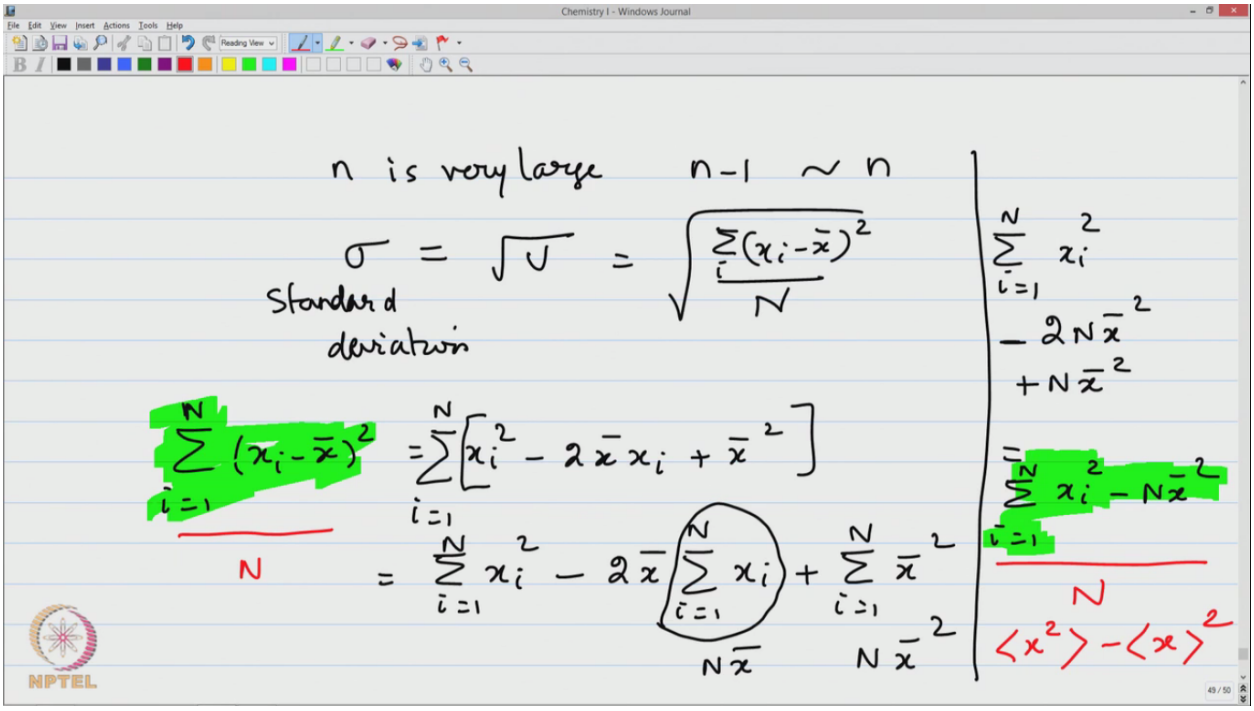
last error cancels the sum of all the others as you have here. Therefore, there is the n minus one and the standard deviation is the variance square square root, sorry. Square root of variance and so you write the formula that it's a square root of sum over i is equal to 1 to n Xi minus X bar square divided by n minus 1.




In the limit of doing this experiment many many many times as n increases to a very large value you can see that we are approaching the true average and if we assume that we finally get the true average then all the errors are independent of each other and therefore the degree of freedom of that system is that very large value of n which is technically n going to infinity the errors become independent of each other and as n goes to infinity or n is very large you can always replace n minus 1 by n and therefore the exact formula for the standard deviation, standard deviation is the square root of the variance and that's square root of sum over i Xi minus X bar whole square divided by n and n is extremely large tending to infinity. Now this formula is the one that gives you that uncertainty that you were using in the previous lectures. How? Let's see that.

Let's expand Xi minus X bar whole square we get Xi square minus 2 X bar Xi plus X bar square. So if you put the sum over i is equal to 1 to n 1 to capital N and if you do that I is equal to 1 to N all of these quantities then what we have is sum over i is equal to 1 to N Xi square minus 2 X bar times sum over i is equal to 1 to N Xi because the averages is independent of the individual measurements in this process and then you have sum over i is equal to 1 to N X bar square. Now you can see that this itself gives you N X bar and this is N times X bar square because X bar square doesn't change for any of the terms therefore there are n such terms so the sum is simply N times X bar square. So what you have come up is if I write it here for this page you have sum

over i is equal to 1 to N Xi squared minus 2 times N X bar squared plus N times X bar square 1 times the N X bar square so the answer is sum over i is equal to 1 to N Xi square minus sum over no there is no sum minus N X bar square. Now this is just the sum all of what we have calculated is only that and that's equal to this number. Therefore, if you have to divide this by N you have to divide this also by N. So you have sum over Xi squared over all the states divided by N what's that?



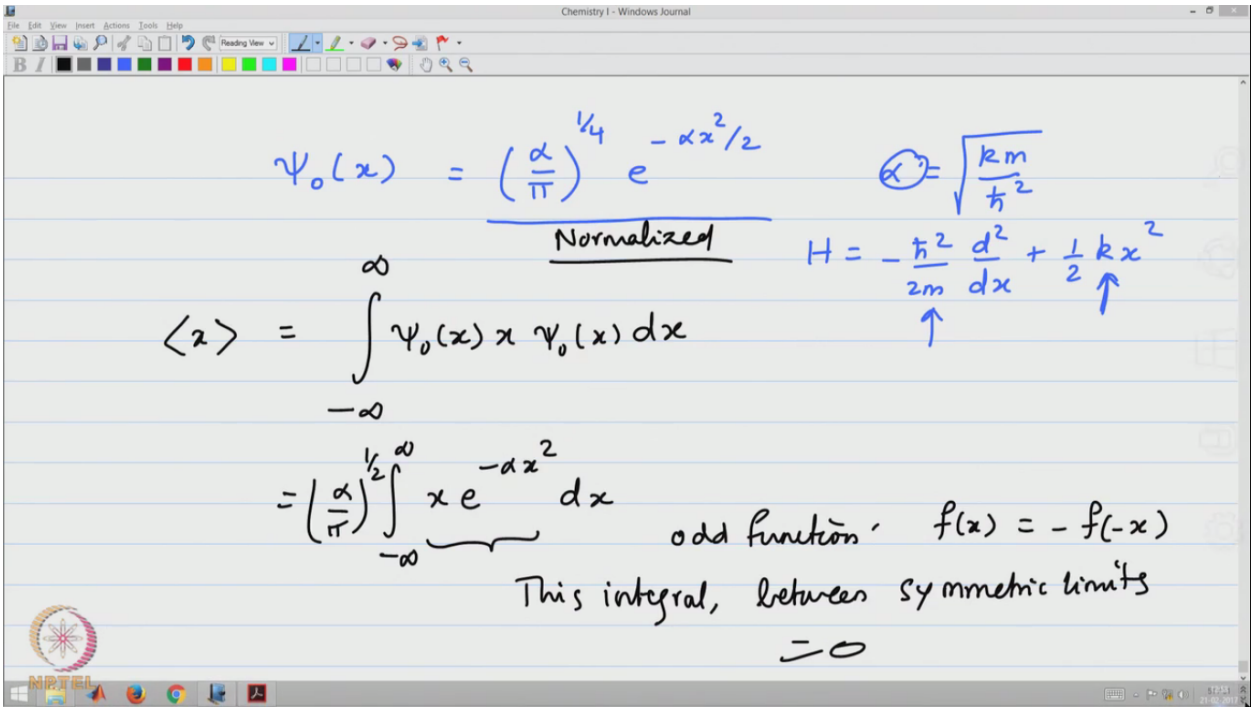

That's nothing but the average of all the squares; square 1, square 2, square 3, square 4 all the entire experimental n times that you have done you have summed over every one of those squares and you would divide it by the total n therefore this is X square average. What is this one. The N cancels out and this is nothing but the X average square. The angular bracket is not needed but the angular bracket is the one that represents the X bar.

So you see right away that in the limit of infinitely large number of repeatable experiments, identical experiments giving rise to some random errors you see that the average becomes the true average and the uncertainty which is a measure of how far the individual experimental result differs from the true average and that's given by the standard deviation and therefore the standard deviation is what is used as the Δ x as the square root of x square minus x average squared. The same way for Δ p square minus whole square. So therefore the origin of the formula is the standard statistics that we all do and the measurement practices that we are familiar with in our schools and colleges, just same practice that is used to define what is called the deviation from a given measurement in terms of a standardized deviation and therefore it's called the standard deviation. Why it is standardized? N is supposed to be infinite okay therefore all the errors will become truly a system only randomized random errors only there is no systematic errors that are

we assume that all these things have been canceled. This is the true formula therefore now we have to show that this Δ x Δ p is greater than or equal to h by 4 π for a Harmonic oscillator system that we have studied so far.

So that's the second part of this lecture. So let's write down the Harmonic oscillator ground state wave function. Remember n is 0 the quantum number is 0 for the ground state and that's given as e to the minus so let me write the normalization constant first. It's α by π if that's a notation I had used 1 by 4 e to the minus α x square by 2 where α is the parameter for the Harmonic oscillator in terms of km by h bar square and you recall that the Hamiltonian is minus h bar square by 2m d square by dx square which is the kinetic energy plus half kx square which is the potential energy and this is a spring constant or the force constant so the k and the m are the two parameters for this Harmonic oscillator therefore our α is defined using those two parameters and the fundamental constant h bar square. This is you can recall. This is what we did in the Harmonic oscillator model and now with this as the quantity let me use black maybe it's brighter on the screen. Let's do the average value X for the Harmonic oscillator.

The average value X is you you know it's ψ naught x these are real therefore I don't need to use complex conjugate. x times ψ naught x dx and you know that the Harmonic oscillator position coordinate goes all the way from minus infinity to plus infinity. So this is the average value. This function is normalized therefore we don't need the denominator okay. that's one. So does the average value and that you can calculate as α by π to the 1 by 2 because there are two functions ψ naught ψ naught square and you have x e to the minus α x square between minus infinity to plus infinity dx. You should know immediately that this is an odd function. Therefore, this integral between symmetric limits that is minus a to plus a minus infinity to plus infinity, is 0. Simple odd integral f of x is – what's an odd function? f of x is minus f of minus x therefore this integral goes to 0. Now for the average value for the position is right in the middle of the x is equal to 0 you have oscillation for the entire positive play positive side of the the X-axis and the entire negative side of the X-axis but right at the middle is what you call is the average position for the particle. What about the average square? The square of the average sorry.



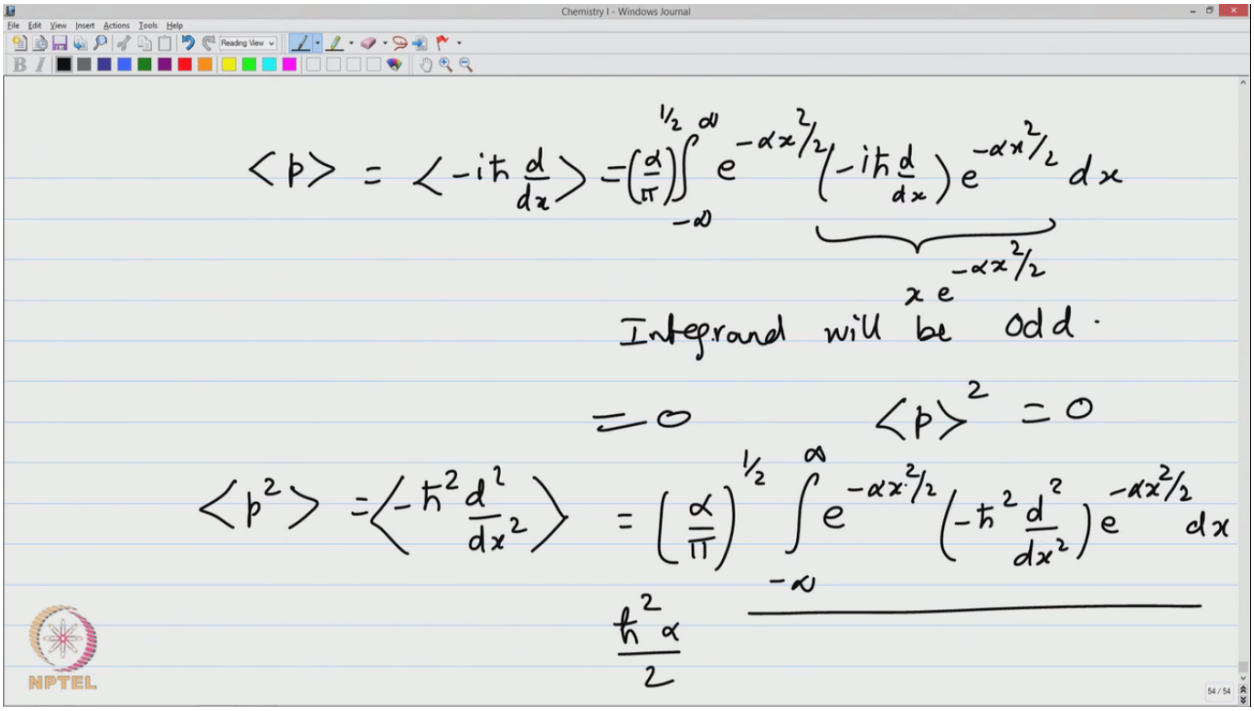

The square of the average therefore is 0. What about the average of the square and that's α by π to 1 by 2 integral from minus infinity to plus infinity e to the minus α x square x square dx because x square simply multiplies the operator x square. This is an operator. Essentially these are all operators because they are all position operator the square of the position operator, the momentum operator and so on. The square of the operator therefore it gives you it only multiplies. So this is the integral. This is an even function. Therefore this integral needs to be evaluated and you must remember that when we wrote α by π 1 by 4 e to the minus α x square by 2 as the normalized wave function what we had used was the fact that minus infinity to plus infinity e to the minus α x square dx is π by α square root and so we have taken the square root of that and divided the function and we used that. So this is known.

Let's do the square average and that's α by π 1 by 2 integral minus infinity to plus infinity e to the minus α x square x square dx and this is you can – this integral can be evaluated using partial integration using UV formula and so let me write this as α by π 1 by 2 integral from minus infinity to plus infinity x times d of e to the minus α x square by minus 2 α. So one of the x is used to write this as a derivative of e to the minus α x square because this will give you minus 2 α x times exponential by minus 2 α. So it gives you the x.

So this is what it is and this integral is since it's a udv type integral between limits this is what its uv between the limits minus vdu between the limits. So if you have to write that it's α by π 1 by 2 you have x e to the minus α x square by minus 2 α between the limits minus infinity to plus infinity plus 1 by 2 α integral e to the minus α x square dx which is that d of x is of course simply dx. This is what dx is. So it's one times dx. So that's what this is and this is zero because the exponential goes to zero because it's x square so the ψ of x is irrelevant. Minus infinity or plus infinity that Gaussian function goes to zero therefore no matter how fast the x increases or decreases this is zero. What is left over here this is square root of π by α times 1 by 2 α. So that

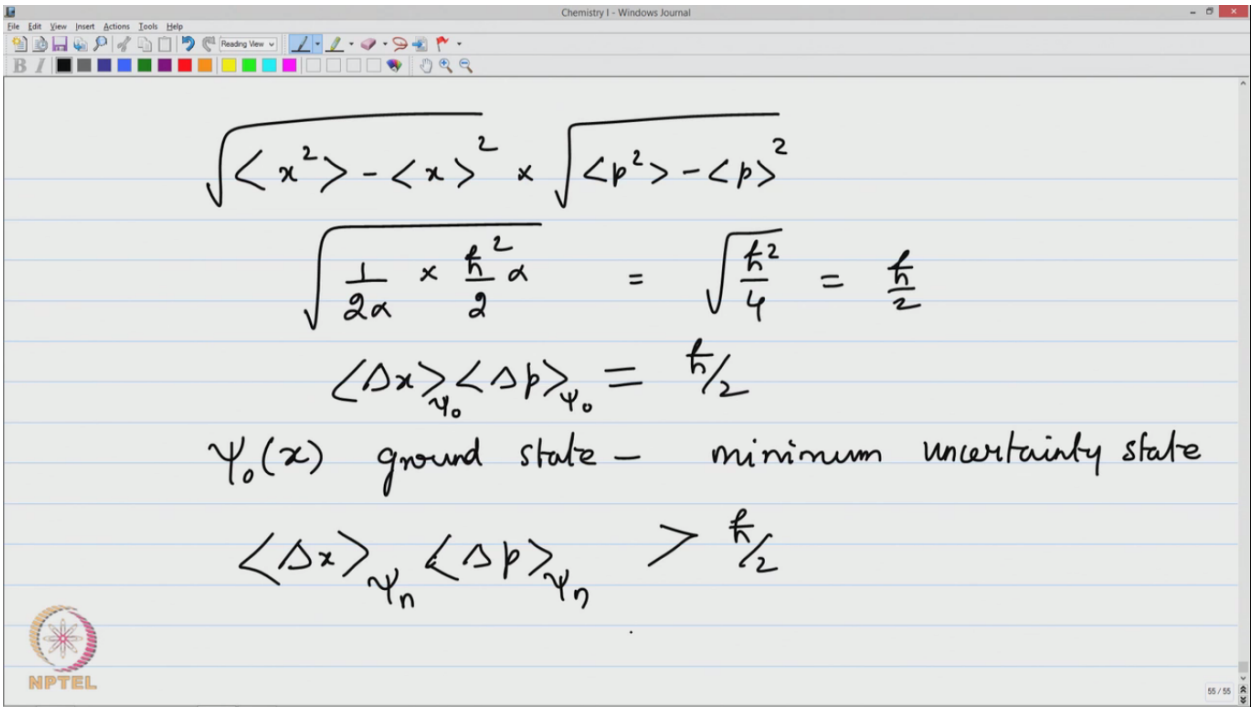
square root of π by 2 α and this α by 2 π both cancel each other and so what is left over is only 1 by 2 α. So the average value x square is 1 by 2 α. The average value x whole square is 0.

Now it's easy to show that the average value of p which is the expectation value of the derivative operator minus ih bar d by dx given by α by π to 1/2 between minus infinity to plus infinity e to the minus α x square by 2 the derivative minus ih bar d by dx e to the minus α x square by 2 dx and there is no problem the derivative of an even function gives you an odd function and this will give you x times e to the minus α x square way to and so this whole integrand will become odd. Therefore this is 0. Therefore the average value of the momentum squared is zero. The average of the square of the momentum is not zero. It is given by minus h bar square d square by dx square which is the operator for the square of the momentum it's the average of that and that if you write down it becomes α by π to 1 by 2 between the limits minus infinity to plus infinity you have e to the minus α x square by 2 and you have the operator minus h bar square d square by dx square e to the minus α x square by 2 dx. This is easy to evaluate. I leave it to you to take the derivative of this and show that this answer is the following. It is h bar square α by 2 that's a simple integral to do. Take the derivative and you will see that it's an exponential and I will leave it to you to do that okay.




Therefore x squared minus x whole square the average the square root times p squared average minus p average square becomes 1 by 2 α because this is 0 and you have h bar square by 2 times α the square root and that's nothing but square root of h bar square by 4 so it gives you h bar by 2. Therefore Δ x Δ p is equal to h bar by 2 and the ψ naught x the ground state of the Harmonic oscillator is called the minimum uncertainty state. If you have to calculate so you have calculated it for ψ naught. you have calculated it for ψ naught if you calculate Δ x for any other Harmonic oscillator states ψ n this uncertainty for any states ψ n it will be always greater than h bar by 2

and therefore the uncertainty principle is obviously obeyed by all the solutions that we have arrived at for the Harmonic oscillator and all the expectation values that we calculate for the Harmonic oscillator. They have the same property that we expect them and they obey this uncertainty relations. So likewise it's possible for us to show uncertainty relations with the not the eigenfunctions.




Please note that the Harmonic oscillator function the exponential minus α x square by 2 is neither the eigenfunction of the position operator nor the eigenfunction of the momentum operator but it's the eigenfunction of the kinetic energy plus the potential energy. So it's always good to have what are called states which are general which are not eigenfunctions of either the x or p or the energy or the T time or the Jx and Jy that is the angular momentum x component and angular momentum y component. It's important to use a general state to show that the eigenfunctions that the Harmonic oscillator the way it satisfies the uncertainty every one of those states will have a minimum uncertainty such as the h bar by 2 or greater than the h bar by 2. Therefore uncertainty principle runs on the core of all of the electronic structure, quantum chemistry, quantum mechanics. So it is important to see the value in terms of a simple calculation. Thank you very much.