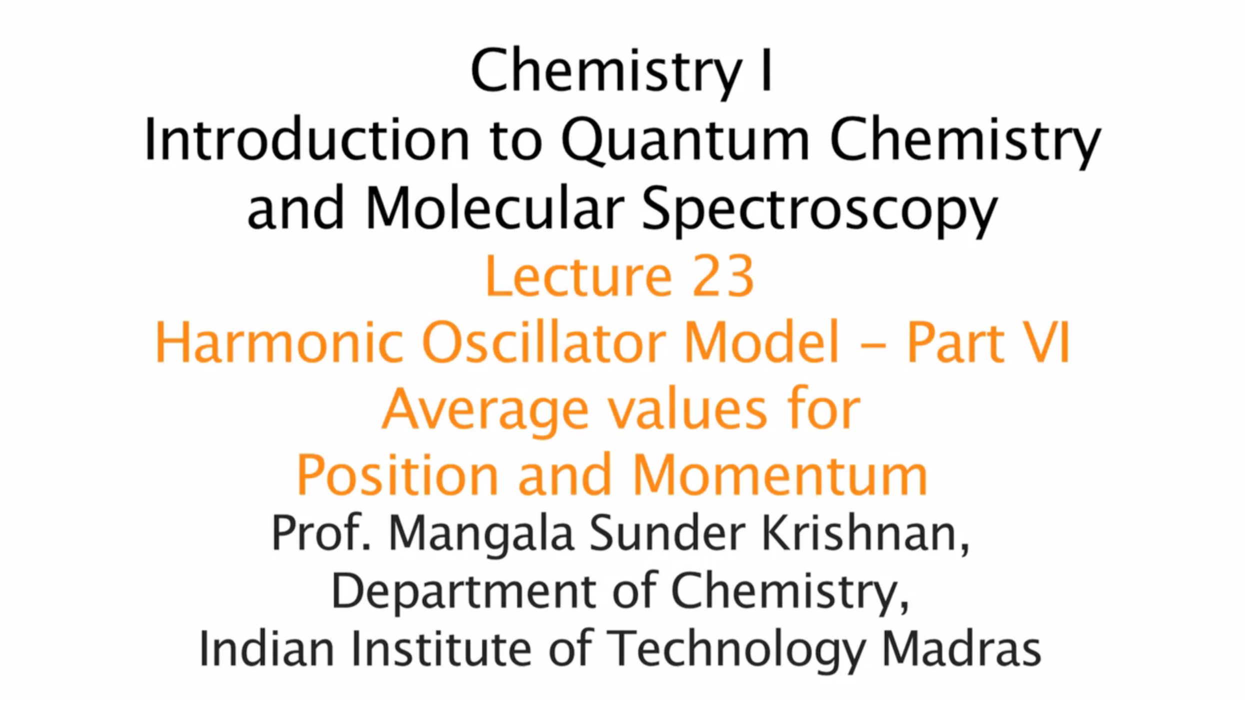

Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 23
Harmonic Oscillator Model – Part VI
Average values for Position and Momentum

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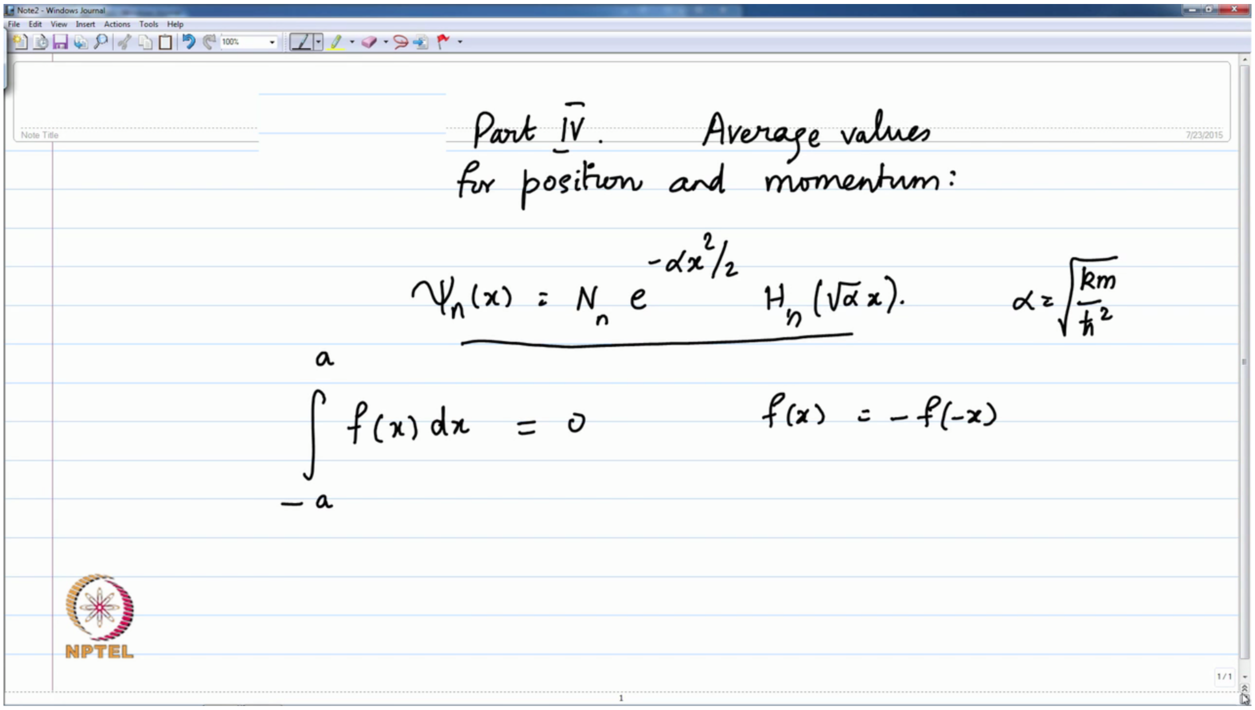
Prof. Mangal Sunder Krishnan: Welcome back to the last part of this elementary lecture on harmonic oscillator. In this part, let me do a simple calculation and demonstrate how to do elementary integrals for spectroscopy in the future, I mean in the next set of lectures when I talk about molecular vibrational spectroscopy, and then be worry the intensity of the vibrational lanes, what goes in there. The mathematical element will be discussed here.



Part IV. Average values for position and momentum:

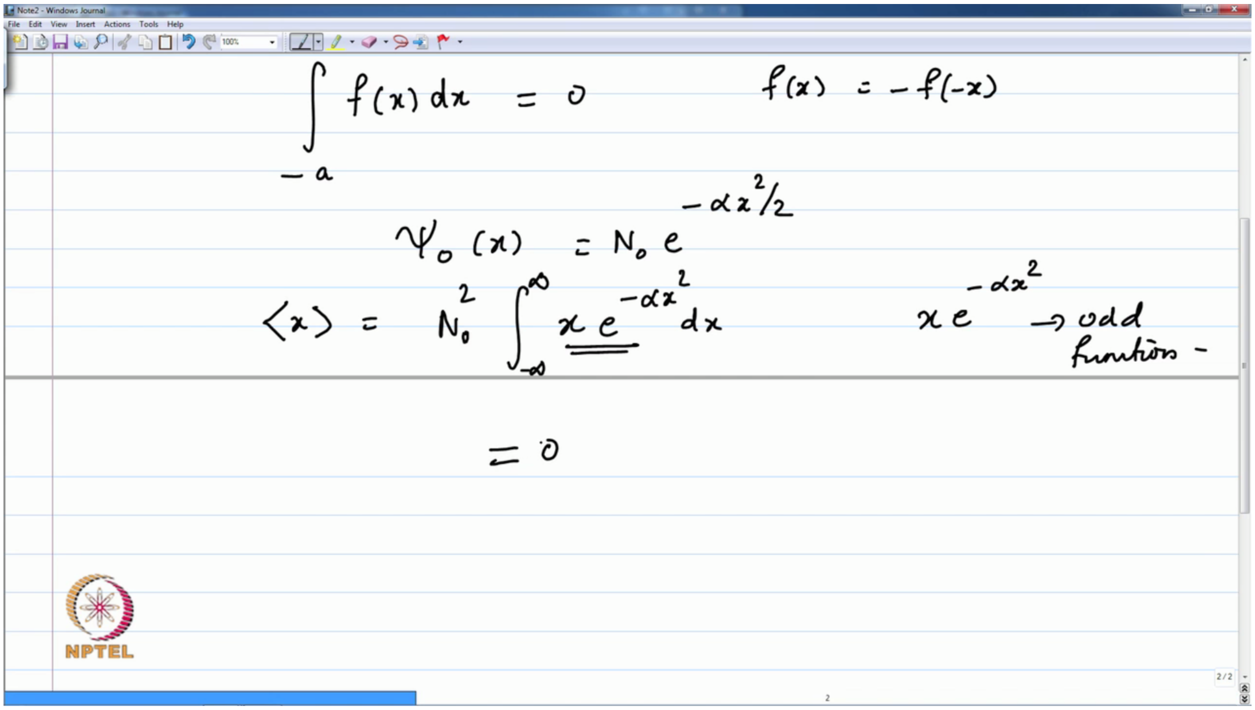
$$\underline{\psi_n(x) = N_n\, e^{-\alpha x^2/2}\, H_n(\sqrt{\alpha}\, x)}. \qquad \alpha = \sqrt{\frac{km}{\hbar^2}}$$

$$\int_{-a}^{a} f(x)\,dx = 0 \qquad f(x) = -f(-x)$$

So this part is on the average values for position and momentum operators in quantum mechanics for the harmonic oscillator. In fact, it's extremely simple. If I have to use the wave functions as given here, I don't think this lecture should be there in the first place, because the average value for the position and the momentum for the harmonic oscillator centered at x=0 is actually 0. Therefore, what are we talking about, okay. We do talk about the average value for the energy partition, if we discuss that.

See harmonic oscillator Hamiltonian has two non-trivial parts, the kinetic energy as well as the potential energy part. The kinetic energy is given by the momentum squared operator divided by twice the mass of the oscillator and the potential energy is given in terms of the harmonic oscillator force constant ½ kx^2. Therefore, some integral calculations involving the Hermite polynomials and the Gaussian functions can become unwieldy as we say when the higher order functions are involved, and there are better ways of handling harmonic oscillator using what is known as the operator representation, or it's also called occupation number representation by some physicists and the others call it as the harmonic oscillator, raising and lowering operators.

So there are many different ways by which we can study them. However, let's stay with the statement that the position and momentum, the average values are 0. How do we show that? It's very easy. I told you that if we have an integral of an r function, f(x) = -f(-x), then this is 0.



$$\int_{-a} f(x)\,dx = 0 \qquad f(x) = -f(-x)$$

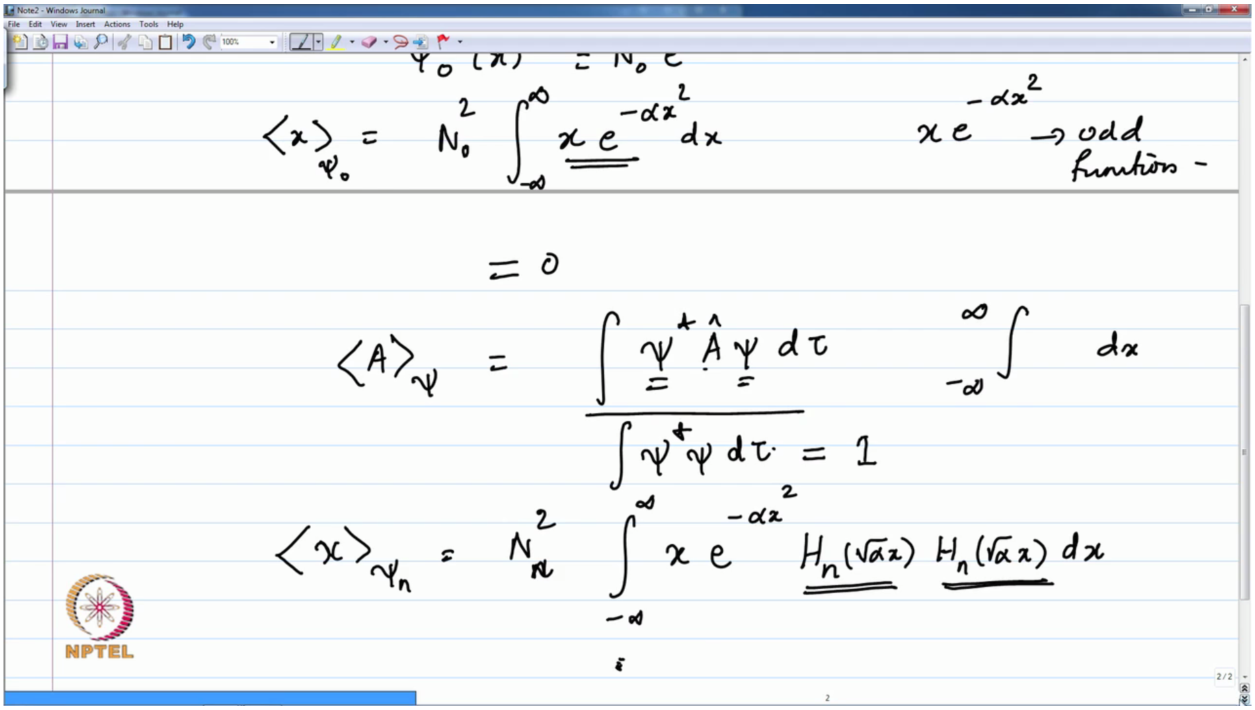
$$\psi_0(x) = N_0 e^{-\alpha x^2/2}$$

$$\langle x \rangle = N_0^2 \int_{-\infty}^{\infty} \underline{\underline{x e^{-\alpha x^2}}}\, dx \qquad x e^{-\alpha x^2} \rightarrow \text{odd function -}$$

$$= 0$$

Now remember wave functions for the -- harmonic oscillators are given in terms of say, let's take, $\psi_0(x)$, $\psi_0(x)$ is given borrowing a normalization constant, which I will write as N_0 is actually α/π 21/4, but it doesn't matter, N_0 $e^{-\alpha x2/2}$. So if we have to calculate the average value for the position of the harmonic oscillator, it's quite obvious. Since the probabilities of finding the oscillator on the +x side for any given x is the same as the probability for finding the oscillator for the -x at that x. The probabilities are evenly distributed. You can easily see that the positions with the value of a -x on the negative side and the +x on the positive side, multiplied by identical probabilities cancel out, okay.

Therefore, if you were to do this, the integral is integral is x, N_0^2, $e^{-\alpha x2}$, because it's a square of the wave function from -∞ to ∞, and you know times dx and you know $xe^{-\alpha x2}$ is an odd function. Therefore, this integral is 0.



$$\psi_0(x) = N_0 e$$

$$\langle x \rangle_{\psi_0} = N_0^2 \int_{-\infty}^{\infty} \underline{\underline{x e}}^{-\alpha x^2} dx \qquad x e^{-\alpha x^2} \rightarrow \text{odd function} -$$

$$= 0$$

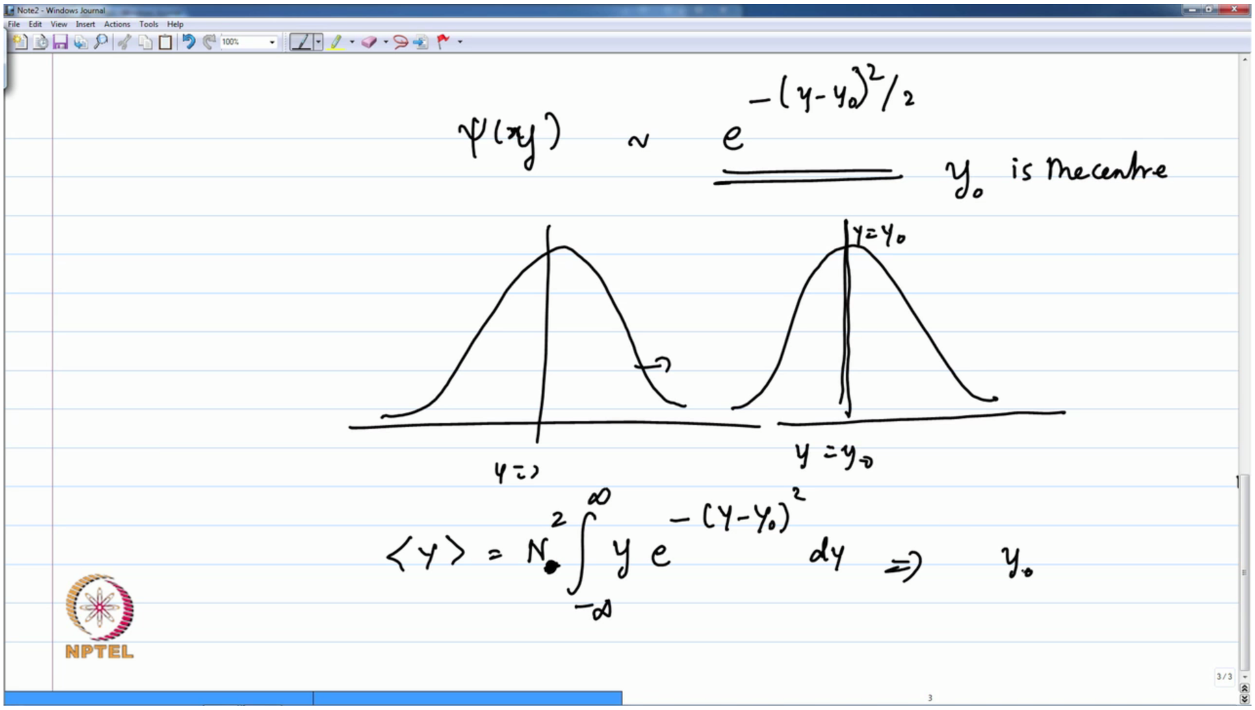
$$\langle A \rangle_\psi = \frac{\int \underline{\psi}^* \hat{A} \underline{\psi}\, d\tau}{\int \psi^* \psi\, d\tau = 1} \qquad \int_{-\infty}^{\infty} dx$$

$$\langle x \rangle_{\psi_n} = N_n^2 \int_{-\infty}^{\infty} x e^{-\alpha x^2} \underline{\underline{H_n(\sqrt{\alpha} x)}}\, \underline{\underline{H_n(\sqrt{\alpha} x)}}\, dx$$

This is true for any wave function. This is at ψ₀, the expectation value is calculated. Please remember the expectation value of any operator in the <x> ψ is given by ψ*A acting on ψdτ / ∫ ψ*ψdτ. So since this is a normalized wave function, for us, this is equal to 1, and here we have put in a as the position operator which is the x itself and the dτ and the limits are from -∞ to ∞ dx, okay. So this is what we had done. Therefore, if you calculate this for any <x>ψn, please remember that it's going to involve this integral, namely N_n^2, the normalization constant, -∞ to ∞ ∫ x $e^{-\alpha x2}$, but now it will involve the Hermite polynomial, $H_n(\sqrt{\alpha}x)$ $H_n(\sqrt{\alpha}x)$ dx, okay.

Therefore, you see that if the Hermite polynomial is odd for any given odd n, then the two odd functions multiplied together gives you an even function, and therefore, you see exponential is already an even function, the product of the two Hermite polynomial is an even function, because they have the same Hermite polynomials of order n and x is odd, and therefore, this is an integral of an odd function, between symmetric limits, -∞ to ∞ ∫ odd function of (x) ds and therefore this is 0.

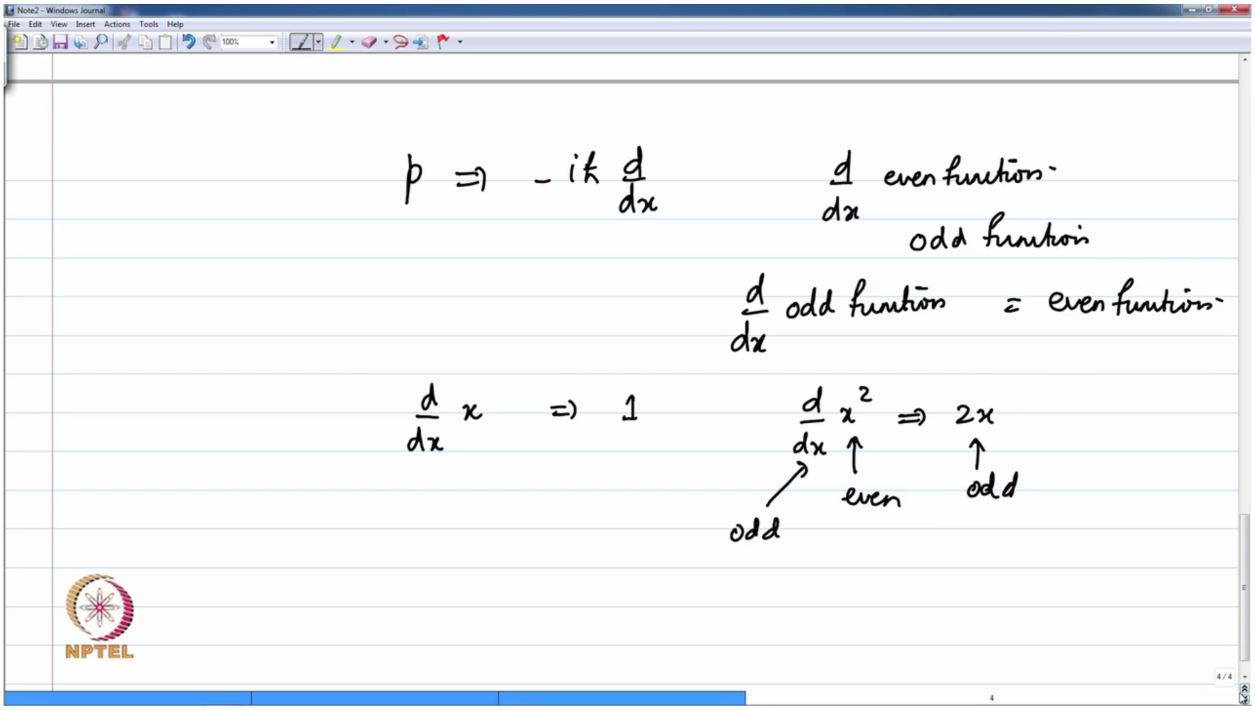
Therefore, the average value for the position of the harmonic oscillator independent of what state the harmonic oscillator is in is always, okay, is always the midpoint, the point where the harmonic oscillator is at equilibrium and the potential energy is 0 at that point.



$$\psi(xy) \sim \underline{e^{-(y-y_0)^2/2}} \qquad y_0 \text{ is thecentre}$$

$$\langle y \rangle = N^2 \int_{-\infty}^{\infty} y\, e^{-(y-y_0)^2}\, dy \Rightarrow y_0$$

Now if the harmonic oscillator for example is not centered at x, but we have a slightly different coordinate system, such that we represent the harmonic oscillator by, say, ψ(y), let us do that, as $e^{-(y-y_0)2/2}$, where y_0 is the center, because you see this function will have a maximum at $y=y_0$, and therefore, this is a Gaussian shifted from y=0 to a Gaussian shifted at $y=y_0$, okay. So if you have it at 0, this is now the Gaussian shifted at y_0, and this point is the midpoint, which is $y=y_0$. Therefore, if you calculate what is the average value for this function for the position, namely what is the average y, if you do that, you can easily show that $\int y\, e^{-(y-y_0)2}\, dy$ between the limits -∞ to ∞, and with the normalization constant N_2, some normalization constant square. You can show that this will give you y_0, which is the value at which the function is on the average as 0 potential energy and it’s the midpoint.



$$p \Rightarrow -i\hbar\frac{d}{dx}$$

$\frac{d}{dx}$ even function·

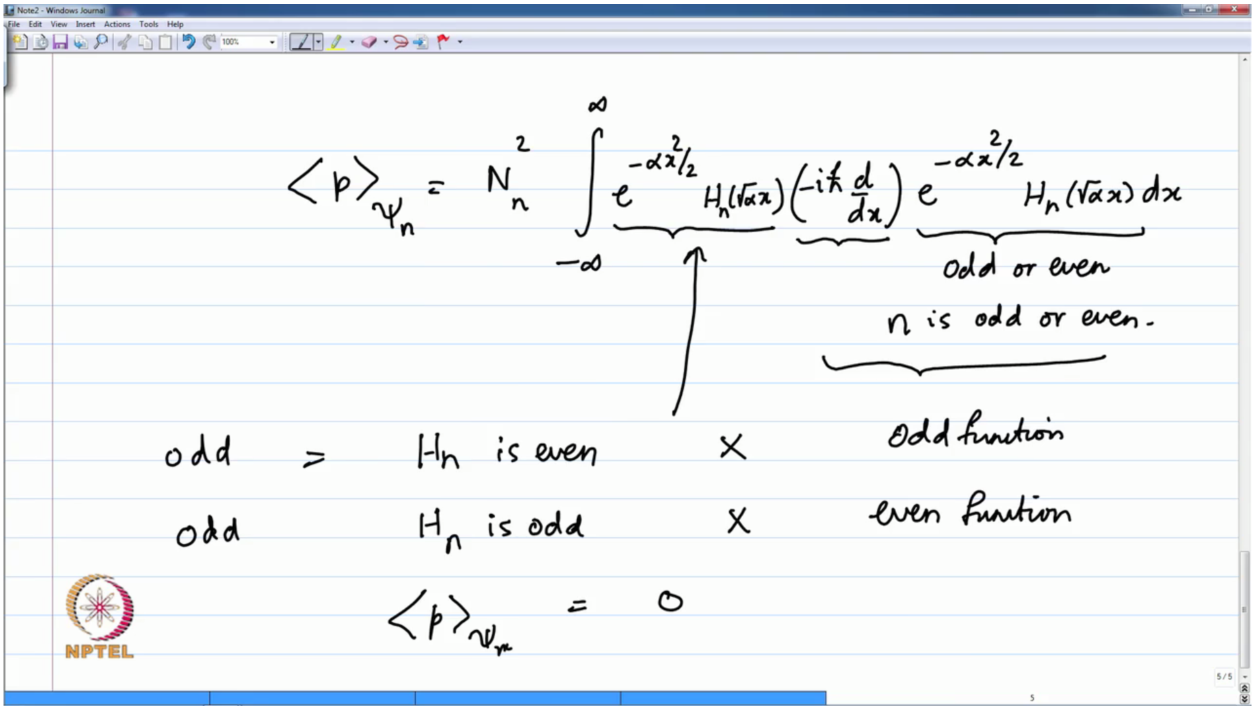
odd function

$\frac{d}{dx}$ odd function = even function·

$$\frac{d}{dx}x \Rightarrow 1$$

$$\underset{\text{odd}}{\frac{d}{dx}}\,\underset{\text{even}}{x^2} \Rightarrow \underset{\text{odd}}{2x}$$

What about the moment? Please remember the momentum operator is -iħ d/dx. It should be obvious that the derivative operator is something like an odd character, because it changes an even function, d/dx of an even function will immediately become an odd function, or d/dx of an odd function will become an even function. For example, if you do the derivative d/dx x an odd function, because it change sign, is going to be one which is even, independent of the sign of x, in this case of course, independent of x as well. But what about d/dx of x^2? It gives you to 2x. This is even; this is odd. In a sense, you can see this because the derivative has the odd character.



$$\langle p \rangle_{\psi_n} = N_n^2 \int_{-\infty}^{\infty} \underbrace{e^{-\alpha x^2/2} H_n(\sqrt{\alpha}x)} \underbrace{\left(-i\hbar \frac{d}{dx}\right)} \underbrace{e^{-\alpha x^2/2} H_n(\sqrt{\alpha}x)\, dx}_{\text{odd or even}}$$

$\underbrace{n \text{ is odd or even.}}$

odd = H_n is even × Odd function

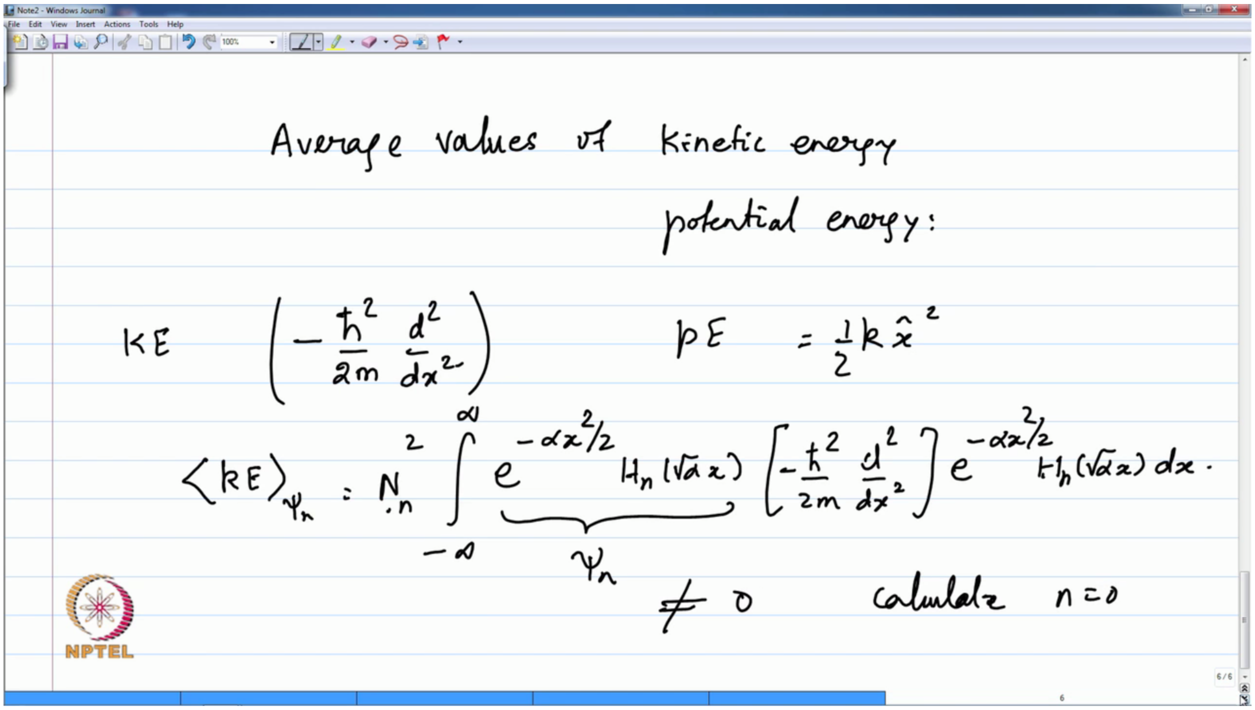
odd H_n is odd × even function

$$\langle p \rangle_{\psi_n} = 0$$

Therefore, you can see immediately that when we talk about the average values for the momentum at any given wave function ψ_n, if we have to calculate the average value of the harmonic oscillator in the state for the momentum operator, then the integral is N_n^2, the normalization constant between -∞ to ∞.

Please remember now momentum being a derivative operator (-iħ d/dx), okay. You need to put the wave function * here and the wave function itself. This is a real function. Therefore, you have $e^{-\alpha x2/2}$ $H_n(\sqrt{\alpha}x)$ that's the ψ_n^* on the site. This is the operator, P, and acting on the wave function $e^{-\alpha x2/2}$ $H_n(\sqrt{\alpha}x)$ dx. Now please remember this is odd or even depending on whether n is odd or even, okay. Therefore, if you take the derivative of an odd function, you will get an even function, but please remember if H_n is even, then the derivative of H_n will give you an odd function. Therefore, the product of the two is odd, okay. If H_n is odd, the derivative of the same H_n here, which is the odd function, will give you an even function, and therefore, the product is again odd. Therefore, the integral for any state ψ_n of the average value for the momentum is also 0, okay.

So I mean it looks like it's a trivial result, but again it's very easy to imagine that if the harmonic oscillator has forward momentum in this direction and if it has a backward momentum in this direction, because momentum is a vector, and therefore, you can always say forward in one direction means backward in the other direction. Since the probabilities for the value, the absolute value, of the momentum for any given x, the probability density is the same for whether it is +x or -x. The averages add with the vectorial sign of P. In the +x direction, the probability remains the same, but the value of the momentum is positive; in the negative x direction, the probability density is the same for that value of x but the momentum is negative, because it has a negative sign, and therefore, the momenta cancel each other for every such value of x and -x, x and -x. Therefore, the integral should be visualized as going to 0, because it has the art character.



Average values of Kinetic energy

potential energy:

KE $\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)$ PE $= \frac{1}{2}k\hat{x}^2$

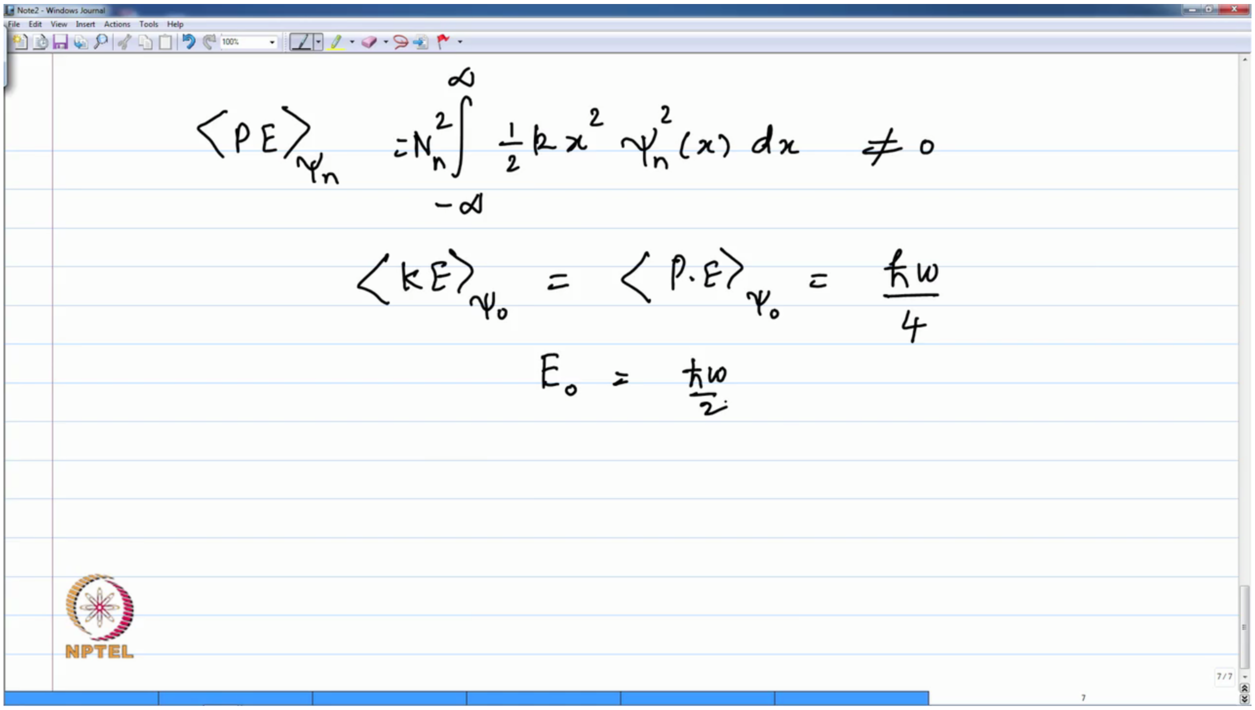
$$\langle KE\rangle_{\psi_n} = N_n^2 \int_{-\infty}^{\infty} \underbrace{e^{-\alpha x^2/2} H_n(\sqrt{\alpha}x)}_{\psi_n} \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right] e^{-\alpha x^2/2} H_n(\sqrt{\alpha}x)\,dx.$$

$\neq 0$ calculate $n=0$

The last important point for the harmonic oscillator has something to do with the average values for the kinetic energy and the potential energy, which I would want you to calculate, but they are not 0. Average values for kinetic energy of the harmonic oscillator and the potential energy of the harmonic oscillator, okay. So the kinetic energy term is given by $-\hbar^2/2m\ d^2/dx^2$. This is the operator for the kinetic energy, okay. The potential energy operator is of course ½ kx^2, x being the operator.

So when you talk about the average value of kinetic energy at ψ_n, you discuss this quantity, namely N_n^2 -∞ to ∞ ∫ $e^{-\alpha x2/2}$ $H_n(\sqrt{}\alpha x)$, this is the ψ_n with the normalization constant N, and then you have the operator, which is $-\hbar^2/2m\ d^2/dx^2$, again acting on the wave function, $e^{-\alpha x2/2}$ $H_n(\sqrt{}\alpha x)$ dx. This integral is not 0, because if H_n is odd, Hn is odd, and therefore, odd times odd function. This is a second derivative. The second derivative does not change the oddness or the evenness of the function if it has that character. An odd function remains an odd function; an even friction remains an even function. Therefore, the kinetic energy, the average value of the kinetic energy for the harmonic oscillator -- after all it's a square the momentum. It doesn't depend on the direction of the momentum. Therefore, for +x and for

-x, they keep adding the momentum for each value of the position. So this is not 0. Please calculate this, and I would suggest that you do this for n=0 or this will be part of one of the quizzes that you will find.



$$\langle PE \rangle_{\psi_n} = N_n^2 \int_{-\infty}^{\infty} \frac{1}{2} k x^2 \psi_n^2(x)\, dx \neq 0$$

$$\langle KE \rangle_{\psi_0} = \langle P.E \rangle_{\psi_0} = \frac{\hbar\omega}{4}$$

$$E_0 = \frac{\hbar\omega}{2}$$

And in a similar way, the potential energy, the average value for ψ_n is given by again from -∞ to ∞, but since it is x^2, you can write ∫ ½ kx^2 and N_n^2, x does not change except to multiply, then you can write the wave function $\psi_n^2(x)$ dx, and again, this is not equal to 0.

For the ground state, the harmonic oscillator average value for the kinetic energy for ψ_0 is equal to the average value for the potential energy ψ_0 and that's equal to $\hbar\omega/4$. And please remember the E_0 is $\hbar\omega/2$. Therefore, the average values for the kinetic energy and the potential energy are exactly distributed as equal contribution to the total energy, but a similar expression can be calculated for various values of the wave functions and the various service of the kinetic energy, and those exercises I believe as exercises for you to work out in detail.

The harmonic oscillator is an extremely important problem as far as the chemists are concerned, in the sense that if you want to study the vibrational spectroscopy, if you want to study vibrational Raman spectroscopy, infrared or Raman spectroscopy, and if you want to study electronic spectroscopy with the vibrational coordinate changes and so on, these are all there in the spectroscopy applications in chemistry. The harmonic oscillator model is crucial. And the fact that the average value of the position goes to zero has something to do with the transition probability connecting two different harmonic oscillator levels. We will see more of that when it comes to the study of molecular spectroscopy, and then we study the infrared spectroscopy.

Until then this is a sort of a very elementary summary for the solutions of the harmonic oscillator and how they behave and what can be learned from them and this can be used to build the next level of study of harmonic oscillator using raising and lowering operator form. And so that will form part of a much more advanced course later that I will be offering. Until then, thank you very much.