Introductory Quantum Mechanics and Spectroscopy
Prof. Mangala Sunder Krishnan
Department of Chemistry
Indian Institute of Technology, Madras

Lecture – 6
Part IV
Average Values for Position and Momentum

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 vibrations in spectroscopy. And when we worry about the intensity of the vibrational lines, what goes in there, the mathematical element will be discussed here.

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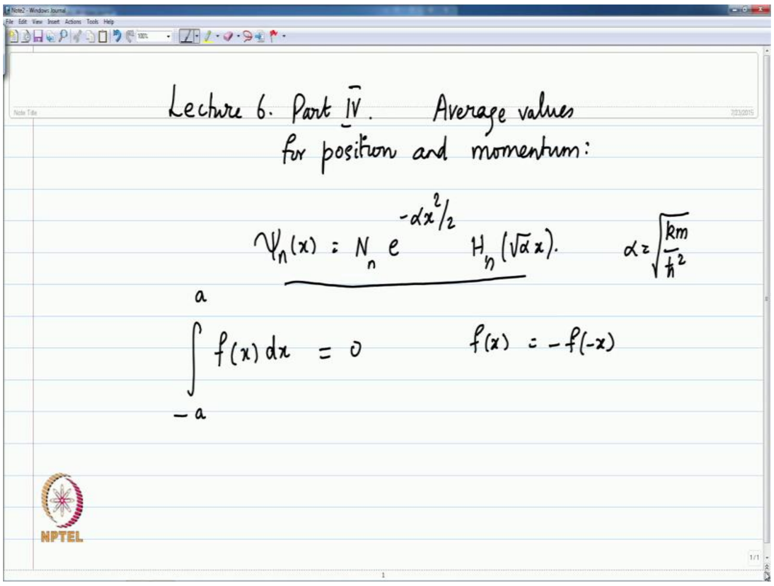

So, this part is on the average values for position and momentum operators in quantum mechanics for the harmonic oscillator. In fact, it is extremely simple. If I have to use the wave functions as given here; I do not think this lecture should be there in the first place, because the average value for the position and the momentum for a harmonic oscillator centered at x is equal to 0 is actually 0. Therefore, what are we talking about? We do talk about the average value for the energy partition, if we discuss that. See harmonic oscillator Hamiltonian has two nontrivial parts: the kinetic energy as well as the potential energy part. The kinetic energy is given by the momentum square operator divided by twice the mass of the oscillator; and the potential energy is given in terms of the harmonic oscillator force constant – half k x square. 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 is also called occupation number representation by some physicists; and the others call it as the harmonic oscillator – raising and lowering operator. So, there are many different ways by which we can study them.

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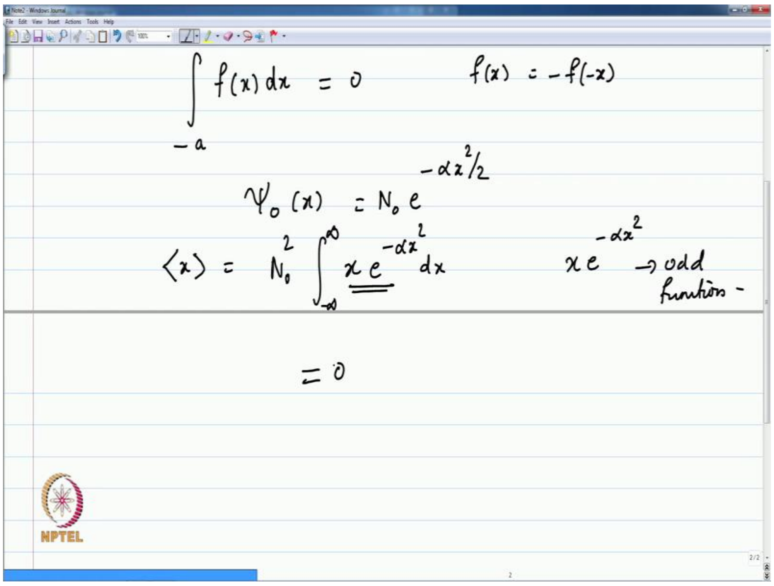

However, let us stay with the statement that, the position and momentum – the average values are 0. How do we show that? It is very easy. I told you that, if we have a – an integral of the odd function f of x is minus f of minus x; then this is 0. Now, remember the wave functions for the harmonic oscillators are given in terms of say – let us take psi 0 of x; psi 0 of x is given baring a normalization constant, which I will write as N 0, is actually alpha by pi to 1 by 4, but does not matter – in ((Refer Time: 03:29)) e to the minus alpha x square by 2. So, if we have to calculate the average value for the position of the harmonic oscillator, it is quite obvious – since the probabilities of finding the oscillator on the plus x side for any given x is the same as the probability for finding the oscillator for the minus x at that x. The probabilities are evenly distributed. You can easily see that, the positions with the value of a minus x on the negative side and a plus x on the positive side multiplied by identical probabilities cancel out. Therefore, if you were to do this, the integral is x N naught square e to the minus alpha x square, because it is the square of the wave function from minus infinity to plus infinity and you know – times dx; and you know – x e to the minus alpha x square is an odd function. Therefore, this integral is 0.

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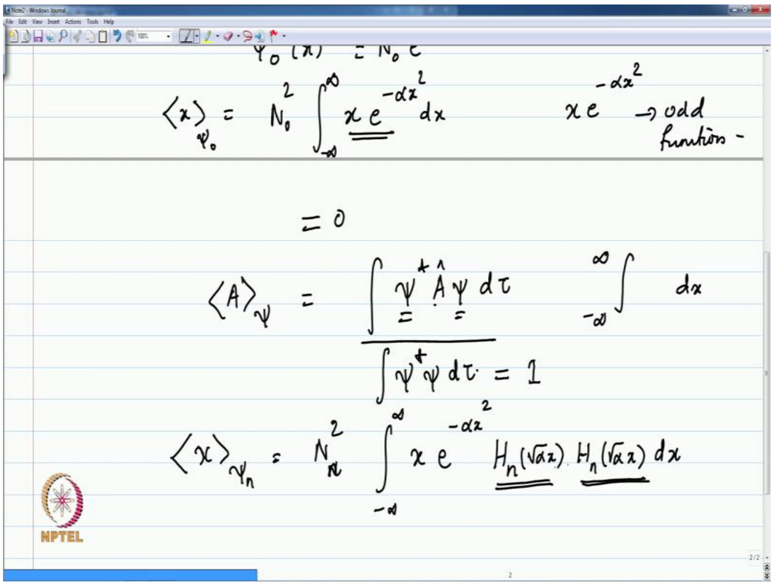

This is true for any wave function. This is at psi 0, the expectation value is calculated. Please remember – the expectation value of any operator in the state psi is given by psi star A acting on psi d tau divided by the integral psi star psi d tau. So, since this is a normalized wave function, for us, this is equal to 1. And here we have put in A as the position operator, which is the x itself. And the d tau and the limits are from minus infinity to plus infinity dx. So, this is what we had done. Therefore, if you calculate this for any state psi n; please remember that, it is going to involve this integral namely, N n square – the normalization constant – minus infinity to plus infinity – x e to the minus alpha x square. But, now, it will involve the Hermite polynomial H n root alpha x times H n root alpha x dx. 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 polynomials is an even function, because they are the same Hermite polynomials of order N; and x is odd.

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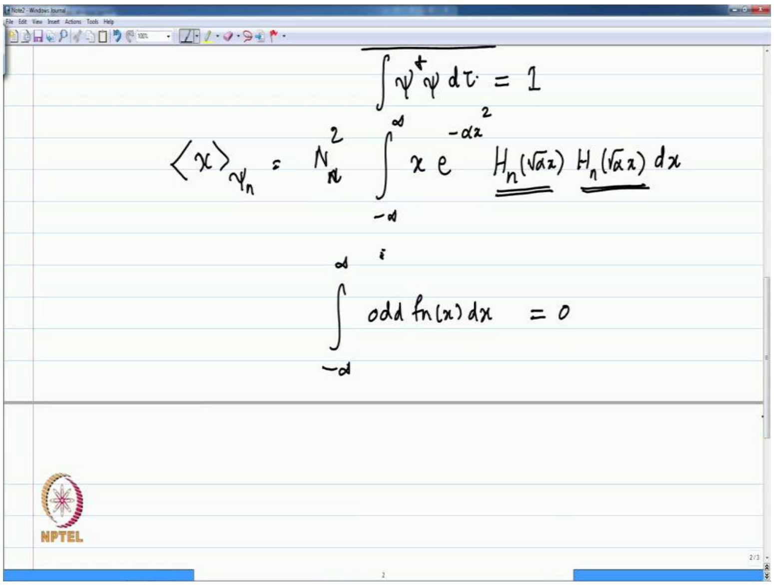

And therefore, this is an integral of an odd function between symmetric limits – minus infinity to infinity odd function of x dx. And therefore, this is 0. Therefore, the average value for the position of the harmonic oscillator independent of what state the harmonic oscillator is in is always the midpoint – the point where the harmonic oscillator is at equilibrium and the potential energy is 0 at that point.

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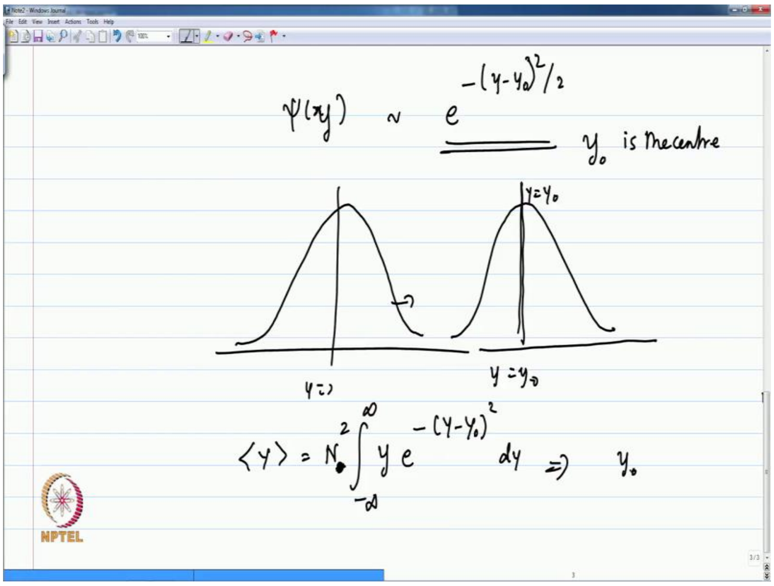

Now, if the harmonic oscillator, for example, is not centered at x, but we have a slightly different coordinate system such that we represent to the harmonic oscillator by say psi of y; let us do that – as exponential minus y minus y naught whole square by 2; where, y naught is the center, because you see this function will have a maximum at y is equal to y naught. And therefore, this is a Gaussian shifted from y is equal to 0 to a Gaussian shifted at y is equal to y naught. 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 is equal to 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, y times e to the minus y minus y naught whole square dy between the limit minus infinity to plus infinity and with the normalization constants are N square – some normalization constant – N square. You can show that, this will give you y naught, which is the value at which the function is on the average as zero potential energy and it is a midpoint. What about the momentum?

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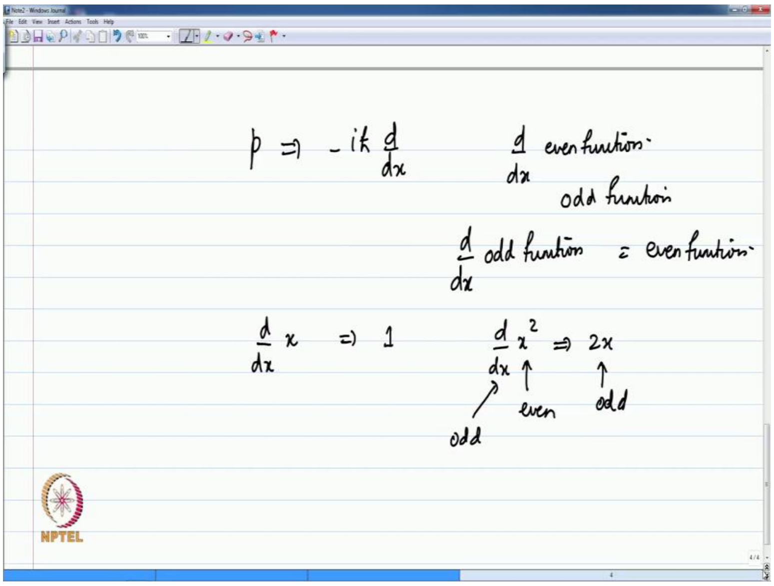

Please remember – the momentum operator is minus i h bar d by dx. It should be obvious that, the derivative operator is something like an odd character. Because it changes an even function; d by dx of an even function will immediately become an odd function; or, d by dx of an odd function will become an even function. For example, if you do the derivative d by dx of x – an odd function, because it changes sign, is going to be 1, which is even – independent of the sign of x; in this case, of course, independent of x as well. But, what about d by dx of x square? It gives you 2x; this is even; this is odd. In a sense, you can see this, because the derivative has the odd character.

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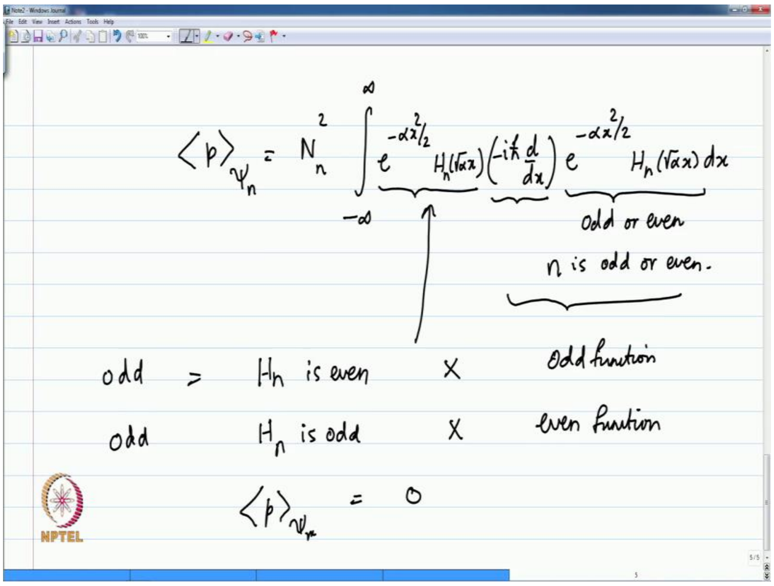

Therefore you can see immediately that, when we talk about the average values for the momentum at any given wave function psi n; if we have to calculate the average value of the harmonic oscillator in the state for the momentum operator; then the integral is N n square – the normalization constant between minus infinity to plus infinity. Please remember now – momentum being a derivative operator – minus i h bar d by dx; you need to put the wave function star here and the wave function itself. This is real function. Therefore, you have e to the minus alpha x square by 2 H n root alpha x; that is the psi n star on this side. This is the operator p and acting on the wave function alpha x square by 2 H n root alpha x dx. Now, please remember – this is odd or even depending on whether n is odd or even. 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. If H n is odd, the derivative of the same H n here, which is the odd function, will give you and even function. And therefore, the product is again odd. Therefore, the integral for any state psi n of the average value for the momentum is also 0.

So, it looks like it is a trivial result, But, again it is 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 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; that probability density is the same for whether it is plus x or minus x. The averages add with the vectorial sign of p in the plus 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 minus x, x and minus x. Therefore, the integral should be visualized as being going to 0, because it has this odd character.

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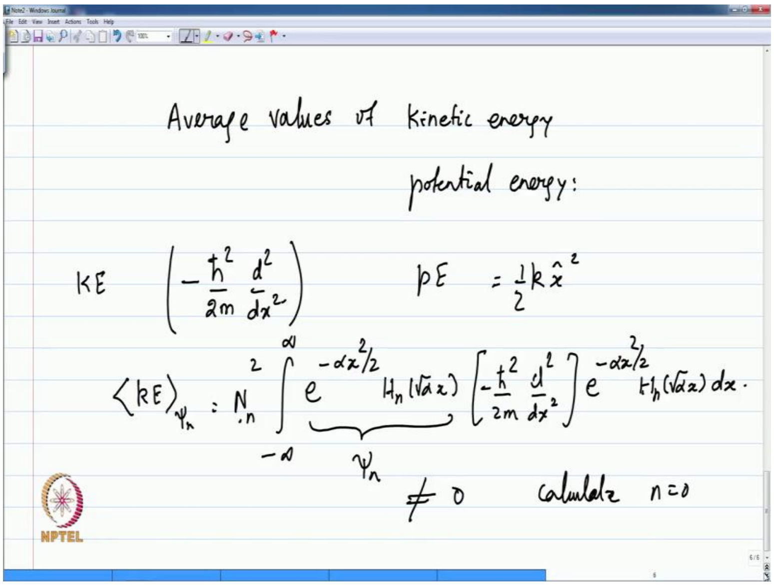

The last important point for the harmonic oscillator has something to do with the average values for the kinetic energy and the potential energy; which I would want you to calculate; but they are not 0; average values for kinetic energy of the harmonic oscillator and the potential energy of the harmonic oscillator. So, the kinetic energy term is given by minus h bar square by 2m d square by dx square. This is the operator for the kinetic energy. The potential energy operator is of course half k x square – x being the operator. So, when you talk about the average value of kinetic energy, that is, psi n; you discuss this quantity namely, N n square minus infinity to plus infinity e to the minus alpha x square by 2 H n root alpha x. This is the psi n with the normalization constant n; and then you have the operator, which is minus h bar square by 2m d square by dx square – again acting on the wave function alpha x square by 2 – H n root alpha x dx. This integral is not 0, because if H n is odd, H n is odd. And therefore, it is an 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 function remains an even function. Therefore, the kinetic energy – the average value of the kinetic energy for the harmonic oscillator; after all, it is a square of the momentum; it does not depend on the direction of the momentum. Therefore, for positive x and for negative 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 equal to 0 or this will be part of one of the quizzes; that you will find.

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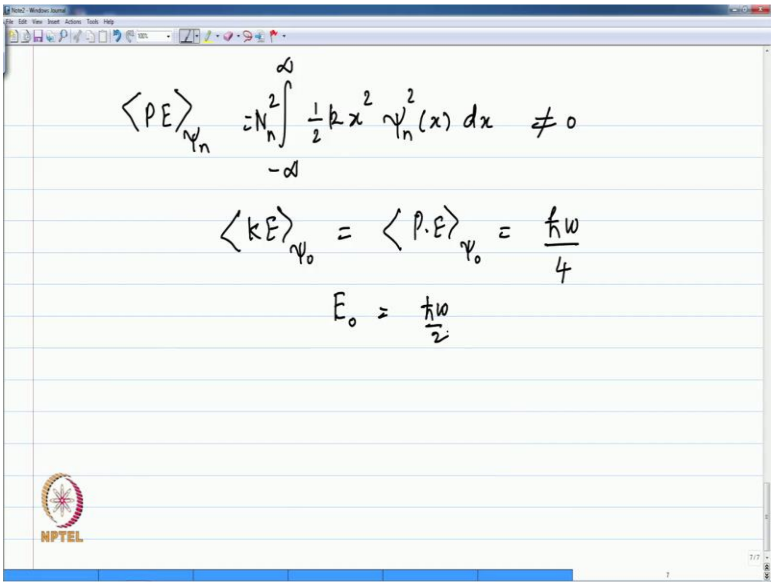

And in a similar way, the potential energy – the average value for psi n is given by again from minus infinity to plus infinity. But, since it is x square; you can write half k x square and the m n square; x does not change, except to multiply. Then you can write to the wave function psi n square x dx. And again, this is not equal to 0. For the ground state, the harmonic oscillator – average value for the kinetic energy for psi 0 is equal to the average value for the potential energy psi 0. And that is equal to h bar omega by 4. And please remember the E 0 is h bar omega by 2. Therefore, the average values for 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 values of the kinetic energy. And those exercise I will leave it as the 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 vibrational coordinate changes and so on; these are all there in the spectroscopy applications in chemistry – harmonic oscillator model is crucial. And the fact that, the average value of the position goes to 0 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 when 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 learnt from them. And this can be used to the build the next level of study of harmonic oscillator using raising and lowering operator formalism; that will form a part of a much more advanced course later that I would be offering.

Thank you very much.