Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 6
Elementary Mathematical Functions – 1

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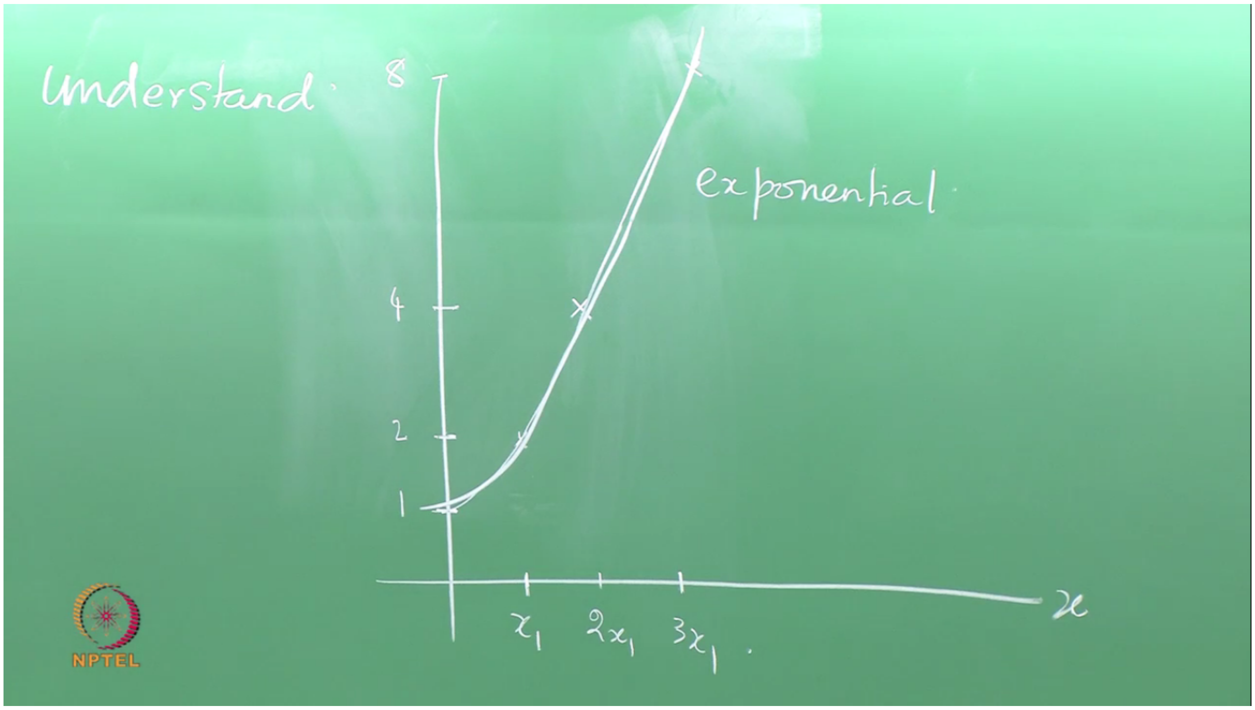
Welcome back to the lectures. The purpose of today's or this lecture is to introduce elementary mathematical functions a few of them that you will need time and again during this course either as solutions for the quantum problems that you study or functions which you will need in order to understand the behavior, the mathematical and the spectroscopic outcomes of experiments and so on. So let me start with something very very elementary and this lecture is titled elementary mathematical functions used in our course. It's not exhaustive in 20 minutes I cannot say too many things. The first function that we will look at are the two sets of functions exponential e to the plus or minus kx. k is if real constants. If k is imaginary or complex it has its own different set of properties. k is real constant. Let us look at what the exponential actually means. I think most of you remember the plot when we picture the exponential as a function of the variable X and you write this the Y-axis as exponential k of x for a given value of k if you plot this function obviously at x is equal to 0 this function has a value 1 so we will start from there here some scale and then you can see that if k is positive k is greater than 0 then this is a growth function. Growth meaning that the function increases in its value as x increases. Now that's for one value of k. Now let me call that k as k zero some constant.

Now suppose I have a different value of k the function may again start from one but it may grow something like this or it may be slower for another value of k or it may be really fast. So let us do it by making this as k0, k1, k2, k3 as some different values of k. What's the relation between these? It's quite obvious that this grows much faster for a given value of x than any other function. Obviously k3 is larger then k2 than k1 then k0. That's a pictorial representation of the function. That's not the understanding of the function.

The understanding of the function is slightly different. I mean if we know that the constants are in this order the function when it is plotted looks like that. What's the understanding of the exponential growth? Let us try and understand this function.



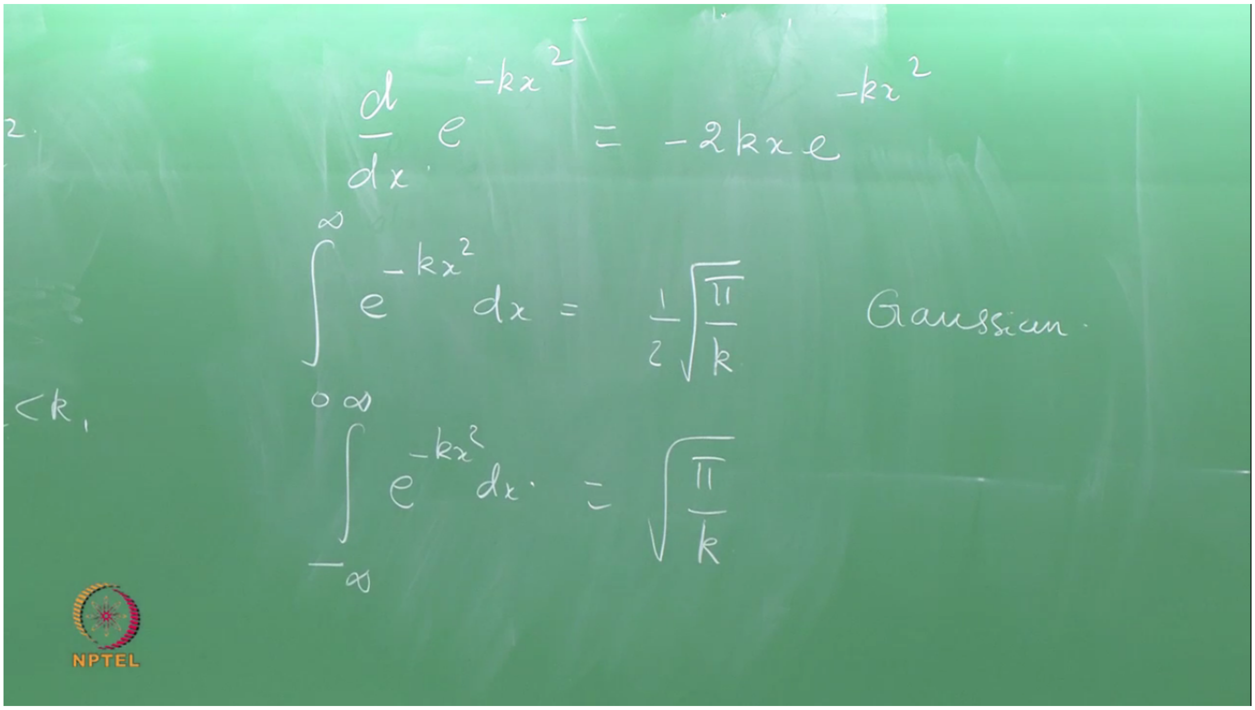
Now the way to see this is to consider this particular case namely for x we start with 1 when x is 0 at a time sorry at a particular value of x the function reaches some value here. When x becomes this is x1, 2xi, 1, 2, 4. 2, 1. At 2x1. So at x1 we have here and at 2x1 the function has the value 4 for example some units and at 3x1 it reaches a value 8 that is every increment, identical increment if the value of the function doubles its previous value such a behavior is an exponential growth, such a behavior exponential. There's nothing special about being doubling being a double or doubling. The function may start with some value in the first interval whatever value that it becomes from 1 it may become 3 but in the next same amount of interval the function 3 becomes 3 square. In the next interval 3 square becomes 3 cube. Such growths are called exponential growth. If you do it for 3 quite obviously it's even steeper or in this picture itself if you do it for 3 you are somewhere here and then 9 you are somewhere here so the point is you have here and for 2x1 you are here and you see that the function grows even steeper. This is what is meant by k. This is what is implied by k. k tells how fast in what ratio that the function grows with respect to the variable x. This is what exponential growth.

Now what about k less than zero that is negative which we call as exponential decay. E to the kx k greater than zero growth, k less than zero is decay. Of course in both cases k , real. So you have e to the minus some value of k whatever is a number of x. So if you plot this it has exactly similar but in an image kind of a picture and start with x and e to the kx is zero that is it's one and suppose for a value x1 the function becomes 1 half, 1 by 2. Then that's the value. For the same interval x1 that is 2x1 the function decreases by the same fraction 1 half becomes one fourth. One fourth in the next interval identical it when 3x1 becomes 1/8 such a behavior if you connect is exponential decay. That's also exponential. That's the nature of the exponential function. The ratio of the function for any given period the ratio is the same from that is the ratio of the value before the value after if you take that ratio that ratio remains for one particular interval ratio.

So here this is what is called the half-life if you are interested in decay processes and the number becomes 1/2 at a particular time t1 if you write the function exponential kt where t is time if you do that instead of the x you use t then you have t1, 2t1, 3t1 and so on. So the exponential is an extremely important function having this specific characteristics and the derivative of an exponential d by dx of e to the kx is k e to the kx that you should know and the integral of 0 to some constant c1 finite value of an exponential k x dx is obviously you can calculate that. If you don't put the limits that is going to be 1 by k times e to the kx. Therefore you have to be careful that this integral is for a finite limit. If you go from and if k is positive if you go from zero to infinity this is infinite. The function is unbounded. The integral is infinite. If it is negative you know that 0 to infinity if you have exponential minus kx you know what the answer is this one.

So the properties of integration, the properties on differentiation and the simple nature of exponential is one extremely important function for you. The second function that you need to worry about is also an exponential but it's not called an exponential it's called Gaussian if it is minus we usually call it a Gaussian function. This is again important in all the quantum and spectroscopy studies that you have.

What's the nature of this function? Unlike what you saw here it's not increasing forever. It's in fact decreasing forever because if k is real and positive this whole thing is decreasing as x either increases from 0 to infinity or x decreases from 0 to minus infinity because the function is dependent on the square of x this is also known as an even function and the shape of this function when you plot it are x this is plus infinity and this is minus infinity. If you do that at x is equal to 0 this whole thing is exponential 0. It is 1 and for all other values of x positive and x negative it is symmetric about to the line and this is obviously bell-shaped even function. Now again e to the minus kx square for one value k1 suppose I want to plot this for another value k2 where k2 is less than k1 it's quite clear that for any given x this will be smaller because k1 is more than k2 this one is smaller this one is slightly larger and therefore you can see that the function that if k2 is less than k1 you will have elaborate a wider function. This is k2. If you have k0, sorry you have k2, it's less than k1 and you have k0 less than k2 less than k1 if you do that then the function is even that zero. So the smaller the value of the exponent the wider, the more extended the function is or the opposite the larger the value of this k the more narrow, the narrower the function is you go in the reverse direction. This is another function which is extremely important for your calculations in spectroscopy and quantum mechanics and again you must know that the derivative of this function e to the minus kx square is minus 2kx e to the minus kx square and the integral of this function from 0 to infinity e to the minus kx square dx is given by 1 by 2 root pi over k. This is a property and this being an even function you can also do the integral of the same function between the entire x coordinate e to the minus kx square dx and that is exactly twice this integral root pi over k.



So these are standard integrals known as Gaussian integral. This is another function that you would need in studying the properties of Harmonic oscillators and quite a lot in understanding spectroscopic line shapes and so on so basic properties you should be familiar with throughout similar functions that we will see which are slightly modified from these functions namely multiplied by a polynomial instead of e to the minus kx we may have an x multiplying e to the minus kx. f1 of x some function we may have x square e to the minus kx and so on. Many many such functions and also for the Gaussian we will have e to the minus kx square and we will have x equal to minus kx square we will have x square e to the minus kx square and so on. These are functions which we will see time and again in the limited six to eight weeks course and the properties and the shapes of these things should be known to you to go back and draw some of these things.

Let me draw two of them before I conclude this small introduction to the mathematical ideas. Suppose we want to plot x e to the minus kx for some value of k and we will do that for the positive segments. Please remember we can't try to do this in the negative segment that is for the negative values of x you see that the exponent this whole thing becomes positive and therefore e to the positive number keeps on increasing therefore on the negative side this function increases beyond limit for very large values. Therefore, we will stay from 0 to some positive values and you can see that at x is equal to 0 this is 1, this is 0 therefore the function is 0 and for any other x as x increases this increases e to the minus kx decreases and therefore there is a competition between x and e to the minus kx upto a point and that point is obviously called the maximum of that function and after that point the exponential minus kx drops off so much more quickly than x increasing that the competition is lost the function decreases forever and therefore there is a maximum and then the function goes to zero. And how do we determine this maximum we take the derivative of this function e to the minus kx x and then set that equal to zero. Then you will find out that the function has a maximum. The derivative of this is clearly it's a UV so you can do that and when you set the derivative to be 0 you will get a value for the maximum.

So that's a maximum here. That's an exercise. Calculate the maximum. And similarly when you go to x square you would say that x square increases again and exponential minus kx decreases since x square increases for larger values of x much more than x itself the competition is taken over for a little longer or a little larger value of x and after that again the exponential wins over. In fact the exponential wins over for all powers of the polynomials of x. If you go sufficiently far enough on the x eventually it is the exponential that will kill the whole thing. It's very very important. Therefore if you think about x square e to the minus kx I can only say that it would be somewhere else the, maximum will be somewhere else, farther away maximum and the value of this will also be different. So these polynomials multiplied by the exponentials are extremely important in understanding the wave functions and the properties of the wave functions for hydrogen atom. The polynomials involving the Gaussian and the polynomials in front of them x and x square and so on are important in understanding the harmonic oscillator and other elementary models in quantum mechanics. Therefore please keep this in mind and please attempt some of the exercises given at the end of this lecture. Until we meet next time thank you.