Chemistry Atomic Structure and Chemical Bonding

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Lecture – 20
Coordinate Transformation

Welcome to the lecture, the topic is on Chemistry and The Atomic Structure and Chemical Bonding. My name is Mangala Sunder. I am Professor in the Department of Chemistry, in the Indian Institute of Technology, Madras. My email coordinates are given here for you to contact, in case you need any clarification or you want to raise questions and things like that, ok.

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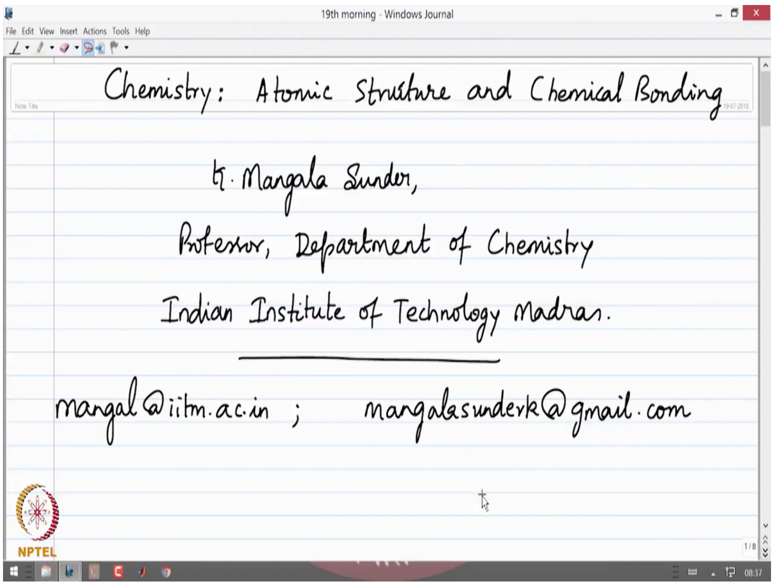

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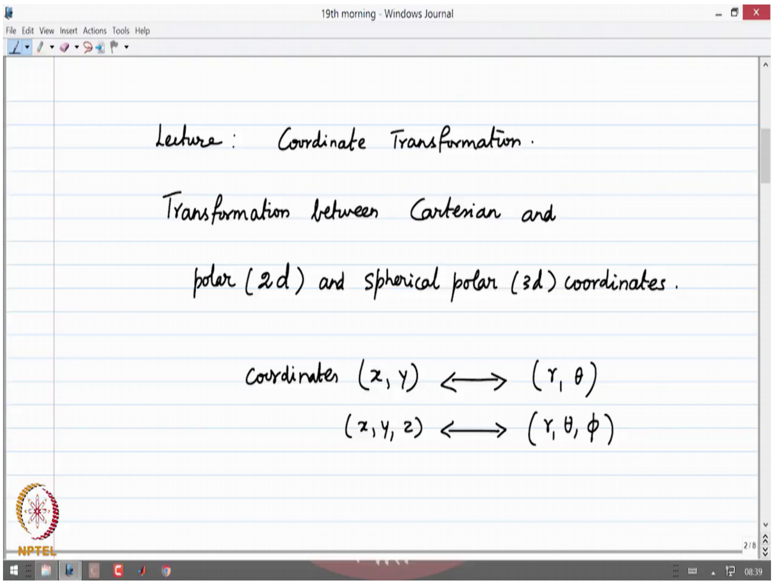

Now, this lecture is on Coordinate Transformation, as has been the practice with the series of lectures, the mathematics would be elementary. But, it is important to be clear of the mathematical details and the Coordinate Transformation is an extremely important process for understanding some of the model problems and solving them in quantum mechanics.

The most important problems in this particular course, are the two problems; namely the particle in a box, a particle in the on a ring as well as the particle namely the electron in the hydrogen atom. The particle on a ring often uses a quasi-one-dimensional variable, namely the angle, it is a polar coordinate system transformation, that we have implicitly used, and in the case of hydrogen atom, we would use a spherical polar coordinate system. Therefore, the quantities and the equivalences between these two coordinate systems should be understood fairly clearly.

Now, in two dimensions, the polar coordinate system transformation between Cartesian and polar, is the transformation between the two coordinates x and y in the Cartesian System and the coordinates r and theta, in polar framework. In the case of three dimensions, it is the transformation between the three coordinates x y z in the Cartesian axis to the three variables or the radius, radial variable theta and phi are the angular variables r theta phi are 3 coordinates.

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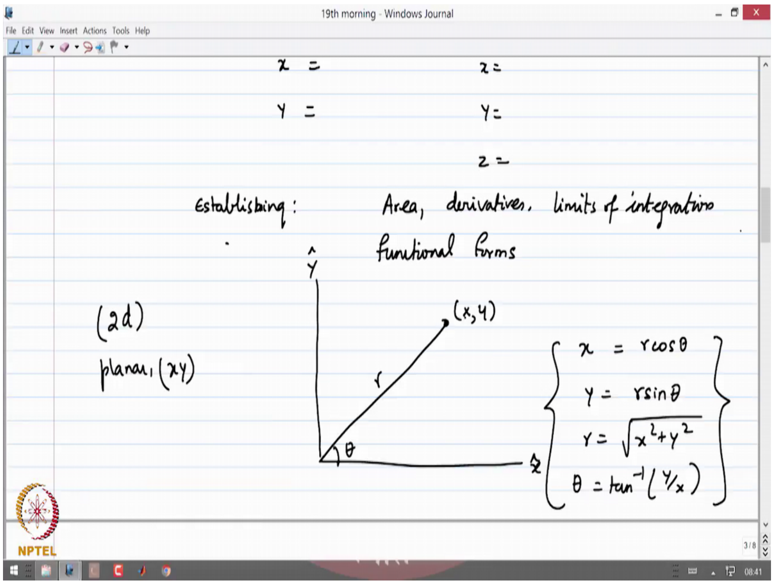

Now, let us start with a simple two-dimensional transformation and what is meant by equivalence, we will see. So, it is equivalence essentially means, we have to establish the equivalence in the areas, the derivatives limits of integrations and functional forms, because we are using all these ideas, in the solution of the Schrodinger equation. Now, in two dimension planar, x and y you can see, that any point any, any function, is a function of the two coordinates x and y and the x and y is they are marked as a point on the two dimensional axis system and the angle, that the position vector makes with the x axis theta as well as the length of this vector are used to define the polar coordinate systems as follows.

The component of x of the component x is given by the radius vector r into cos theta and the component y is given by r sine theta and therefore, this is the transformation from Cartesian to polar. What is the inverse transformation? If you take the squares of these and add them up and you take the square root, you see that r is equal to square root of x square plus y square and taking the ratio of y by x you get tan theta and therefore, theta is equal to tan inverse y by x.

Therefore, the coordinate system and transformation and the inverse are defined for polar system, likewise other coordinate systems are used. Cylindrical coordinate systems are often used, in some of the problems, then various other systems there are some 10 to 11 coordinate systems, that we may use in quantum mechanics, but for our problems these two would do, ok.

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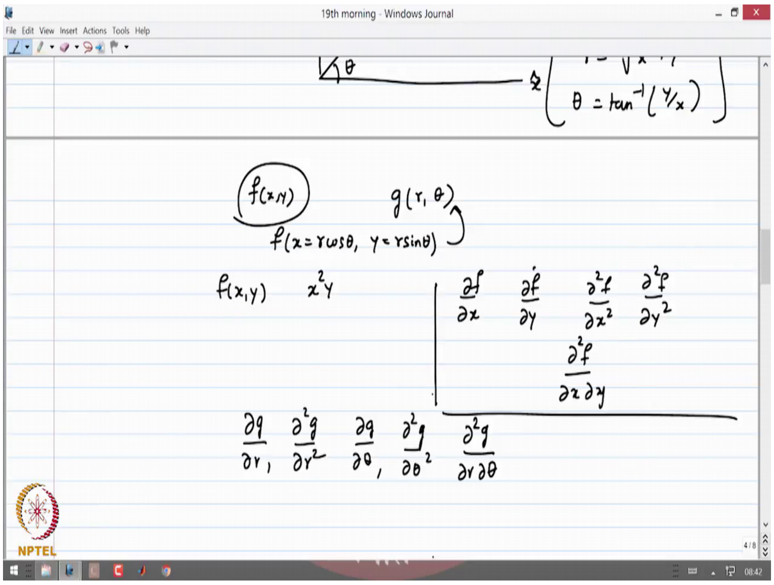

Now, the a function in x and y and the corresponding function in r and theta, obtained by substituting x is equal to r cos theta, y is equal to r sine theta, their derivatives and the area elements are something now we will look at. Now, let us take an example of x square y as f of x y ok; now in the xy framework, we have partial derivatives dou f by dou of x dou of f by dou y and dou square f by dou x square, dou square f by dou y square and dou square f by dou x dou y and so on.

Now, likewise the corresponding function f, also has dou g by dou r dou square g by dou r square and dou g by dou theta, dou square g by dou theta square and likewise dou square g by dou r you know theta and so on. So, these are the partial derivatives in the polar coordinate system and these are the partial derivatives in the Cartesian coordinate system. How do we relate them, because we mean for use the transformation from one coordinate to other? The derivatives should also be transformed to the coordinate system, that we use.

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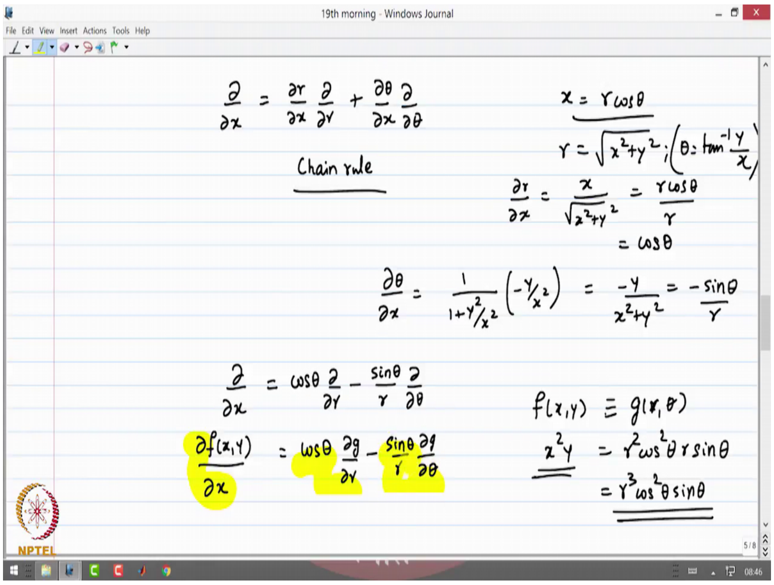

So, here is an example for the two-dimensional system. The partial derivative dou dou of dou x is written in terms of the partial derivatives of r and theta using chain rule in calculus, ; and that is given as dou r by dou x dou by dou r plus dou theta by dou x dou by dou theta, because x depends on r and theta, ok. Therefore, both the derivatives are here.

Now, you see you need the derivative dou x by dou r or the inverse know r we know x and that is easy to calculate, because you know r is equal to square root of x square plus y square. Therefore, dou r by dou x is x by square root of x square plus y square and that is r cos theta by r that is cos theta ok, likewise dou theta by dou x is, if you recall theta is tan inverse y by x and therefore, the derivative of that is tan inverse is of course, 1 by 1 plus y square by x square times minus y by x square this gives you minus y by x square plus y square and in terms of the r and theta it gives you minus sine theta by r.

Therefore, the derivative dou by dou x in the Cartesian coordinate system is equivalent to the derivative, cos theta dou by dou r minus sin theta by r dou by dou theta, ok. Therefore, if you do dou f of x y dou x, you calculate that to calculate the corresponding quantity using g. You must actually do cos theta dou g by dou r minus sine theta by r dou g by dou theta where f of xy and g of theta are equal r and theta are equal. So, here if it is x square y, the corresponding g r theta is x is equal to r cos theta. Therefore, it is r square cos square theta r sine theta which gives you r cube cos square theta sine theta. These functions are equivalent and therefore, these derivatives are also equivalent. The derivative dou by dou x is given by, in this system by this and also by this, ok.

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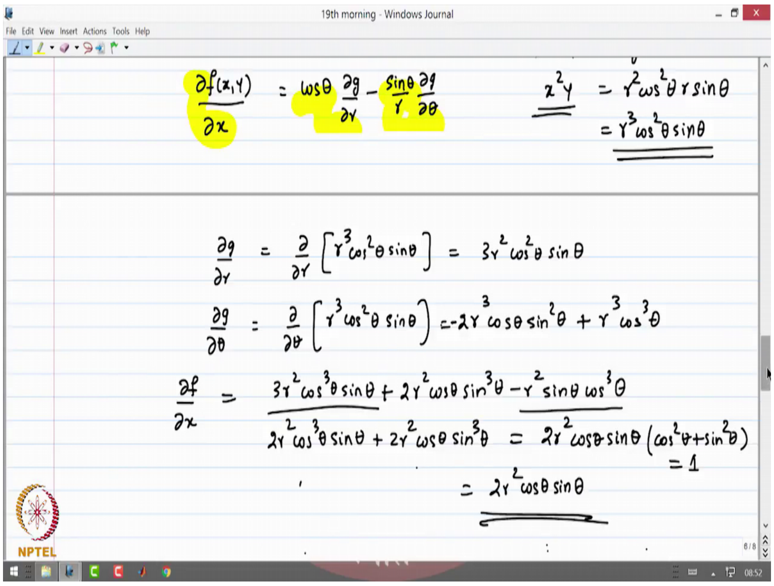

Let us calculate and see that it is true, ok. So, let us take the derivative dou g by dou r, which is dou by dou r of r cube cos square theta sine theta and that is three r square cos square theta sine theta and dou g by dou theta is dou by dou theta of r cube cos square theta sine theta. So, that is given, as r cube into two cos theta sine theta. So, this becomes a sine square theta and with a minus sign, and the other derivative is the derivative, with respect to sine theta which gives you r cube cos cube theta.

Now, if we calculate dou f by dou x, then it is equivalent to doing this multiplication. So, multiply cos theta with dou g by dou r. So, you get three r square cos cube theta sine theta and then you have a minus and sine theta by r you have therefore, that is minus plus two r square cos theta sine cube theta plus with a minus sign r square sine theta cos cube theta, ok.

So, you can see immediately that, the 3 r square cos cube theta sine theta minus r square cos cube theta sine theta gives you 2 r square cos cube theta sine theta plus 2 r square cos theta sine cube theta and, that can be simplified immediately as 2 r square cos theta sine theta times cos square theta plus sine square theta, which is 1, which is 1. Therefore, the derivative is 2 r square cos theta sine theta, ok.

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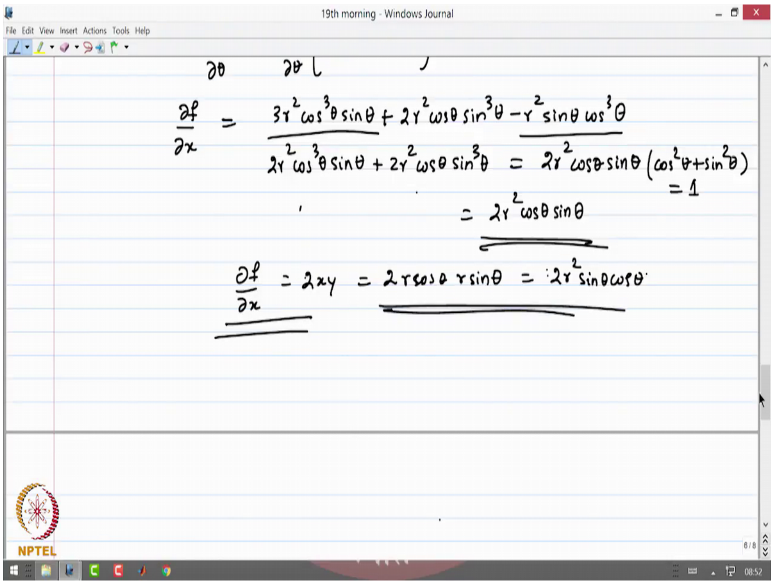

Now, that is exactly, what you would have got; if you took the derivative of x square y with respect to the f of x dou f by dou x is 2 xy and the 2 x y would be 2 or sine cos theta and or sine theta which gives you 2 r square sine theta cos theta.

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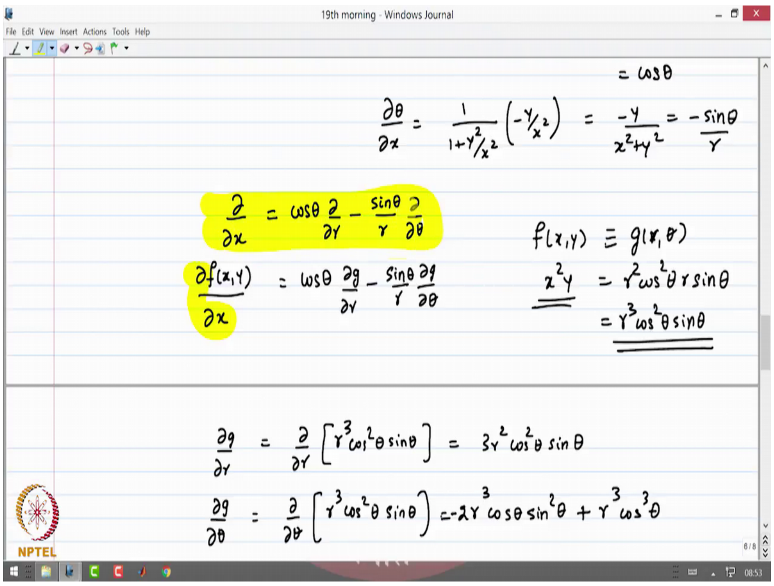

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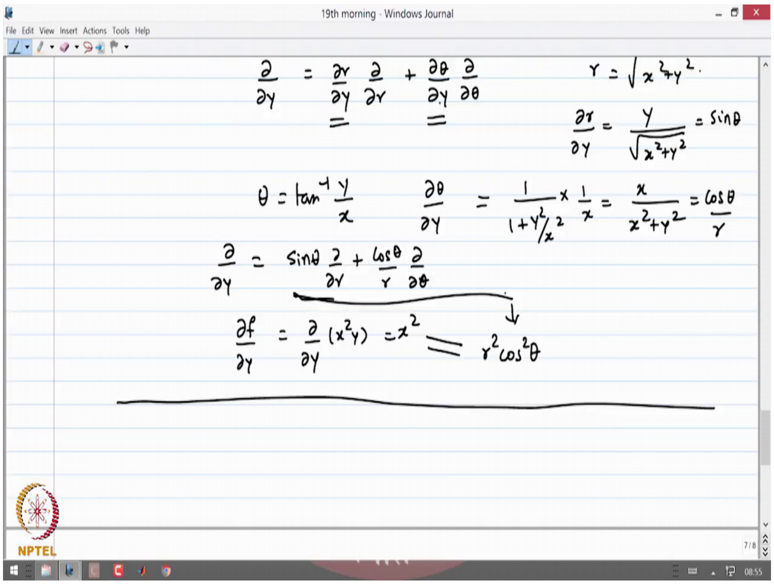

Therefore, you see that, the equivalence of the derivative is given by this expression or dx, likewise for the y you can calculate immediately. The derivative dou by dou y is dou by dou r dou r by dou y plus dou theta by dou y dou by dou theta, ok, and again, now, you have to calculate these derivatives and you know that r is square root of x squared plus y square. Therefore, dou r by dou y is going to give you y by square root of x square plus y square and that is sine theta by r. And likewise, dou theta by dou y thus, knowing that theta is tan inverse y by x. This is equal to 1 by 1 plus y square by x square times 1 by x. So, this will give you x by x square plus y square, ok, and that is cos theta by r.

So, the derivative dou by dou y now, is given in terms of r and theta as dou r by dou y, which is saying, sorry this is not sin theta, ok; it is sin theta dou by dou r plus cos theta by r dou by dou theta. So, in a similar way, you can also establish the derivative dou f by dou y, which is the derivative dou by dou y of x square y and gives you x square. You can get exactly, this expression to give you r square cos square theta which is x square.

So, this is what is called the equivalence of the derivatives from between the 2 coordinate systems and this is important, because the kinetic energy operator involves the second derivative with respect to x and the second derivative with respect to y, if you remember dou square by dou x square and dou square by dou y square. Therefore, to calculate mathematically these quantities the transformation of coordinates is important.

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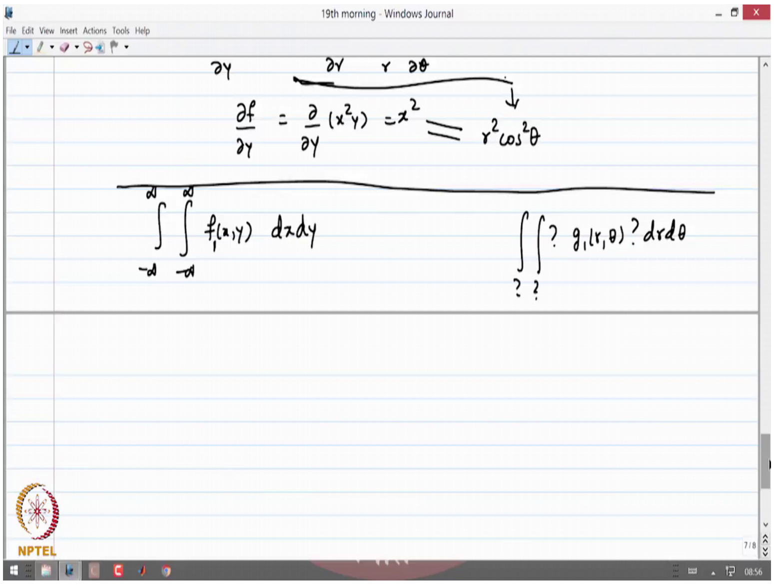

The other equally important aspect is the element, dx dy. If we have a function f of x y something else, some other function say, f one of x of y and we have an integral between minus infinity to plus infinity, minus infinity to plus infinity for x and y. What is the corresponding expression for the g one of r theta d r d theta; is there anything else to be taken and what are the limits, ok.

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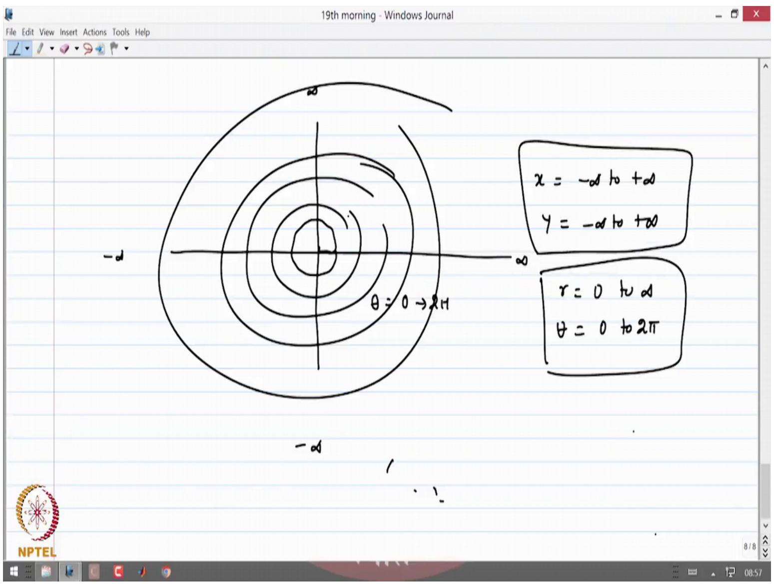

Then, it is easy to see that, because when you say, you are integrating between x and y with minus infinity to plus infinity, minus infinity to plus infinity, you are integrating over the entire plane and the same integration can be carried out by integrating over all angles of theta from 0 to 2 pi, starting from some, some angle here and 0 to 2 pi and then integrating from r equal to 0 to infinity, because then you have concentric circles of that.

And therefore, the integral x, with the limits x is equal to minus infinity to plus infinity and the limits y is equal to minus infinity to plus infinity, yes equivalent to the integral with the limits r equal to 0 to infinity and theta is equal to 0 to 2 pi for each r therefore, r goes from 0 to infinity. Therefore, the integration over the entire plane is done by either this, in the polar coordinate system or done by this in the Cartesian coordinate system.

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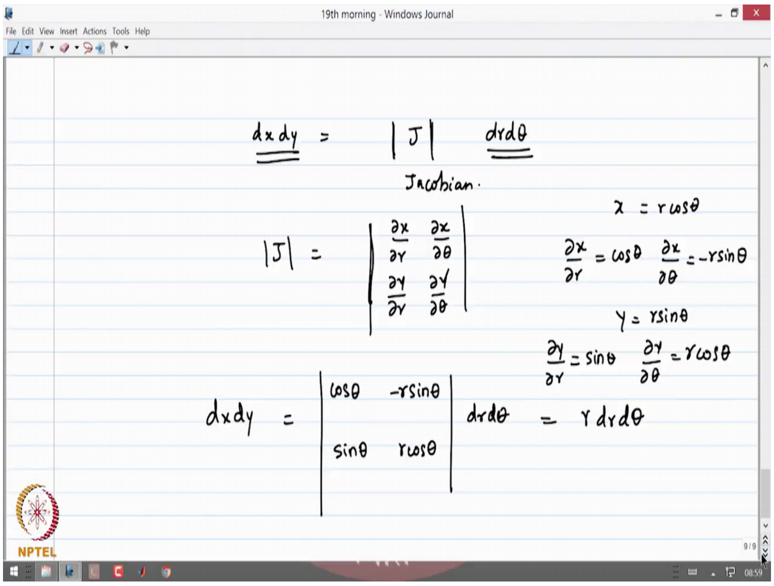

The only other thing, that we need to worry about it, what is dx dy; in terms of d or d theta and that is a very simple mathematical relation and you have been introduced probably earlier, what is called the Jacobian and this is the sine less, that is the absolute value of the Jacobian, connects the area element in the cartesian coordinate to the area element in the polar coordinates. And the Jacobian is given by the determinant dou x by dou r dou x by dou theta, dou y by dou r dou y by dou theta and these derivatives are already known, because you know x is equal to r cos theta.

Therefore, dou x by dou r is; obviously, cos theta, dou x by dou theta is minus r sine theta and y is equal to r sine theta and therefore, you have in a similar way, dou y by dou r is sine theta and dou y by dou theta is r cos theta.

So, if you substitute these values into the Jacobian determinant, dou x by dou r is cos theta and dou x by dou theta is minus r sine theta and dou y by dou r is sine theta and this is r cos theta times d r the theta is equal to dx dy and, that immediately gives you r cos square theta plus r sine squared theta. Therefore, it gives you all the r d r d theta.

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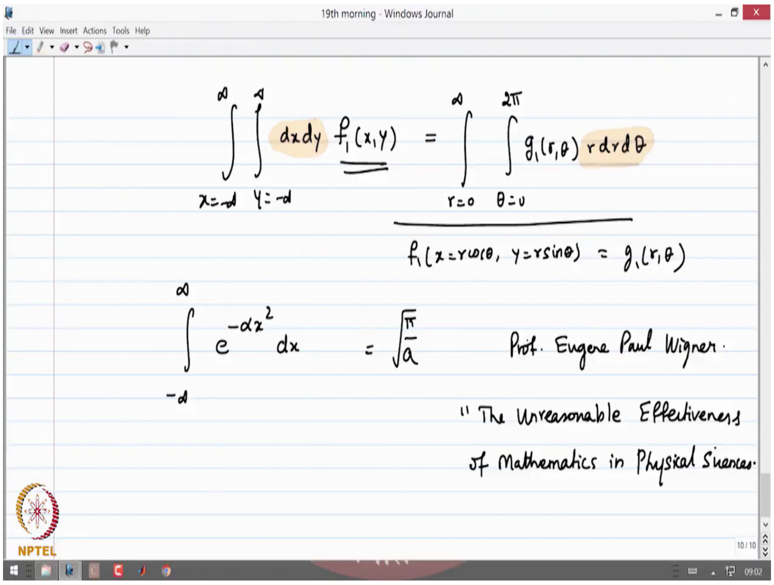

Therefore, you can see, that the integral x is equal to minus infinity to plus infinity y is equal to minus infinity to plus infinity dx dy f 1 of x y whatever that function may be, assuming that this integral is finite, is equivalent to the integral r is equal to 0 to infinity. Theta is equal to 0 to infinity, it is g 1 of r theta, which is obtained by substituting f 1 x is equal to r cos theta y is equal to r sine theta and that gives you g one of r theta, and this is r d r d theta. So, this is the integral.

Therefore, the equivalence is dx dy is r d r d theta as the area element and the limits of the integration have now, been converted to the corresponding limits here, namely r is from 0 to infinity theta is equal to 0 to 2 pi, I am sorry this is 0 to 2 pi, ok. So, that is one example, but which I will close this lecture, namely the calculation of the integral e to the minus alpha x square dx from minus infinity to plus infinity.

This is a very standard integral and all of you know, the answer is as root pi by a. In fact, there is a fantastic story about this whole thing in one of the, most beautifully written articles, by Professor Eugene Paul Wigner, in a or in an article, known as the Unreasonable Effectiveness of Mathematics in Physical Sciences.

I suggest every one of you, pull this article from the internet and read the first paragraph of how the pi in a probability distribution comes out as the circum, the ratio of the circumference of the circle to its diameter, is connected to the population distribution and that is very beautifully written article, ok.

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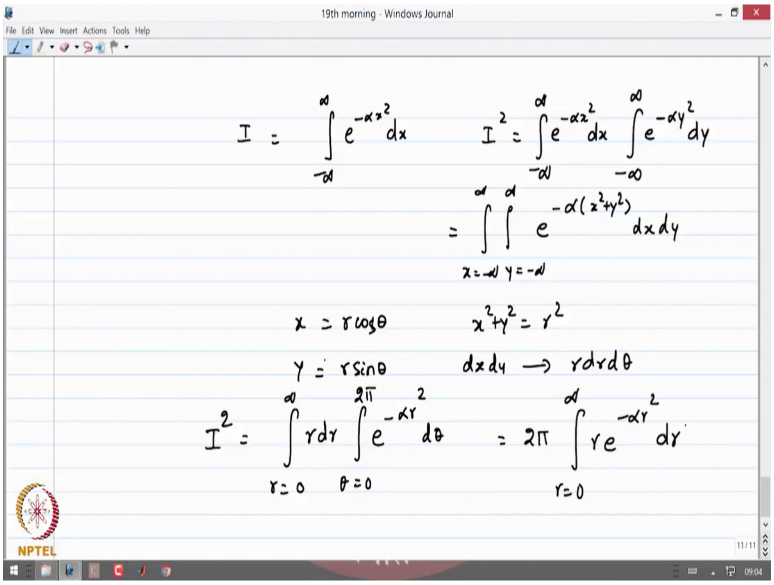

Now, this integral I, if we write this as minus infinity to plus infinity e to the minus alpha x square dx. To calculate this, let us do I square, namely multiply this integral by its own, alpha x square dx and since the variables are, these are variables inside the integral, we have to use a different variable namely alpha y square dy, ok. That is also between 0 and infinity, minus infinity and infinity. So, this gives you the double integral x is equal to minus infinity to infinity y is equal to minus infinity to infinity e to the minus alpha x square plus y square dx dy.

Now, remember that if we make the transformation x is equal to r cos theta and y is equal to r sine theta, then we know, that x square plus y square is r square and then, we know that dx dy needs to be replaced by r dr d theta. Therefore, the integral I square, is now given by the corresponding limits, namely r is equal to 0 to infinity r d r theta is equal to 0 to 2 pi e to the minus alpha or square d theta. Now, the integral with theta, d theta this function does not depend on theta. Therefore, it is nothing, but the integration of d theta from 0 to 2 pi.

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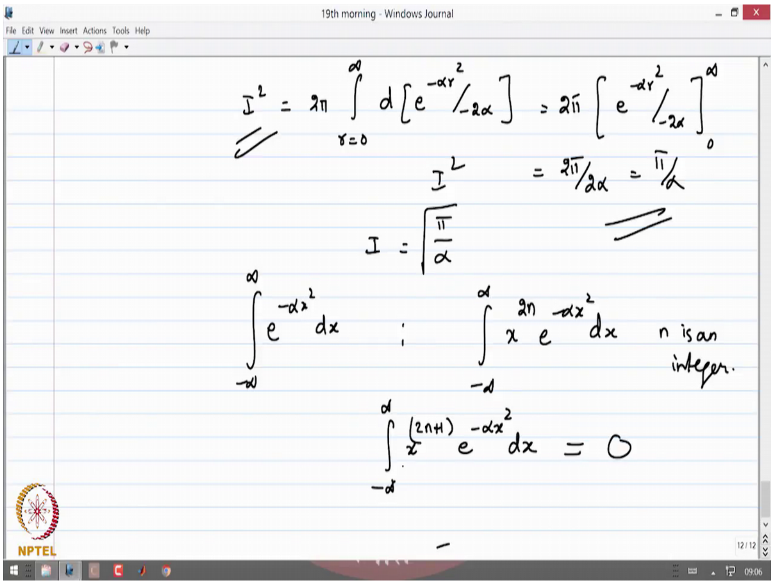

Therefore, it gives you the answer 2 pi times the integral r equal to 0 to infinity r e to the minus alpha r square d r and that is a very easy integral to evaluate by partial integration, namely I square is 2 pi times r equal to 0 to infinity, d of e to the minus alpha r square by minus 2 alpha. This is the differential form the, fully differential form exact differential form integrated between r equal to 0 to infinity is the same as that. Since, it is a differential, perfect differential the answer is basically 2 pi times e to the minus alpha r square by minus 2 alpha between the limits 0 and infinity. And at infinity r is of course, infinity.

So, this function goes to 0 and at r equal to 0 this function is 1 by minus 2 alpha, but there is a minus sign therefore, this becomes 2 pi by 2 alpha and that is I square which is pi by alpha. Therefore, I is equal to root pi by alpha and once you know this integral e to the minus alpha x square dx from minus infinity to plus infinity, you can calculate any number of them, namely minus infinity to plus infinity x raises to 2 n e to the minus alpha x square dx.

By simply repeating, the partial integration, until you reach the point with no other polynomial of x, but accept e to the minus alpha x square dx at that point you have (Refer Time: 24:50), so, pi over alpha. Therefore, you can generate the entire integral series using this elementary, but one of the most important integrals.

We will use this in harmonic oscillator and of you do not need to calculate this integral x raise to 2 n plus 1 this is n is an integer I did not say, but that is what is implied, and if it is an n is an integer x raise to 2 n plus 1 e to the alpha x square dx is 0. Therefore, you do not need to calculate. For these are all important later in the computational chemistry in the Gaussian programs and many others and therefore, it is a Coordinate Transformation of a two dimension, which is to be understood fairly clearly and the rules for transforming the derivatives, transforming the area elements and transforming the integral limits, they all should be clear.

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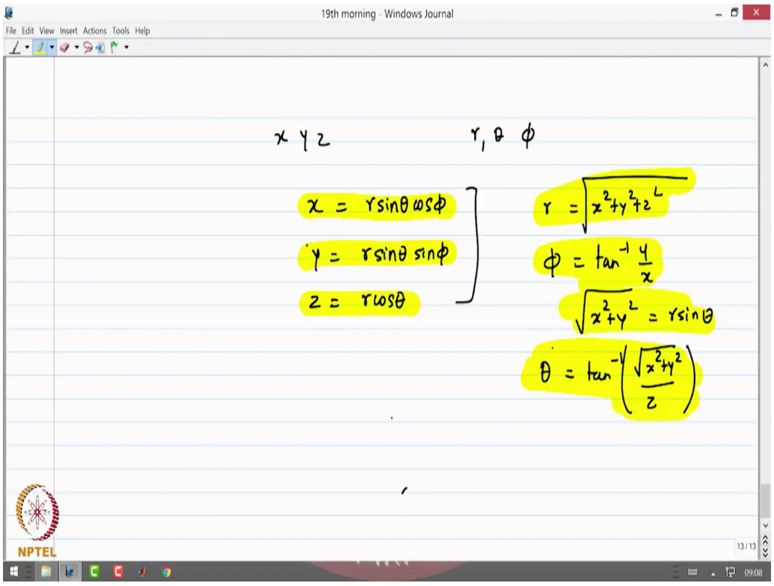

For the three dimensional system, where we have x y z connected by r theta and phi, the lectures on the hydrogen atom contain some of the details with the coordinate equivalence x is equal to r sine theta cos phi, y is equal to r sine theta sine phi and z is equal to r cos theta and the inverse transformation, that r square is equal to x square plus y square plus z square.

Therefore, r is square root of that and the ratio of y by x is tan phi therefore, phi is tan inverse y by x and to calculate to the theta x square and y square If you take the square root that gives you r, that gives you r sine theta and therefore, theta is tan inverse square root of x square plus y square by z, ok, r sine theta by r cos theta is tan theta therefore, theta is tan inverse that.

Therefore, the transformation, given by these equations x y z and the inverse transformation given by these equations for r phi and the theta determine the three-dimensional problem which would be studied in the case of hydrogen atoms and the hydrogen atom Hamiltonian would be transformed into a spherical polar coordinate System, because the potential energy of interaction between the electron and the nucleus is physically symmetric and spherical polar coordinates would be used.

There I would discuss the transformation more in detail with respect to the partial derivatives and the equivalence of the volume elements and the Jacobians etcetera. Therefore, this lecture may be kept in mind, when you read that particular lecture for the study of the hydrogen atom in detail. We will continue with the course, with the solution of the model problems in quantum mechanics, elementary modern problems in quantum mechanics in subsequent lectures until then.

Thank you very much.