Mathematics for Chemistry
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Lecture - 8

Today, we are going to do application of line integrals, and this application is something that you probably have seen before and it is called potential theory.

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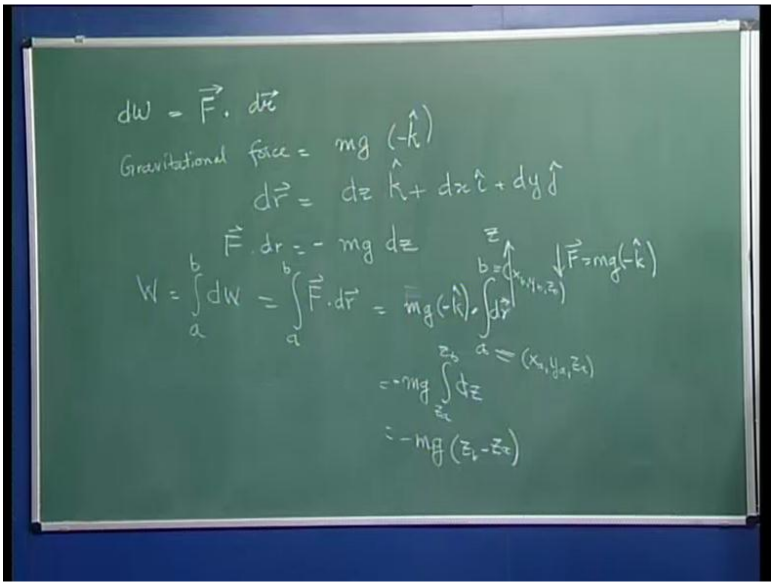

So, the idea is suppose, you have a force F acting on a body and due to this force, the body is displaced by a distance d r, then the work done in this process is d w, which is a scalar, which is F dot dr. So, this is what you learn in your standard mechanics course, we are assuming that, this d r is an infinitesimally small displacement and for this infinitesimally small displacement d r, the force is a constant. So, now what happens when you take a body from one point to another by application of this force.

So, we look at specific example, suppose you have a gravitational force. Now so the body is attracted towards the ground and the force on the body is just the mass of the body, and times the acceleration due to gravity and it is acting in the minus k direction that is, it is acting downwards. So, we assume that this is the plus k direction, this is the force that is acting downwards, and suppose you assume that you are displacing the body by some amount, then the if this displacement of the body is given by d z k d y j then you will say that F dot d r equal to mg d z, minus mg d z.

So, if your d z is negative then the force does work in pushing the body down, if your d z is positive that is, in the upward direction then you have to do work to push this body. So, what we assume is that, this is a z direction and the force is acting on this direction g times. So, if d z is negative then you have to do work whereas, if d z is positive then the force or sorry if d z is positive, you have to do work. So, the work done by the force will be negative and if d z is negative then the force does work so it is going down and the force is doing work of m g times d z.

Now, this is an example of a force, which is constant everywhere so if am looking at this body, if I am looking at this piece of chalk, it is when I leave it, it will drop down by gravity. Now, it does not matter whether I am here, here, here, here wherever I am, the force is a same so the force is independent of where you are in space.

And so in this case, if you are doing work in going from a point a to point b then this is just the total work done in going from a to b, is just the integral of d w. And the integral of d w, in this case will just be integral F dot d r from a to b and this will just be equal to, since F is a constant, you can take it outside the integral. So, it is just F, F is just mg to minus k hat, doted into integral d r or integral d z or d r from a to b.

Now, if this point a is denoted by coordinates (x a, y a, z a) and this point b is denoted by Coordinates (x b, y b, z b) then the value of this is just minus mg d z from z a to z b so it is independent of x a and y a, and this is just equal to minus m g. So, what we found was that, you can calculate the work done by this force in a straightforward procedure now, in this case, the force was constant everywhere.

So, it was the same force so you could take it outside the integral and this integral of d r just become a straight forward r at the boundaries. It was just value of r at the boundaries and since you had a dot product, we just needed to worry about the z component. Now, but there are many cases, many situations, in which this force might not be a constant, force might depend on where you are. So, suppose, you have a situation where, the force at this point might be different from say, the force at this point or it might be different from here and so on.

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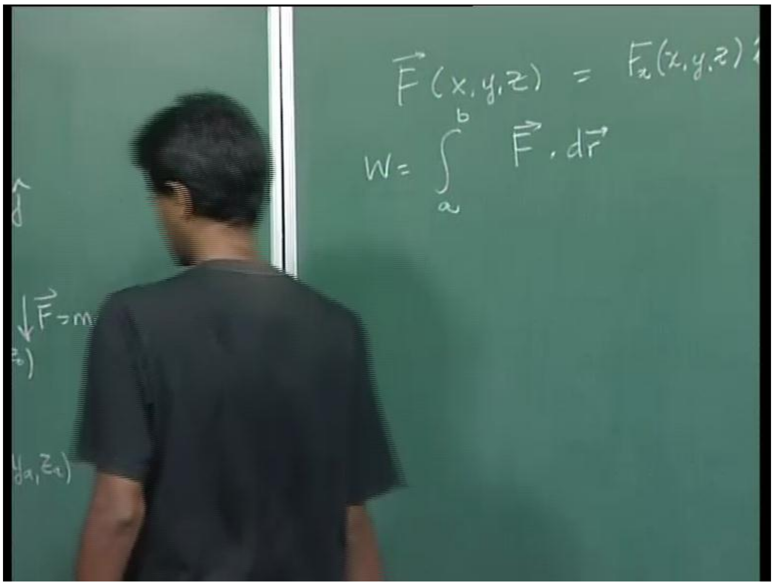

And so this implies that, force is a vector field so force depends on x y z so force is a vector field and it has components. So, the force is given by this vector field in this case, it was just a constant, so these two components was 0 and this was equal to minus mg. So, if force is a vector field then how do what happens to this integral and the answer is fairly obvious so then your W just becomes integral a to b, F dot dr.

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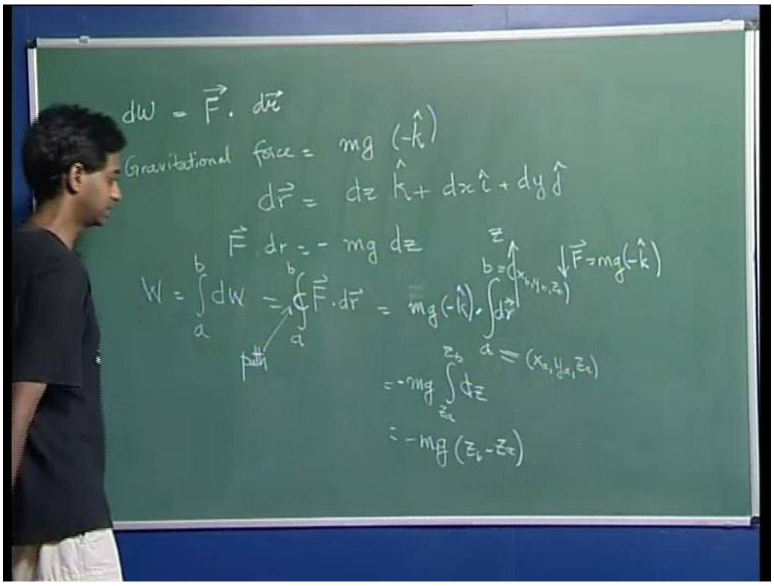

And one point that, we have to mention here is that, even in this case, we moved along a path but since only the z coordinate was changing, the path was, just you could just think of the path as depending upon the final and initial states.

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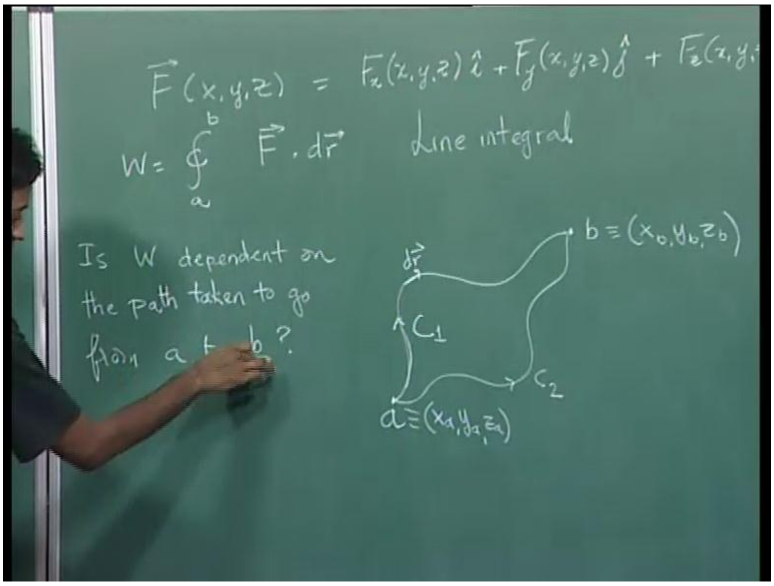

In this case, it depends on which path you are taking, so you are going from point a to point b along a certain path, if I show the displacement, so you have a d r and this d r is part of this path. So, you are going from a to b, point a to point b, these are two points in three dimensional coordinate space and this is the path which is called C so this is the path c and you can clearly see that, the work is nothing but a line integral.

Now, you might ask, when does this line integral dependent on the path so suppose, I go from a different path. So, if this is C 1, this is C 2, is the work done the same or is it different so is W dependent on path. So, you start at the same initial point and you end at the same final point but you ask a question is the work done by the force dependent on, which path you take and the general answer is, yes it depends on, which path you take.

There are certain kinds of forces, for which this work is independent of path and this is what, we want to explore in this lecture. So, now, we want to say that, this work done in going from a to b, it may or may not depend on the path and in some cases, it depends and in some cases, it does not depend. And so if you ask, what is the feature of F, what is the feature of this force field that makes it path dependent or path independent. So, that is what, we are going to explore in the next few minutes so if you notice that, the force is different at each point and so if you want to calculate the work, you have to do this line integral.

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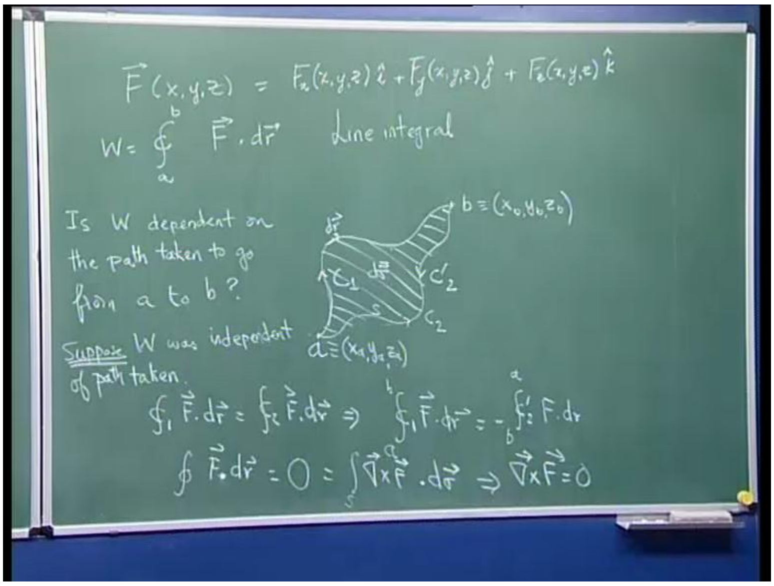

Now, suppose, W was independent of path so suppose, this W was independent of paths taken so what happens in this case, now, you say that the work done in going here to here is same as work done going from here to here. Now, so you say that, integral over C 1 F dot d r is equal to integral over C 2 F dot d r and this implies, integral over C 1 F dot d r equal to minus integral over C 2 prime F dot dr. So, this is from a to b, this is from b to a so what is this C 2 prime, so C 2 goes from a to b along this path, C 2 prime goes from b to a backwards along the C 2 path.

So, if C 2 is in this direction, C 2 prime is in this direction and the limits of integral are from b to a. And it is fairly obvious that, this integral going from a to b of F dot d r along C 2 should be negative of the integral going from b to a of the same F dot dr. So, now, this implies that the sum of work done in these two paths is 0, so integral so the first path, you go from a to b along C 1 and then you go along C 2 prime from b to a.

So, the total work done in this path is 0 so it is a sum of these two so that is 0 so what you get is, that the closed integral of F dot d r so is equal to 0. So, and you can show that, this is true for any two paths, if F is, if this work is a path independent function then any two path, any path you take, any closed path you take then the work done should be 0 so work done in any closed path should be equal to 0.

Now, since this is true for an arbitrary close path, we can use Stokes theorem to say that, this closed integral is equal to, if this path, you can take a path that encloses a surface, surface d sigma then you can say that, this is equal to integral over the surface S of del cross F doted into d sigma. So, this is true for any closed path and so we can use Stokes theorem to say that, this is equal to the curl of the force field, the integral of the curl of the force field over this surface.

Now, since we said that, if work is a path independent function, you can choose any path and so this your surface can be completely arbitrary. And so if this is to be true for all possible surfaces then this implies del cross F equal to 0.

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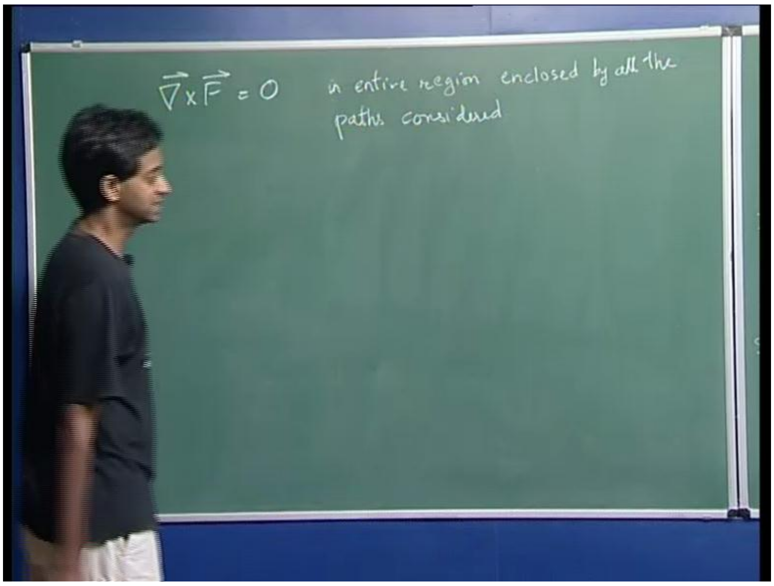

So, the condition for path independence is del cross F equal to 0 now, it is important that, del cross F should be 0 in the entire region, region enclosed by the path so enclosed by all the paths considered so I will just explain, why I put this qualifier.

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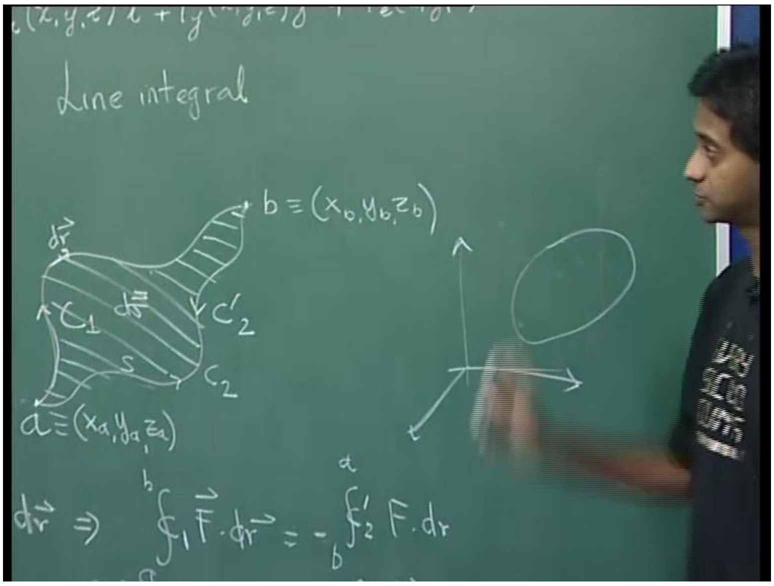

It could be that, W is path independent in one region so in this region your work could be path independent whereas, outside, it might be path dependent. Therefore, the condition is that, we are restricting ourselves to this region where, the work is path independent. And so everywhere in this region, the curl of F should be 0, so wherever the work is path independent, the curl of F should be 0.

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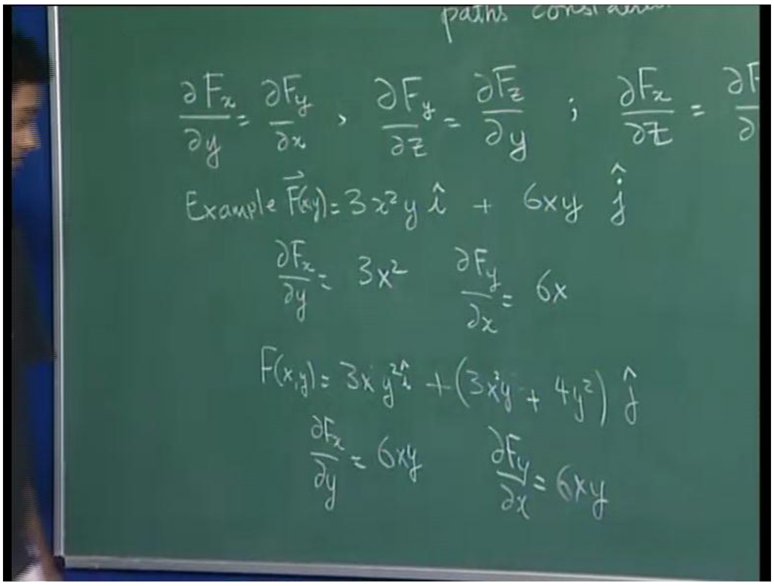

And this leads to the condition it is, if you, dou F x by dou y and these are the components of the curl and so each of the components should be equal to 0. Therefore, you have these identities, so the fact that, your work done is path independent implies that, the force field has to satisfy these conditions. So, if you take any arbitrary force field then it need not satisfy this condition but if it does satisfy this condition then it is in the path independent so the work done will be independent of path.

So, let us take an example, suppose, I take 3 x square y I, F of x y is equal to, 6 x y j so suppose, I take this as a force field now here, I have restricted myself to a two dimensional problem instead of the full three dimensional problem. But, if I take this as a force field then you can see that, 6 x y dou F y by dou x is equal to 6 x and these are not equal to each other everywhere.

So, if you consider any arbitrary region, the work done by this force in different paths will not be the same on the other hand, if you had F of x y is equal to 3 x square y plus. Now, if I take the derivate of this with respect to y, I will get 6 x sorry if I take the derivate of this with respect to y is, there is a correction, I should get 3 x square and if I take the derivate of this with respect to x, I should get 6 x. Now, if I take 3 x y square plus may get three x square y.

So, if I choose this function then the derivative with respect to y is 6 x y and here, the derivative with respect to x. So, if I differentiate with respect to x, this term contribute 0, this term contribute 6 x into y so it is equal and therefore, this will be path independent.

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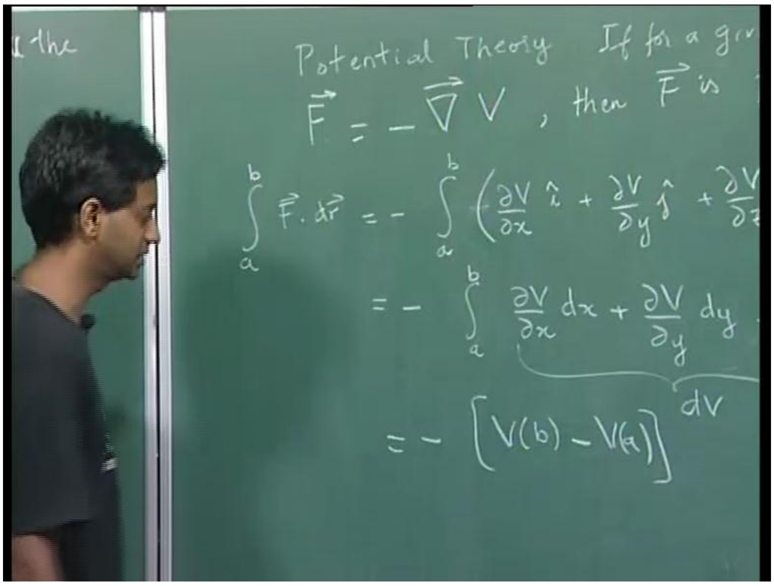

So, this leads us next to, what is called as potential theory, which states that suppose, I have an F that can be expressed. So, suppose, there exists if for a given F, there exists V of x y z here, F is also force field such that, F is equal to gradient of V. So, if there exists a scalar field such that, if I take F and if I take the negative gradient of V then I get F then F is path independent.

And the negative is just out of convenience, you could always I mean, the negative sign is not really important in this case, it is just that, V is usually defined as a potential energy and the force is defined as a negative gradient of the potential energy. So, the point is that, if there exists a V such that, F is minus grad V then the force is path independent.

So, how do we understand this now, we can say that, we look at integral F dot d r from a to b, this is equal to now, if F can be expressed as minus grad of this then this is minus integral a to b now, F is minus grad V. So, dou V by dou x i plus dou V by dou y j plus dou V by dou z k, this whole thing is dotted into d r, d r is dx i plus d y j plus d z k. And we can go ahead and do the dot product, and we will get minus integral a to b, dou V by dou x d x plus dou V by dou y d y plus dou V by dou z d z and V is a function of x y z.

If V is a function of x y z this is nothing but the total change in V so if V is a function of x y z then d V is the partial with respect to x times dx, partial of V with respect to y times d y plus partial of V with respect to z times dz. So, this whole thing is nothing but d V and so the integral will just give you minus V of b minus V of a. So, the point is that, if your force can be expressed as a negative gradient of the potential so if there exists a function V such that, F equal to minus grad that then the total work done in going from a to b is just a difference in potential energy.

And this is something that, we have seen before that suppose, I want to know, how much work I need to do, to lift this chalk then you say that the difference in potential energy out here it is mg times the height here, out here it is mg times the height here and that difference, gives you the work done by this force. So, now, the point is that, if F is path independent, it can be expressed as a gradient of potential and vice versa, if F is expressible as a gradient of potential then it is path independent.

Now, this potential theory is something, that has lot of applications in different areas and even the idea of path integral, path independence is something that, we encounter frequently when we are in thermodynamics, when you calculate the pressure volume work done in changing the state of a gas under various conditions. Now, when we say that, the force is negative gradient of potential, we should always be a little careful when you write this and just to illustrate this point, I will take an example.

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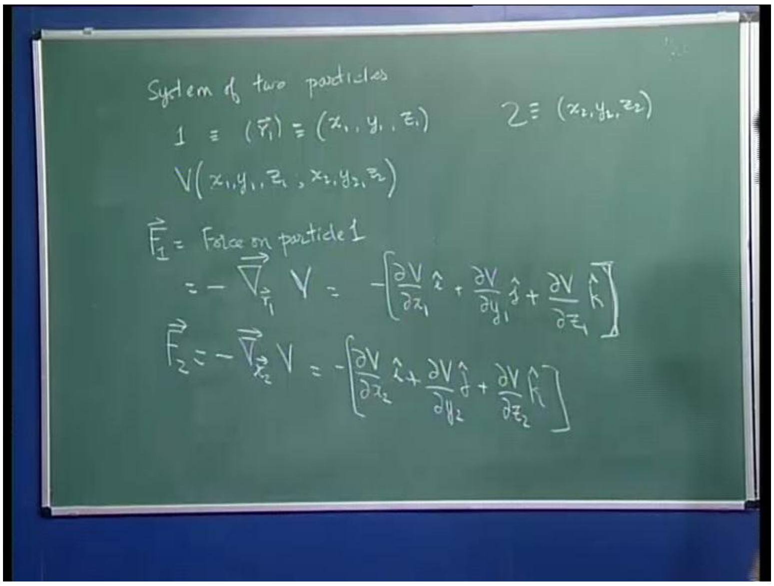

Suppose, there is a system of two particles, particle 1 is located at r 1 that is, (x 1, y 1, z 1) and particle 2 is located at (x 2, y 2, z 2) and typically if you look at the potential energy, the potential energy will be a function of the positions of both the particles. So, the potential energy is the energy, that the system has on account of the position of the particles so the potential energy will be a function of (x 1, y 1, z 1, x 2, y 2, z2).

So, in general, if you write any potential energy of the entire system, it should depend on where each particle is located, not just where one particle or not just, where the second particles is, it should depend in general, on where both the particles are located. Now, you can ask, what is a force and then if somebody ask, what is a force then you should ask, the force on what.

So, now, if you ask, what is the force on particle 1 so this is the force on particle 1 now, the force on particle 1 is given by minus gradient with respect to r1 of V and this is equal to minus dou V by dou x 1 i plus dou V by dou y1 j z 1 k. So, this is the force on particle 1, notice I am taking a gradient with respect to x 1, y 1 and z 1 so only the coordinates of r 1 are involved, when you calculate the force on particle 1.

Similarly, when you calculate the force on particle 2, it is a gradient with respect to r2 that appears and this is. So, you should always be careful when you write the force, you should not simply say it is a gradient of a potential, it is what you really mean, is a force on one particle, is a gradient with respect to the coordinate of that particle. Now, if you just have a system of just one particle and you just have a force field for F of x y z, as we had in the previous case then the force can be thought of, as a gradient of the potential.

But, in all other cases, you have to be careful, you have to say, the gradient with respect to which coordinate. Let us look at a particular kind of force, which is very common in fact, it is most commonly force, that you encounter in various areas of chemistry.

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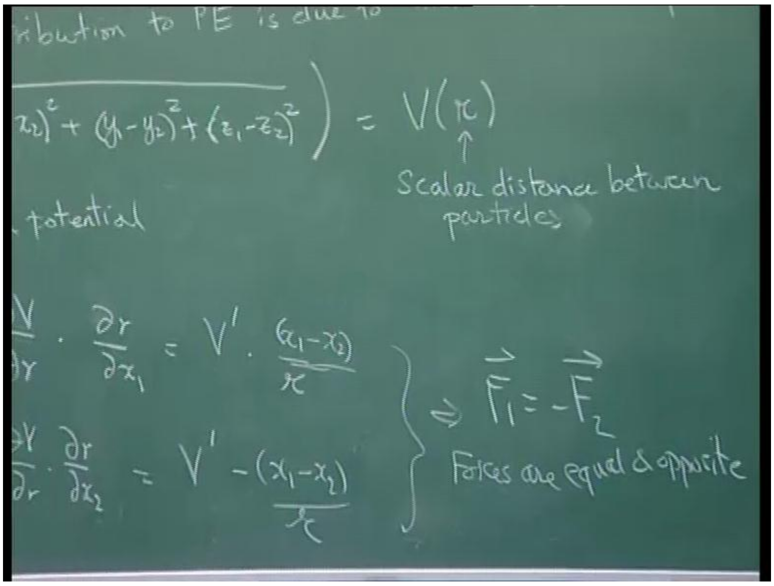

Now, in most cases, the particles 1 and 2, the force between them, the value of the force just depends on the distance between the particles. So, what I mean is that, if the potential energy of the system, the total potential energy of the system, if the only contribution to potential energy is due to the interactions between the particles. So, if the only contribution to the potential energy of the system is due to the interaction between the particles and that means, the particles are not in any external field or anything.

So, you assume that, let us say, if you have two particles, two charge particles then the only force is due to the attraction or repulsion between these charged particles. You do not have any other contribution, you do not have an external electrical or magnetic field, you do not have any gravitational field or anything else. And this is a case that, we typically encounter in various areas of chemistry for example, if you take the nucleus and the electron of the hydrogen atom, the only interaction is due to the, is the only contribution to the potential energy is due to interaction of the electron with the nucleus.

So, in such a case, your potential energy, which depends on the coordinates of both the particles can typically be expressed in this form. So, if you had two particles and the potential energy is only due to the interaction between the two particles then the potential energy is a function only of the distance between the particles, such a potential is called a central potential.

And in fact, most of the potentials that we know, whether it is gravitational potential of two bodies attracting each other due to gravitation or the columbic, the electromagnetic forces between bodies, they are all in the form of central potentials. Now, in case you have a central potential then what happens is that, if you take d V by dx1 so d V by dx1 is equal to partial derivative of V with respect to r, times partial derivate of r with respect to x 1.

Now, you can see that, partial derivative of r with respect to x1 is nothing so this is d V by d r and I will just call it V prime, V is only a function of r. So, I can write it as V prime, this is the derivate of this function times d r by dx1 and if you calculate that, you will get, this will just turn out to be x1 minus x2 by r. So, if you take d by dx of this quantity, it is 1 over twice square root of this one over twice r times 2 x1 minus x2.

And if you calculate d V by d x 2, this will come out to be d V by d r times dou r by dou x 2 and dou r by dou x 2 is minus of this quantity because you have a minus sign in front of x 2. So, this just turns out to be V prime into minus x1 minus x 2 by r and you can take this argument through, and you can show that, the force acting on particle 1 will be the negative of the force acting on particle 2.

So, the forces on the two particles are opposite so F 1 equal to minus F 2 so this implies so forces are equal and opposite. And this is the characteristics of this central potential so when you have a central potential of interaction between the two particles then the force on 1 due to 2 will be equal and opposite to the force on 2 due to 1. Now, let us do an example where, we calculate a line integral of a certain force along two different paths.

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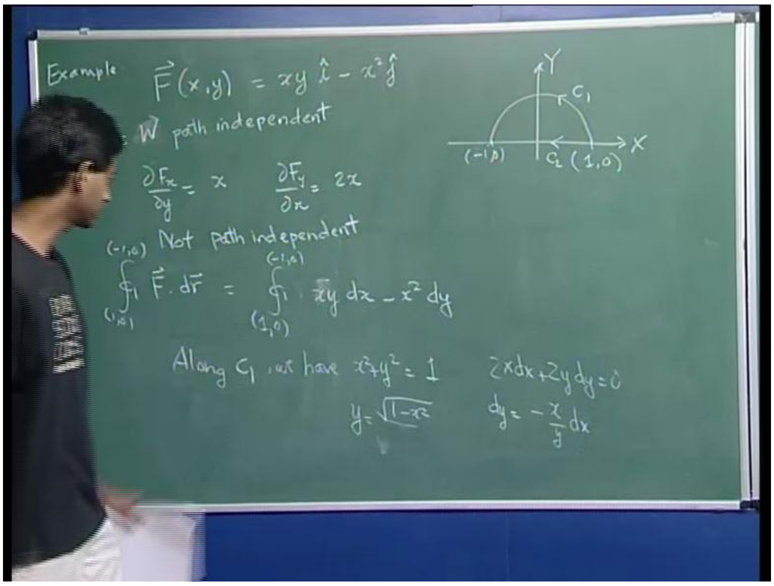

So, the force is given by F of x y, this problem is an two dimensional, in two dimensions x y i minus x square j and you calculate the work done in going from the point (1, 0) to (minus 1, 0). Along two paths, the first path C 1 is a semicircular path C 1 and the second path C2 is a path along the x axis. So, calculate the work done in moving a particle from 1 0 to minus 1 0 along these two paths so the first thing you will check out is, if W was path independent.

And in order to, check that, you take the y is equal to x 2 x, so it is not path independent. So, in general, the work done is not path independent now, let us calculate the work done. So, the work done is so integral over C 1 F dot d r from (1,0) to (minus 1,0) now, in this case, what you will say is that, this is equal to 0 and here, d r is, d r in this case will have two components, it will have d x and it will have d y.

So, and if I substitute for this, this is x y d x minus x square dy and remember, d x and d y are not completely independent because we are going along this path. And so along the path, along C 1, we have x square plus y square is equal to 1 so we have x square plus y square equal to 1 and therefore, we have 2 x dx plus 2 y dy equal to 0 in other words, d y is equal to minus x by y d x. So, the rate of change of y along this path is related to the rate of change of x along this path and moreover, y is also related to x, y is equal to square root of 1 minus x square.

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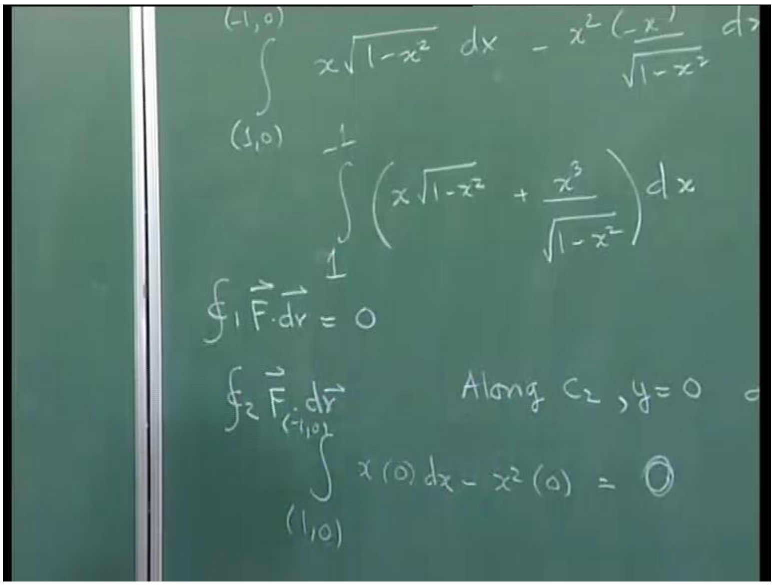

So, putting all this together, we will get this as, integral from (1,0) to (minus 1,0) so the first term x now, y is square root of 1 minus x square d x, the second term is minus x square now, d y is minus x by y. So, minus x by square root of 1 minus x square d x so I can take all this together and I can write this as integral. Now, I do not have to worry about y at all because I have already taken into account that, y is along this path and the rate of change of y.

So then I can just write this as, integral 1 to minus 1 of x square root of 1 minus x square plus x cube divide by square root of 1 minus x square d x. And you can go ahead and work out this integral, it is fairly easy to show that, the value of this integral should be 0 because you are integrating from 1 to minus 1 and the integrand is an order function of x. So, if I change x to minus x then the integrand changes sign and therefore, this is equal to 0 so you can evaluate this integral and you will get it equal to 0.

Now, suppose, you go therefore, you will say that, integral over C 1 F dot d r equal to 0 now, what about integral over C 2 F dot d r and you can go head, and you can follow the same procedure so you write your path now. So, along C 2, y equal to 0 so along C 2, the y component is 0 and d y equal to 0 so if you substitute these two then you come back to your F so the only path that will contribute since dy is 0, only this part will be non-zero and here too y is 0.

So, since y is 0, you just have integral and this will be (1, 0) (minus 1, 0) x into 0 dx minus x square 0 so this is equal to 0. So, each of the terms is 0 and therefore, this whole integral gives you 0, and what you notice is that, even though your function, even though the derivate said that, the work should be path independent, the work done along these two paths is identical. So, the point is, work done along C 1 and C 2 is identical now, this does not mean that, the work is a path independent function, what it means is that, these two are just special paths where, the work done is the same.

However, if you take any arbitrary path, the work done will not be equal to this or it would not be equal to 0, for any arbitrary path. So, in general, this is not a path independent function but for these two paths, the calculated work turns out to be the same.

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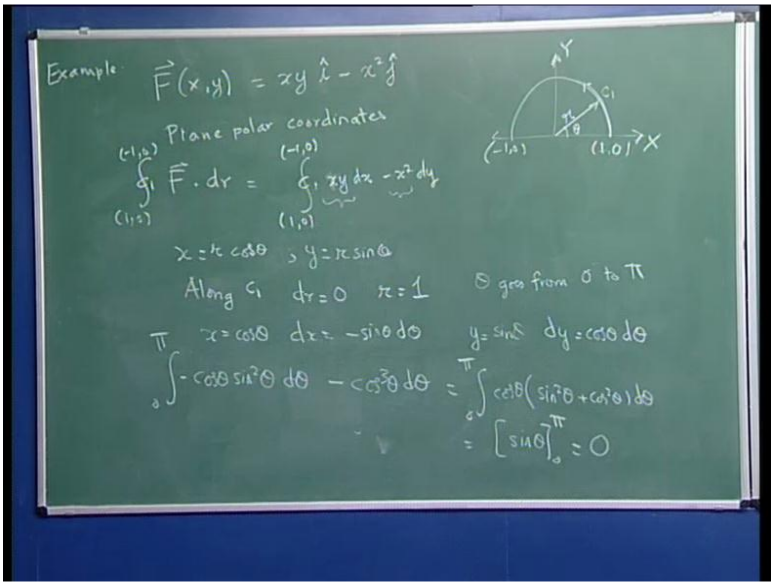

Now, just one more thing I wanted to mention about this, is along the path C 1, we calculated the work by using the equation of the semicircle and substituting for y. Now, you could have done this in plain polar coordinate and I will just illustrate this because this is a trick, that will be used quite often. So, often it is easier to solve some integrals in plan polar coordinates and especially, when you have a path that is, that traces out a circle then it is better to go to polar coordinates.

So, how would you do this integral in polar coordinates so first thing, you will write F dot d r from, integral x y d x, x square dy along C 1. So, in polar coordinates you say, x equal to r cos theta, y equal r sin theta and along the path C 1, we notice that, d r equal to 0. So, along this path, your distance r theta so this distance r does not change, d r equal to 0, r equal to 1 and theta goes from 0 to pi. So then what you can write is that, x equal to cos theta, dx equal to minus sin theta d theta, y equal to sin theta, dy equal to cos theta d theta.

So, the entire curve C 1 is just parameterized by a single variable theta so instead of, changing both x and y, you just change theta from 0 to pi and you trace out the entire curve C1. So, you substitute this over here, and what you will get is, integral x into y so that is, cos theta minus sin theta and d x is, d x is sorry cos theta sin theta minus sin theta. So, you get minus cos theta sin square theta d theta and this next term is minus x square, x square is cos square theta into cos theta, so that is cos cube theta, theta from 0 to pi.

And if I take the cos theta common then I have so this is equal to integral cos theta sin square theta plus cos square theta d theta from 0 to pi and this whole thing is just equal to 1 so this is integral of cos theta is sin theta from 0 to pi is equal to 0. And what this illustrates is that, going into polar coordinates is a one way to do this integral and you can imagine that, if you had more complicated function then doing it the other way in the x y coordinates might not be as simple.

Whereas, going to planar polar coordinates, we can do it even if, we can calculate this integral even, if these are more complicated functions, even if we had more complicated functions here, we could calculate this integral much more easily in polar coordinates.

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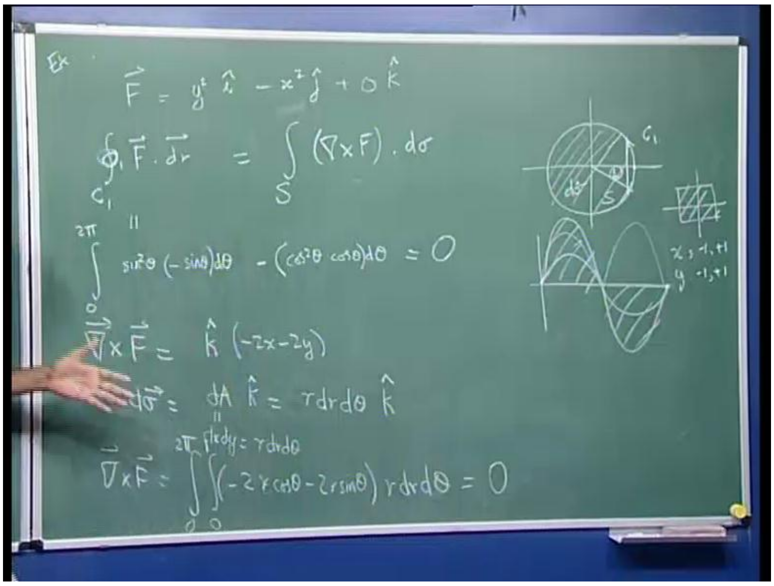

So, the last thing I want to show is an illustration of Stokes theorem so let us look at F is equal to y square i minus x square j plus 0 k. So, now, you are asked to calculate the closed integral along C 1 and compare it to the area integral over S. So, you are asked to calculate integral F dot d r along C 1, this is a closes loop along C 1 and show that, this is equal to integral del cross F dot d sigma over S. So, this is what, we are going to show and in this way, we are going to illustrate Stokes theorem.

So, let us so now, this line integral is something, that we should be able to calculate easily, again we will go to polar coordinates. So, this line integral will be equal to integral now, y square is sin square theta and what you will have is sin square theta d x. So, d x is minus sin theta d theta and the limits of integration of theta, if this let us assume that, this is a unit circle so the limits of integration of theta are from 0 to 2 pi.

Now, you have to go a full circle so that is the limits of integration of theta and the other term is minus x square is cos square theta and then you will have a d y, dy as cos theta d theta and you are integrating again from 0 to 2 pi. Now, both sin and cosines are periodic functions and so sin square and sin cube are also periodic functions of 2 pi so this integral is equal to 0. So, the area under sin function from 0 to 2 pi is and if you take sin square, sin cube will look like this so you will have a plus part and a minus part.

Similarly, cos cube will also have a equal plus and minus parts so both these integrals work out to be exactly equal to 0. Now, if you calculate the surface integral so in order to calculate that, you need to look at del cross F, del cross F is k into and if you calculate this, you will get an answer of minus 2 x minus 2 y. So, you can take the curl of this force field and you will get this answer so since the vector field is localized to the x y plane, the curl will be localized to the z direction.

And now, what you have to do is, you have to calculate the surface integral now, the surface integral you have to put the limits carefully so that, you trace out the entire circle. Now, d sigma is equal to d a so it is the area times the normal vector now, the normal vector to the surface is along k. So, it is d a times k hat and your d a in plane polar coordinates can be written as r d r d theta times k. So, d a in polar coordinates is, d a in Cartesian coordinates, this is equal to dx dy, in polar coordinates, this works out to be r d r d theta.

So, if you put this together, what you get is del cross F is equal to and now, your area integral, you have to integrate over this entire area and the way to do that is, to have integral so del cross F dot d sigma. So, you have minus 2 x minus 2 r cos theta minus 2 r sin theta that is, minus 2 x minus 2 y, I wrote in polar coordinates and instead of, d a what I have is, r d r d theta and I have to integrate both r and theta to get the full area integral. So, I have to integrate over this entire area and that, corresponds to r going from 0 to 1 and theta going from 0 to 2 pi.

So, that corresponds to the entire area and you do not need to do too much work, you can just do the theta integral, it is just cos theta, and cos theta and sin theta, when you integrate from 0 to 2 pi, you just get 0. So, this illustrates stokes theorem and what it also illustrates is that, when you calculate this surface integrals or line integrals, you have to use the best method available. And sometimes, it might be polar coordinates sometimes, it might be Cartesian coordinates and you have to put the limits very carefully.

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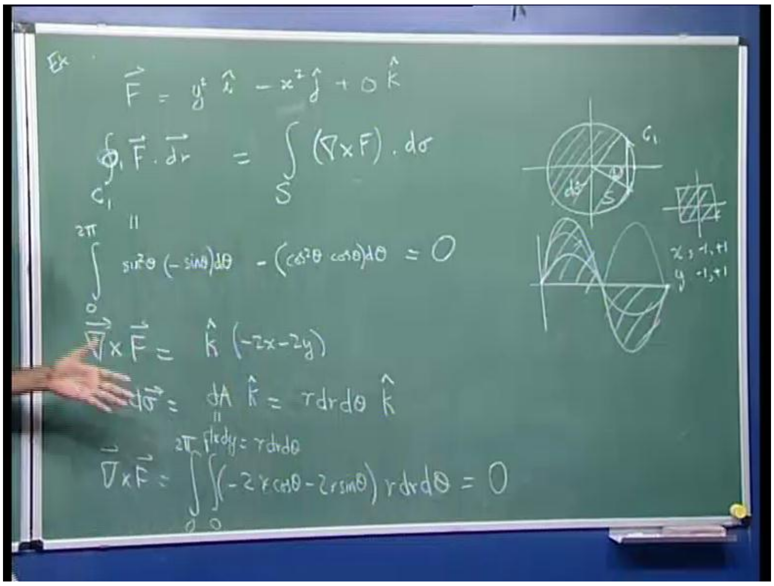

So, notice that, it was very easy to give the limits in polar coordinates now, if I was using Cartesian coordinates then the limits of x, x goes from minus 1 to 1 but y goes only from here to here, y does not go from minus 1 to 1 in general. If I had put x going from minus 1 to 1 and y going from minus 1 to 1 then I would have got an square area y. So, you have to be very careful, when you put the limits of integration, y only goes from minus square root 1 minus x square to plus square root 1 minus x square.

So, it is usually, a slightly more tricky problem to do this in a Cartesian coordinates so in the next class, we will change here and we will go to matrices. So, I hope, these lectures on vector analysis have been fairly simple to understand, it is important that, you try lot of different problems and you especially, when you calculate line integrals and area surface and volume integrals. Some of the techniques you learn, as you practice more, so it is important that, you get lot of practicing by doing various solved examples.

Thank you.