Mathematics for Chemistry
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Lecture - 7

In the last class we studied, we looked at various ways of defining derivatives with respect to a vector, in this class we will look at integration with respect to a vector. Now, when you are integrating a function of a single variable you think of that as the area under the curve.

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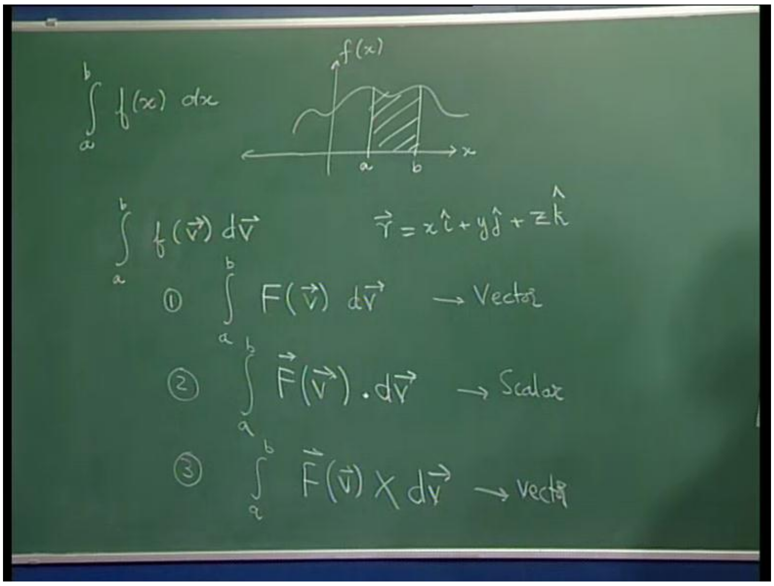

So, for example, if you had a function f of x of one variable and if you are looking at integral f of x d x from a to b, we think of this as the area under the function f of x from a to b. So, if you have x and if you plot f of x, f of x might have some graph like this if this point is a and this point is b, then the integral is defined as the area under this function here. Now, we want to extend this to the case, where instead of having x here what we have is a vector, so we are integrating with respect to a vector quantity.

So, you can have something like integral a to b, and what we have is a function of a vector and integration with respect to a vector. Now, it turns out that there are a few different ways this can happen, for the sake of arguments will restrict our self either to vectors of the form r is equal to x i plus y j plus z k. And occasionally we will just work in two dimensions, where you just have r is x i plus y j, but in general we will restrict our attention to vectors, where this vector is basically of this form.

So, now I had said that there are many ways you can define these integrals. Now, if you look at this you will say that what you have is a function of a vector and we already saw that there are two types of function, there is some something called the scalar field, where f is a scalar and there is something called a vector this field, where f itself is a vector. So, then this integration there are few different integrals that appear and I will just write down all of them the first is an integral from a to b, where you have scalar function F of v.

So, this is a scalar function and this scalar function is multiplied by this vector element by vector element and so the result of this is a vector. So, you have a scalar function multiplied by this vector to give you a vector, the other integral that will commonly appear is, where you have a vector function and this is dotted into this differential vector element this gives us scalar. And the third are just where you have a vector function but now instead of dotting it to get a scalar you take a cross product with this vector element to get a vector.

So, we can easily see that these three kinds of integrations that will appear. Now, this is not the whole story there are lot of things that we have to specify here and I look at each of them in detail.

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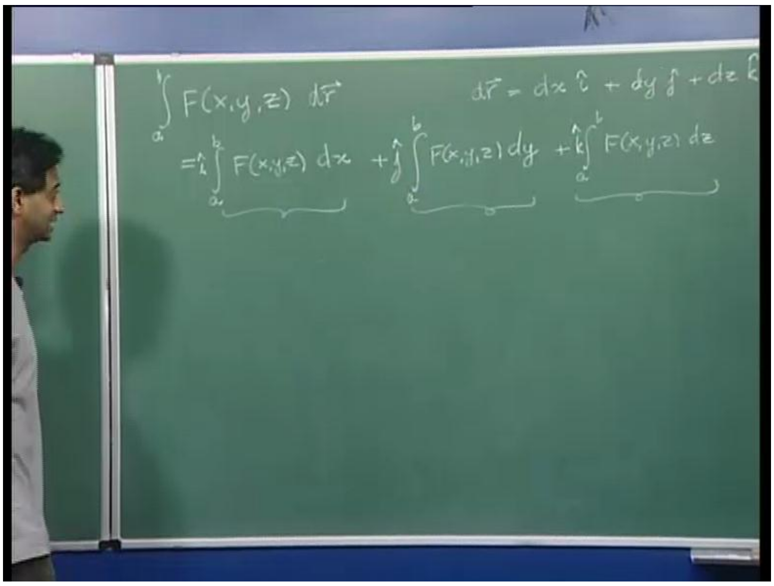

So, let us take the first case a function of a vector a scalar function of a vector is essentially a function of x y z, so we are restricting our attention to the case where this vector is x i plus y j plus z k, so function of this vector is juts f of x y z. So, now we have an integral I will just call it a to b, I will come back to the limits of this integration and the nature of this integration. And what you have is your d vector, d vector is your d r vector and d r is a vector with 3 components.

The x component is d x and the y component is d y and the z component is d z, so d r is a vector of this form. So, when you multiply these two you will essentially you will get 3 integrals integral a to b f of x y z d x this multiply by i plus integral a to b f of x y z d y, this thing multiply by j plus integral a to b f of x y z d z multiply by k. So, we have used here the fact that these unit vectors they do not change as you go from one point to the other, so they can come outside the integral sign.

So, we can take these unit vectors outside the integral sign and you just get this form, gives you a vector with 3 components the x component is this, the y component is this and the z component is this. So, you start with a function of x y z, which is a scalar function and you end up with a vector, where each component is an integral over one of the 3 variables. So, this is the first type of integral.

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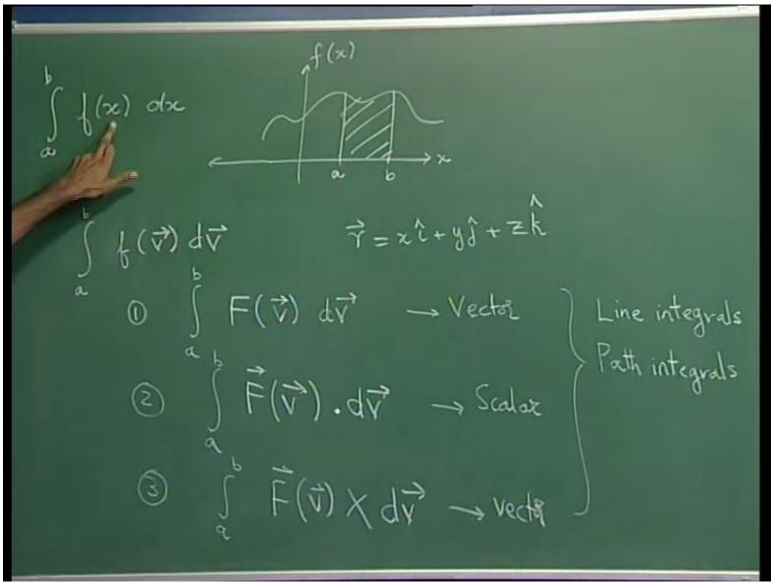

Now, all these integrals are of the form are referred to as line integrals and the significance of this will become clear why it is called a line integral or sometimes they are also called as path integrals. This will become clear once we think about what do we mean by a and b. Now, when you had a function of just one variable then a was just one value of x b was one value of x, but now the argument of the function is not is not just one variable but it is 3 variables argument of the function has 3 components x, y, and z. So, your point a will have 3 components.

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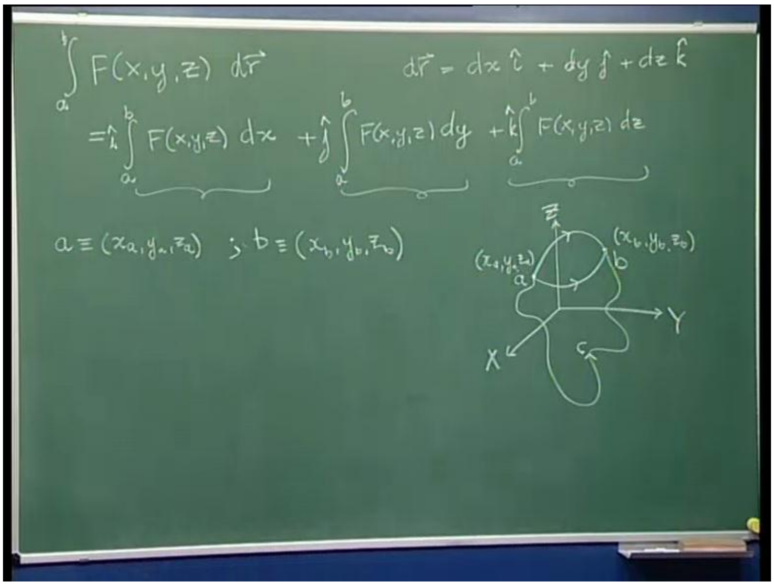

So, for example a can be 3 components x a, y a, z a and b can have 3 components x b, y b, z b, so we have 3 components for a and 3 components for b. Now, this is not the entire story in this case for a very special reason in this, in the case of a single variable you just specify the initial point and the final point. And that defines exactly what your integral is but here when you have more than one variable, then you have to specify something else. To see this you can think of the coordinate system and you have one point, let us say here x a, y a, z a and you have a second point this is a and this is b. And your function has a certain value here it has a value your function F has a value for each point including a and b.

So, for each point in this three dimensional space if you take any point with any value of x, y, z with this function F has a certain value. Now, if you imagine integrating f from a to b then you have to see how the function changes as you go from a to b, so just as in this case you have to see how the function changes as you go from a to b. Now, going from a to b in the case of one dimension, so was straight forward, because you just go from a straight to b this way, there is no other way to go from a to b.

In this case it is not, so straight forward you can go from a to b along this path, you can go along this path, you can go along some path that looks like this. So, you have various path going from a to b and therefore, the complete specification of the integral needs you to specify which path your following. So, if you are following a path c you need to specify that, you are following the path c and when we look at examples this will become clear that, what it means it is called a line integral, path integral or even sometimes a contour integral.

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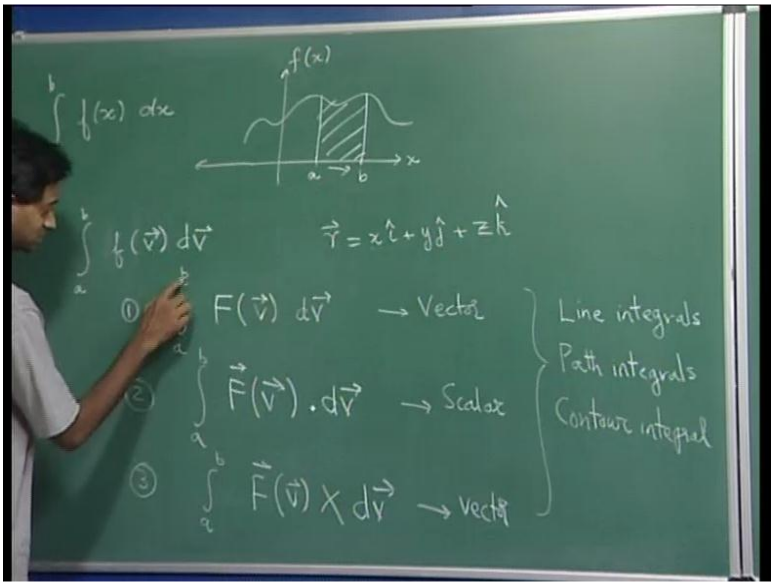

And this basically emphasizes that you are taking a path to go from a to b. So, it is not enough just say a and b, a has these coordinates, you have to say b has these coordinates and there is along a path c.

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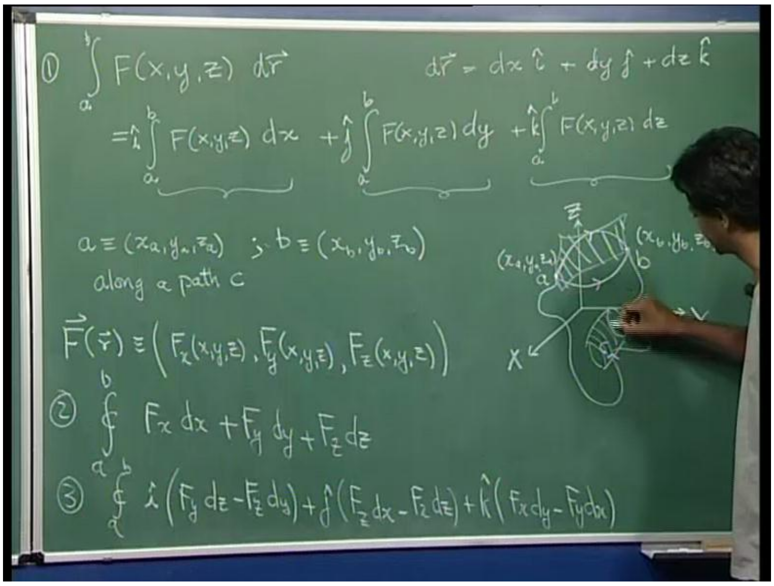

So, the correct way to write this is a to b along c and this is one way of defining the line integral. So, now the next two definitions will become fairly obvious, the second definition is when we have when your F itself is a vector function. So, F has 3 components F of r has 3 components F (x) of x, y, z F (y) of x, y, z and F (z) of x, y, z. So, F has 3 components and now what you going to do is take an F and dotted with d r, now d r already mention here has these 3 components d x, d y and d z.

So, if I take the dot product in I just get F x into d x plus F y into d y plus F z into d z and so this integral becomes, so this is line integral one, this is the first definition, the second definition has integral. And now again you have to specify the contour a to b and you have F x into d x plus F y into d y plus F z into d z. So, notice its not a, what you get is the scalar. So, these are just multiplying it does not have any components you take the x component and you integrate over d x, take the y component of f integrate over d y, take the z component integrate over d z and these are the usual one dimensional integrals.

Only thing is when you put the limits you have to make sure that you are following the path c, so this is the second definition of this integral. And the third definition is actually simply related to the first definition, in this case you take a cross product of F and d r, F and or d v instead of multiplying F x by d x, what you will do is, you will do F x d y minus F y d x and that will be the k component. So, you can think of this as integral a to b and what you have is F cross v.

So, F cross v is has 3 components the ith component will essentially if I think of F has this 3 components d r is the this 3 components so you just take a cross product of the 2. So, then the ith components of the cross product will be F y d z minus F z d y, so you integrate F y with respect to z, F z with respect to d y these are the F x, F y and F z. Then the j th component will have F z d x and the k th component will have F x d y F y d x and once again you will integrate along the a path c.

So, these are three definitions of what are called as line integrals, where you integrate with respect to a vector and you are just integrating with respect to a vector. And since a vector in this case we will restricted ourselves to vectors of the form r is equal to x i plus y j plus z k occasionally we will just be working in two dimensions. So, r will have only the these two components in that case the cross product will not to be defined and so this definition of line integral will not be used, so this completes the discussion of line integrals.

Now, you can you can think of other integrals involving vector quantities, now since you said that these vectors they from a three dimensional space. So, instead of just integrating from a to b along a line, you can imagine more complicated things you take the integral value of the function over a certain area. So, you look at the values of the function at each of these points and the integral that gives you the sum of values of the function over all these points will be like an area integral.

And then you can extend it to even volume integrals where you look at the value the function in an entire closed volume so you can imagine that you have a little tube or some sort of volume here and you look at the value of the function everywhere inside this. So, at each point inside this volume the function has a certain value and the integral will be the sum of the values over all these points. So, these are next two types of integrals we will define will define the area integral about the surface integral and the volume integral.

So, we have seen various definitions of the line integral and now the question is, where is this used and it turns out that one of the most important applications of this line integral is to calculate the work done by a force.

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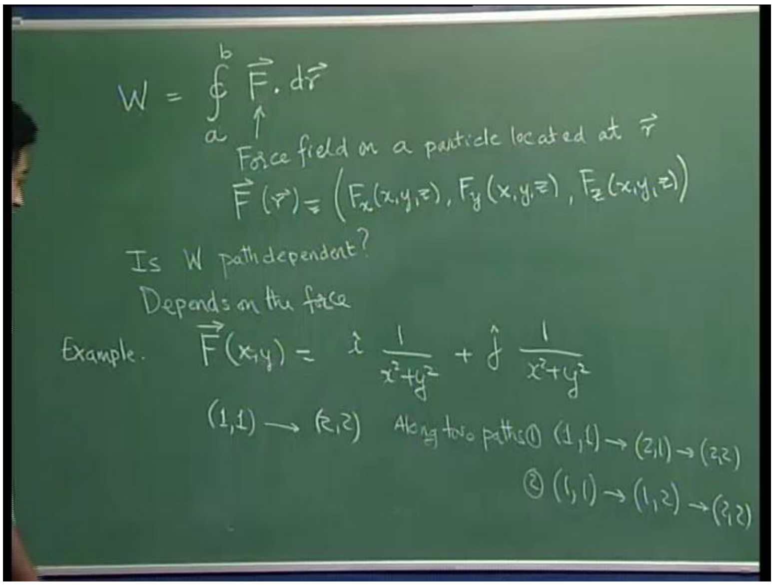

So, the work done by a force is wave force in moving, so by a force field in moving from one point to another. So, we have a point a to a point b move it along a certain path the work done by this force is given by f dot d r. So, this is the one of the famous applications what you have here is the force field, so it is a force field on a particle located at, so this is the on a particle located at r.

So, what you have is F force r this has three components x, so it is a vector field and the three components of the vector field are F x, F y and F z in each of these depend on where you are in space, so these each of them are functions of x, y and z. So, the force field on a particle located at r, so essentially you have this region and wherever the particle is it feels some force. So, depending on where it is it feels a force and due to this force the you move the particle in the presence of this force.

Now what is the work done and that is given by suppose you move from a to b along a path c, the work done is just line integral, so this is very important application. Now, suppose you imagine that here is a particle that is a lying in the force field and the force field that it is lying in it is a gravitational attraction of the earth. So, then you can ask what is the work done in taking a particle from here to here I am moving against the gravity, so what is the work done when lifting the particle from here to here.

So, this is the simple example and the and the way you will do it here you will write an expression for the force as a function of x, y, z and you integrate this expression going from here to here. Similarly, if you have a particle in an magnetic field or in a electromagnetic field, then you can similarly, calculate this if you have a particle in a fluid of varying density then the force at the particle fields at each point will be different and so you can again calculate the work done in moving the particle.

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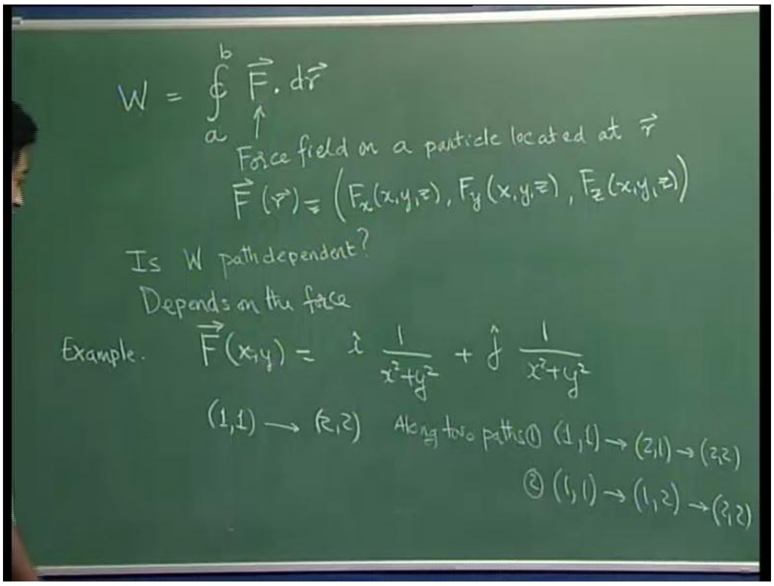

So, that we ask a lot is suppose I go from a to b along one path and I go from a to b along a different path, so is w path dependent. So, if I go from two different paths do I get the same value of the work or do I get different values. And this turns out to be a fairly important question and you have seen you have seen some bits of the this in your thermal dynamics forces but and the answer is it depends on the force and we will look at this in a little more detail in the next lecture.

But, what I want to say is that there are certain forces for which the work is path independent and there are certain forces for which the path depends on the force. And when I say force, I mean a real force field that has three components each component depends on x, y, z. So, there are some theorems that we will discuss in the in the next class on which cases is this work path independent and you have encountered some of this in this thermal dynamics courses.

So, you have seen the work in you have seen that in general it depends on the path but there are some particular cases, some specific cases when you can actually construct work that is path independent. So, the next integral that we will be looking at before, we are look at that, let us look at an example of how you do this line integral. So, an example let us say F of x, y is equal to, let me take F of x y is has 2 components I am just take at two dimensional force, so it has two components i times.

So, what is the work done by this force in going from a point, so you are going from point (1, 1) to (2, 2) and you go along two paths the first path and so you are going from points (1, 1) and (2, 2) along two paths. So, the first path is (1, 1) (2, 2) (1, 2) (2, 2) along straight line. So, you go from (1, 1) to (2, 1) along a straight line and then you go from (2, 1) to (2, 2) along a straight line. So, this is the first path, second path you go from (1, 1) to (1, 2) along a straight line and then from (1, 2) to (2, 2) along a straight line. So, these are both straight line paths and you are asked to calculate the work done.

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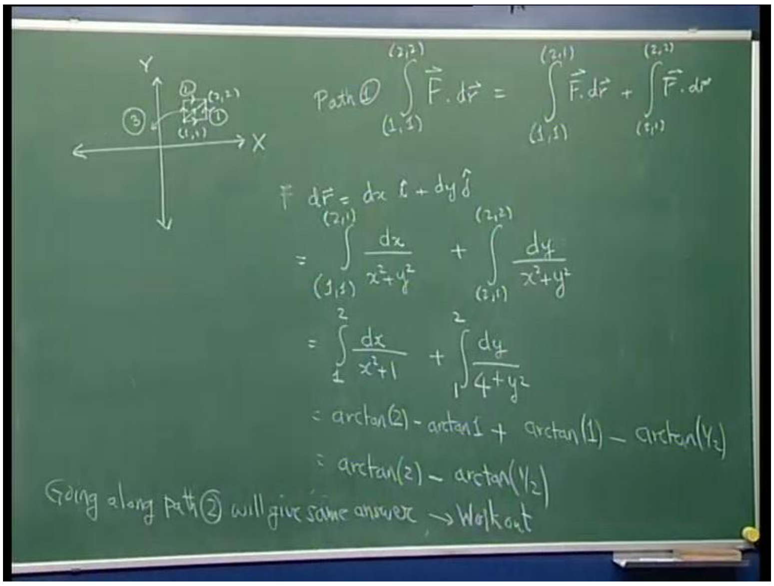

So, just to show you these paths, so if you have x and y and this is (1, 1) this is (2, 2). So, you can go either this way or you can go in this way and either and you have to calculate the work done in moving the particle under the influence of this force from (1, 1) to (2, 2) along these two paths so this is path 1. So, let us start with path 1, so for path 1, we can write integral F dot d r from this is along (1, 1) to (2, 1) plus integral from (2, 1) to (2, 2) so you first go from 1, 1 to 2, 1 and then from (2, 1) to (2, 2). So, you write this integral as a sum of these two integrals.

Now, the path going from (1, 1) to (2, 1) so in general d r is equal d x i plus d y j now along the path going from (1, 1) to (2, 1) your d y you are change in y as 0, so y has a fixed value. So, you can write this as in this case d y is 0, so it is just f, it will just be the x component of the force multiplied by d x and along this path d x is 0. So, this is just be the y component of the force multiplied by d y. So, to put it all together you write this as integral from (1, 1) to (2, 1), now f of x y I will just put the x component to the force, it will just be d x y square and the second integral is integral.

Now, what you should do is you should put the in this case along path is not only is the y constant but the value of that constant is 1. So, I can write this as integral the y is fixed at 1, so am just integrating over x from 1 to 2 d x divided by x square plus 1. And in this case x is equal to 2, so this become integral d y 2 square is 4 y square integral y from 1 to 2 and this are your usual one dimensional integral.

So, the value of this is arc tan 2, arc tan 1 the value of this is, now this will be 2 by 2 which is 1, minus arc tan 1 by 2 is half. And if you add all these together will just get inverse tangent of two minus inverse tangent of half, that is the value of the line integral along path 1. Now, what happens when you go along path 2 and in this case again it is not to difficult to show that in this case you will go from (1, 1) to (1, 2) instead of (2, 1) you will go to (1, 2) and you will have a d y and instead of instead of x you will have x fixed at one.

So, it will look exactly like this but instead of x will have y and you will have you look exactly like this but instead of y you will have x. So, you can show that when you go by this path you will get exactly the same answer as this. So, whether you go by (1, 1) and (2, 1) to (2, 2) or you go from (1, 1) to (1, 2) to (2, 2) you should you will get exactly the same answer and that is very easy to show if you follow exactly the same steps. Only thing when you go from (1, 1) to (1, 1) then x is fixed but y varies. So, then this term would not be there only this term will be there and x is fixed at 1, so it is not fixed at 2 it is fixed at 1.

So, it turns out to be exactly the same as this integral and you can show that going along either path gets a gives the same answer. So, going along path 2, will give same answer and this I leave it to you to work out, so you should work this out, so what we notice is that going along these two paths you get the same answer but is are these two the only path and the answer is no you can consider many other paths for example, if you consider a path going from (1, 1) (2, 2) along the straight line, so if I call this path 3.

So, if I look at path 3, where you go from 1 to 2 along a straight line and I will just work out the path 3 now. So, along path 3 the work done will be in this case both x and y are changing but they are changing in the equal rate it is moving from (1, 1) to (2, 2) along this 45 degree line and so both x and y are changing in the same rate.

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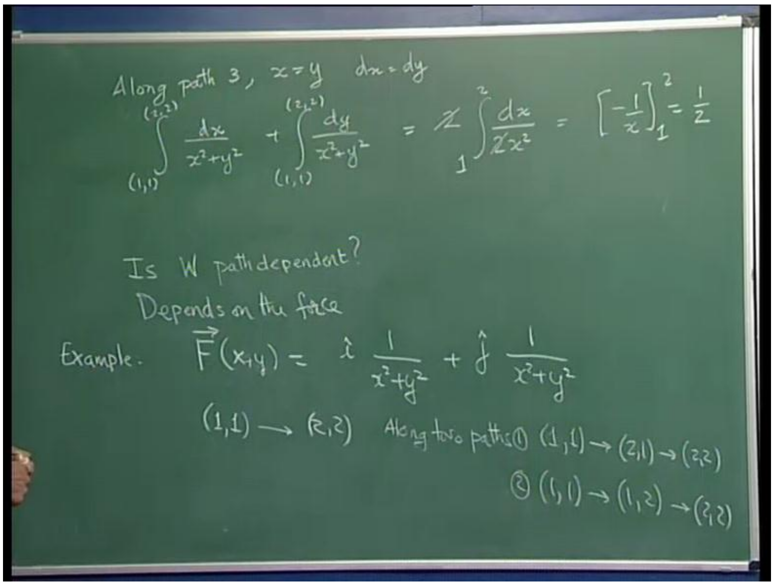

So, notice that along path 3 x equal to y and d x is equal to d y and now if you substitute if you substitute in this what you will get is integral F x is 1 over x square plus y square d x both of them going from (1, 1). So, in this integral I will put y equal to x, so if I put y equal to x and I will get d x over 2 x square and then this integral will just be d x over two x square from x equal to 1 to x equal to 2. In this case I will get d y over 2 y square from y equal to 1 to y equal to 2 and both these integrals have the same value so they have the same value.

So, this will just be twice d x over 2 x y and integral from 1 to 2 and if you cancel this you will just get 1 to 2 and this is equal to, so this is equal to half. Notice that the integral going from path 3 is not the same as going from path 1 to path 2, path 1 and path 2 had the had the same value for work, but path 3 had a different value. So, it turns out that we your conclusion will be that this force field is not a path dependent force field, the work done dependents on which path you take it turned out that these two path had the same work. But, this path had a different work and in general if you take two different paths they will not have the same work.

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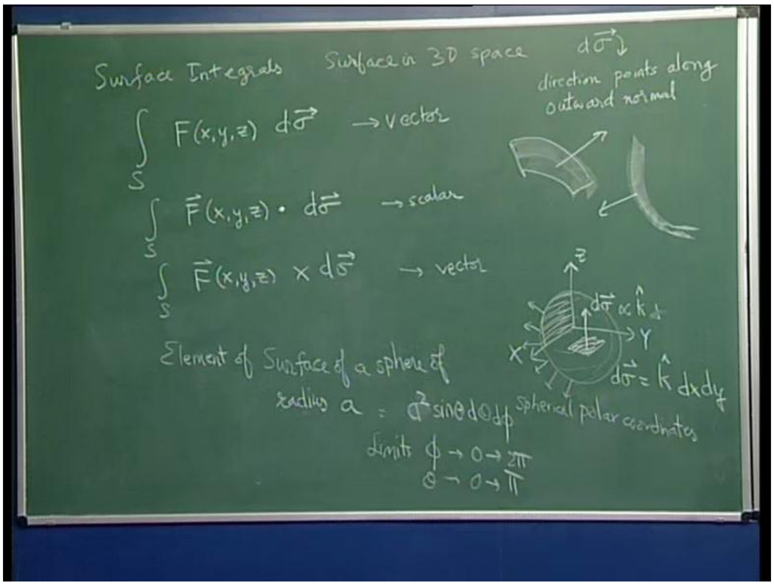

So, next type of integral we have we have seen line integrals now let us go into surface integrals. So, again here you have a surface, so your surface in 3 D space and we use the symbol d sigma and this is a vector, so this, so the surface is a vector the direction points along outward normal. So, it is the direction that points in the direction in the outward normal to the surface so if I have a surface like this then the outward normal is what defines a direction of d sigma so if you had a surface like this then this point in the direct outward normal.

On the other hand if you had a you had a surface like this of and this will be direction of k sigma. So, there are some conventions to do define what you actually mean by outward but we would not get into that we will just assume that the at least for all the surfaces that we use the definition of outward is very clear. But, essentially this points in a direction normal to the surface. So, now you can again it is possible to define three kinds of surface integrals and the first integral will be integral over some surface s F is d sigma vector.

So, where you have a scalar field multiplying a vector surface to give you surface integral so the, so the result will be a vector. The next will be integral where you start with a vector and you dot take a dot product to this scalar and this is the one that that we will be using the most. The third integral we mention it just for completeness is F and this gives you a vector you start with a vector field you cross with a vector that corresponds to the surface normal and you get another vector field, which is the surface integral and this integral is over the entire surface.

So, and each of these can be calculated using almost the same techniques that we used for line integrals, at least the definitions are very similar to line integrals. Actually implementing and calculating the surface integral turns out to be slightly more tricky you have to use some ideas from multi from calculus of many variables. So, for example, if you had this three dimensional space and your surface could be something simple like this could be a surface.

So, your surface is in the x y plane if, so your surface is in the x y plane at z equal to 0, so your surface is defined as this region in the x y plane bounded by the these points and it is where z equal to 0. So, then you have to define the surface element accordingly in this case your d sigma will point this is direction of d sigma, will point normal to the surface so it points along k. So, if you had write d sigma what you will write is an along the surface only x and y are changing.

So, will just say you will write d sigma equal to k hat d x d y and you will put the appropriate limits for x and y, so that you just cover this surface region. So, it could be something simple like that for more complicated surfaces for example, you could take a surface which is surface of a sphere, so it is one quadrant of the surface of a sphere and in that case again you have to define your surface integral appropriately. So, it need not be such a simple looking surface it can be more complicated surface, it can be curved, it can be curved in it need not be flat plane it can be curved plane and the bounding region need not be straight bounding region can be curved.

So, for example, you can ask what is the integral over the surface of a sphere, so you have a sphere what is the integral over a surface of that sphere. And in this case the outward normal at each point will be different in this case you had just only one outward normal but here depending on where you are you have a different outward normal. And in each case you have to use different tools to define to represent your surface; for example, for the surface of a sphere it turns out to be more convenient to use spherical polar coordinates, which was discussed in an earlier lecture.

So, if you want to parameterize this surface and you want to write a simple way of writing d sigma then if you are working with the surface of a sphere it is best to use spherical polar coordinates; in each case you have to choose what coordinates you will use. So, for example, surface of a sphere of radius a and you can show that this can be represented by is the element. So, it look at the element of surface of a sphere and this element will just be given by in this case a will be fixed.

So, you have a and a theta d pi, so it will be a square sin theta d theta d pi. Now, when you are working in spherical polar coordinates and it is usually easier to put limits on theta and pi, in this case pi will vary from 0 to 2 pi and theta will vary from 0 to pi and that will give you the entire surface of a sphere. So, limits pi goes from 0 to 2 pi, theta goes from 0 to pi and this covers the entire sphere of radius a. So, if you want to do an integral over a surface of a sphere it is better to use spherical polar coordinates and in each case you will choose the coordinates system that is most convenient for solving that integral.

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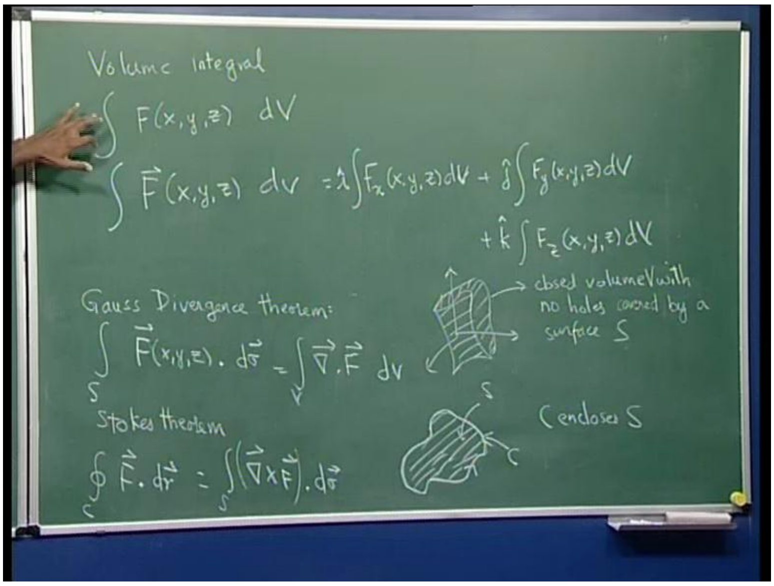

Now, the third type of integral is something called a volume integral and in this case since volume is scalar, this volume integral there is only one definition of a volume integral. So, if you had a scalar function F of x, y, z then you can define integral d v f of x y z. Similarly, if you had a vector function then you can define integral this will just be a vector with 3 components so it will have 3 components F x d v times i no plus j. So, you just integrate each of these components separately, so it is a this gives you a vector with 3 components corresponding to integration of the individual components.

So, these are the three kinds of integrals that we often encounter when we are working with functions of vectors now you can ask questions like what is the relation between a surface integral and a volume integral. And there are two interesting theorems that relate various kinds of integrals the first theorem is called the Gauss Divergence theorem. So, this has to do with a volume integral with this relates a volume integral to a surface integral.

So, the idea is that suppose you have a volume a closed volume with no holes and it could be an arbitrary shape. So, this is a closed volume with no holes covered by a surface S. So, the surface of this volume is S, so you have closed volume and you have a surface S closed volume let us call it v with no holes and when I say no holes I mean I do not have holes here.

So, the surface is continuous as and the volume is also continuous. So, in this case Gauss divergence theorem relates the volume integral to the surface integral, now if you had any field F, now the surface integral of F dot d sigma over S. Now, notice that S is a closed surface that covers the volume V this is equal to integral over the volume V of del dot v d v del dot f. So, if you want to find the surface integral but it turns out that it is easier to calculate the volume integral, then you just take the divergence of f and you find the volume integral and that is equal to the surface integral.

But, importantly S should be the surface that encloses the volume V. So, this is the Gauss divergence theorem the other theorem is called the stokes theorem, stokes theorem relates the surface integral to a line integral. So, in this case you have a surface s you have a smooth continuous connected surface S and you have this you have this path C that covers that encloses, so C encloses S and both are smooth connected and without any holes.

So, now in this case the stokes theorem relates the line integral and the surface integral and what it says is that the line integral, integral over C is a closed path F dot d r is equal to the integral over the surface S but at the it is a integral of del cross F d sigma. So, it is the is the surface integral of the curl of F, so it is not related just to the surface integral of F with surface integral of the curl of F. And these two theorems are extremely useful many times it is much easier to describe a region by using the volume.

And so instead of doing surface integral you can do a volume integral of the divergence it turns out to be easier to do that in some cases. So, in that case you use the stokes, you use the gauss divergence theorem. Similarly, sometimes it is easier to do an integral over a surface rather than doing this line integral and so you use stokes theorem to go to that. And if you can look at various examples of usage of each of these theorems and you will definitely encounter lots of volume integrals during a quantum chemistry course.

Occasionally, in advanced courses you will also encounter some surface integrals, the line integral are things that you keep encountering in your in thermodynamics and also the other areas of mechanics.