Advanced Mathematical Methods for Chemistry
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Module - 01
Lecture - 05
Recap of Week 1, Practice Problems

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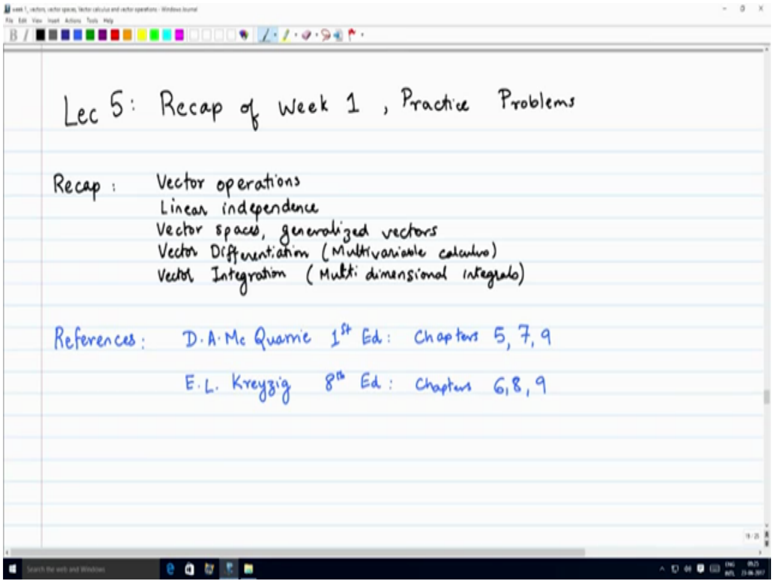

So in lecture 5 we are going to recap everything that we did not week 1 and then I will do a few practice problems. So, just to recap quickly, so in this week we learnt about vector operations, we learnt about linear independence, we learnt about vector spaces and generalized vectors. So, we saw that you do not need to think just about 2D and 3D vectors you can think about generalized vectors.

Then we learnt about vector differentiation and there we saw how multivariable calculus comes naturally. So, partial derivatives comes come very naturally when you are doing vector differentiation and then we learnt about vector integration and again here we saw multi dimensional integrals comment. Lot of all this material can be found in Macquarie’s book which was told to you as one of the reference books. So, in the first edition there were chapters 5, 7, 9 and similarly Kreyzig’s 8th edition has this material is there in chapters 6, 8 and 9.

And again the let me emphasize that I have not done all the material in these chapters I have only taken part of the material. Now there are certain fairly advanced topics like greens theorem and stokes theorem which I did not touch upon and they will not be required for this course, but some of the more basic topics like what is a vector space, the axioms of vector space these are things that it would be in your interest to understand them. So, now, let us go to discuss a few practice problems and I will try to give examples that are relevant to topics in chemistry as far as possible.

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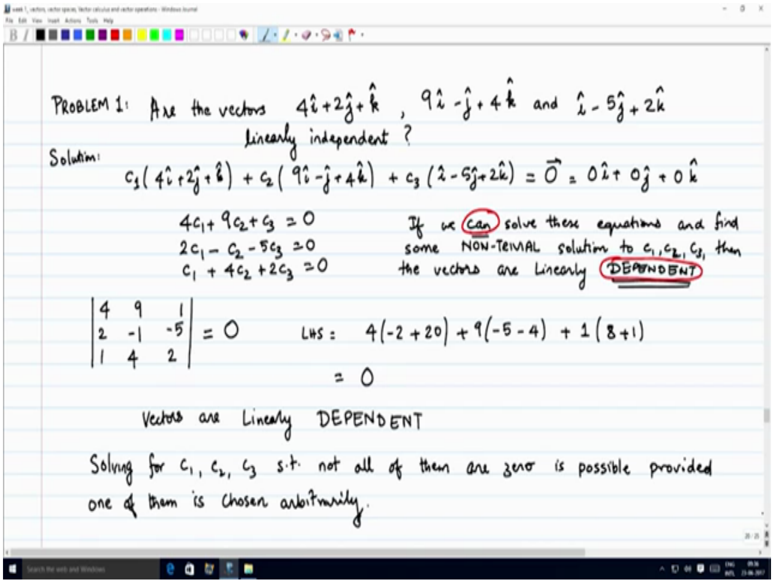

So, let us start with a very simple problem. So, the here is a question about linear independence. So, the question asks are the vectors for i plus 2 j plus k, 9 i minus j plus 4 k and i minus 5 j plus 2 k are these vectors linearly independent. So, let us try to solve this.

So, the solution is the following. So, what we will say that we check what is the condition for linear independence. So, linear independence means suppose you have a constant c 1 times 4 i plus 2 j plus k plus c 2 another constant times 9 i minus j plus 4 k plus c 3 times i minus 5 j plus 2 k. So, if you had this condition if this was equal to 0 and let me put a vector on 0. So, if you had this condition now what you see is that now there is a i component, there is a j component and k component. So, basically the 0 is I can write as 0 times i plus 0 times j plus 0 times k. Now these 3 are independent components. So, I have 3 equations and if you write out the equations you will get the i component, so

I will write the i component. So, the i component will look like 4 c 1 plus 9 c 2 plus c 3 equal to 0, the j component j component equation will look like 2 c 1 minus c 2. So, you have minus 5 c 3 equal to 0 and the k component will look like c 1 plus 4 c 2 plus 2 c 3 equal to 0.

So, I have 3 equations and 3 unknowns and the question is can we solve. So, if we can solve these equations and find some non trivial, non trivial means see some solution, so if you look at this equation c 1 c 2 c 3 are equal to 0 will trivially is a trivial solution. So, if you find some non trivial solution to c 1 c 2 c 3 then the vectors are linearly dependent, dependent. So, if you can find a solution, if you can find solution then the vectors are linearly dependent and let us it is again these things are very important. So, if you can find a solution then they are linearly dependent.

So, now how do you know whether you can find a solution that is non trivial and the answer is quite straightforward. So, there is a condition if you want to have a non trivial solution for these set of equations then it must be true that the determinant 4 9 1, this determinant 2 minus 1 minus 5 and 1 4 2. So, if you have such equations whether such linear equations where the right hand side is 0 are referred to as homogeneous equations. So, if you have a set of homogeneous equations then the condition for existence of a non trivial solution is that this determinant should be 0. So, the determinant of the coefficient should be 0. This is a rule that you will be using in many places when we use it a lot in quantum mechanics and when you are doing the variation theorem, you also use it in lot of cases when we are setting up ensembles in statistical mechanics we sometimes use a formulation that where you end up with linear equations.

Now, so let us verify do we get 0. So, what is the left hand side? So, the left hand side equal to 4 into minus 2. So, it is of the way you will take the determinant plus 20 plus 9 into minus 5 minus 4 plus 1 into 8 plus 1 and you can easily you can do this and you will find that this is equal to 0. 18 72 minus 81 plus 9, so it will get 0. So, that therefore, you conclude that vectors are linearly dependent. This is very interesting because what we saw is that if you can just take the vectors as they are, just take the each of the components and just make a matrix make a determinant with them and you check whether it is 0 and it immediately tells you whether they are linearly dependent or not.

Just to emphasize these are vectors in 3 dimensional space. So, you have i j k. So, it is a 3 dimensional space. So, you cannot have more than 3 vectors set are linearly independent, if there were 4 vectors then they would necessarily be linearly dependent. So, if you have 3 vectors in 3 dimensional space they may or may not be linearly independent and that linear independence can be checked just by doing this determinant. If you try to solve for c 1 c 2 c 3, if you try to solve these simultaneous equations for c 1 c 2 c 3 you will find that one of them can be chosen arbitrarily. So, one of the 3 can be chosen arbitrarily because there are 3 equations and 3 unknowns, but it is a homogeneous system. So, other than trivial solution if you want to have then actually you will find that one of the coefficients can be chosen arbitrarily.

And again these are things that you will see very often when you when you work out these equations in various areas of chemistry. So, let me emphasize that vectors are linearly dependent now topic - solving for c 1, c 2, c 3 such that not all of them are 0 is possible provided one of them is chosen arbitrarily. So, in other words when you say that these vectors are linearly dependent; that means, these equations are not independent of each other. So, effectively you only have 2 equations and 3 unknowns. So, one of the code, one of the constants can be chosen arbitrarily.

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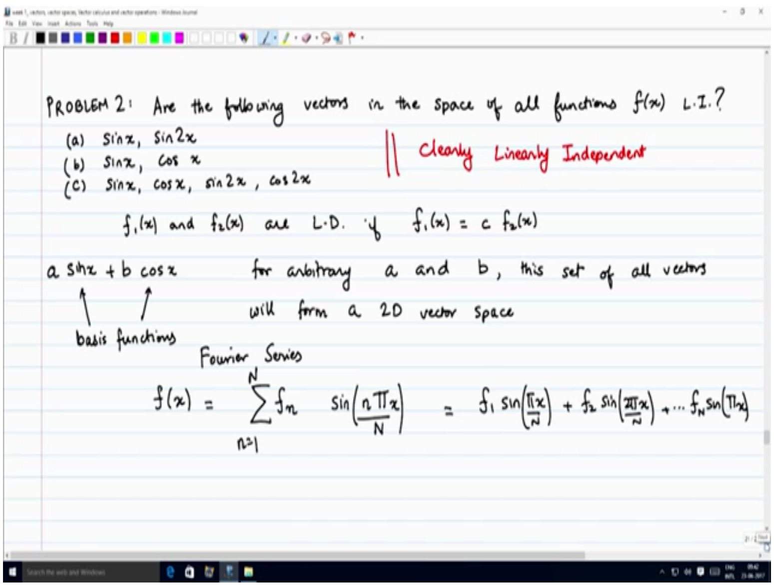

So, now, next I will do the next problem which is also based on the idea of lineal independence and here the question are the following vectors in the space of all functions f of x linearly independent, LI stands for linearly independent. So, here we are looking at the space of functions. We already emphasize that is a vector space and we took 2 functions sin x and sin 2 x and then the next set I gave was sin x and cosine x, the third set I gave was sin x, cosine x, sin 2 x, cosine 2 x.

Now 2 functions are linearly independent, are linearly dependent if one is proportional to the other. So, f 1 of x and f 2 of x are linearly dependent if f 1 of x equal to some constant times f 2 of x and this constant should be independent of x.

Now, clearly all these all these functions are these are clearly linearly independent and I emphasize that it is very clear because I cannot write sin 2 x as a constant time sin x similarly I cannot write cos x as a constant time sin x. Similarly I cannot write any of these functions as a linear combination of these functions. So, clearly they are linearly independent and why I emphasize this problem is the following that that the idea of, so suppose you take suppose you take sin x and cosine x since they are linearly independent I can take something like a sin x plus b cosine x and this for arbitrary a and b. So, if you let if you let a and b any arbitrary scalar. So, this will give, this set of all vectors will form a 2D vector space.

So, I can just take a linear combination of sin x and cosine x and if I let take all possible linear combinations then I will get a vector space because sin x and cosine x are linearly independent and this is just, this is a 2 dimensional vector space. So, this is an idea of this. So, in this 2 dimensional vector space, in this 2 dimensional vector space is a space of all functions that can be written in this form, these sin x and cosine x are basis vectors or basis functions and what is important is that you can use this idea of basis functions in I mean you mean this idea is very powerful, basis functions they just have to be linearly independent and you can take an entire, you can take the space span by these functions and that vector space is a vector space.

Now, this idea of basis functions is you is what is used in Fourier series. The fact that sin x and sin 2 x are linearly independent, so in Fourier series what is done is you write a function f of x as a linear combination. So, and what is done is you write it as a linear combination of sin n pi x by capital N sum over n equal to 1 to N and you have some coefficient that coefficient I will write it as f n. So, what is done is this is the nth coefficient. So, basically this is can be written as f 1 times sin pi x by n plus f 2 times sin 2 pi x by n plus dot dot dot f n times sin, n pi x by n is same as sin pi x.

So, this sort of expansion in terms of sins is called a Fourier series and what is important is that each of these functions is s sin pi x by N, sin 2 pi x by N n so on are linearly independent. So, the idea of basis functions is something again that you will see a lot in indifferent courses and you know it is all based on the ideas of linear independence.

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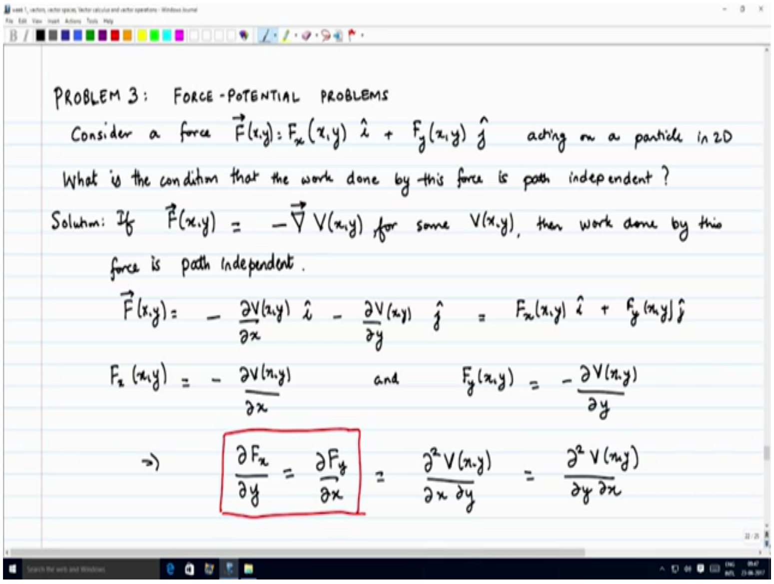

Next problem will take is a force potential problem. So, consider a force and here when you say force f of x acting on a particle. So, what you mean is that you have a particle in 2 dimensions this is in 2 dimensions. So, you have a particle in 2D and based on where it is in space its acted upon by a force and the force has this form force is a function of x y, it has 2 components F x of x y times i and F y of x y times j. So, force is clearly a vector field and now you are asked to find what is the condition that the work done by this force is path independent.

Now, the solution is the following that we know that if F can be written as can be written as minus the gradient of some potential V of x y some scalar field, V of x y for some V then work done by this force is path independent. So, if you want to know whether the work done by the forces path dependent or not then you should check whether it can be written as a negative gradient of some potential some potential function V, V of x y and notice I really emphasize in the dependence of variables when I write the functions. So, when I write force I explicitly have written that it is a function of x y. So, this is actually a very good habit to get into, when you write equations you have to write what these are functions of.

Now, if you can write F as negative gradient of V then clearly I can say that F of x y is equal to minus dou V by dou x, now I am not I will write the x y i minus dou V by dou y x y j and this is equal to F x of x y i plus F y of x y j. So, therefore, we conclude that F of F x of x y should be equal to minus dou V of x y by dou x and F y of x y is equal to minus dou V of x y write dou y. So, the condition turns out to be that the x component of the forces is derivative with respect to x of some potential function V and the y component should be derivative with respect to y of some function V.

Now, what this implies is that if I take dou f x of divided by dou y, here I am suppressing the dependence on x y, I am not showing the x y dependence, but, but you know you can show it, but if you wish. So, if you take dou f x by dou y that will be the second derivative of V with respect to x and with respect to y and this should be equal to dou f y by dou x. So, this is both these are equal to dou square V of x y by dou x dou y which is the same as dou square V of x y by dou y dou x. So, the order of partial derivatives does not matter if V is a well defined function and so this is the condition. So, what we have is here is a condition just based on the component of the force. So, this is the condition that we are interested in. So, the x component of the force you take the derivative with respect to y that should be the equal to the derivative of the y component with respect to x.

This is a very useful condition and will see an application of this in the next part of this problem.

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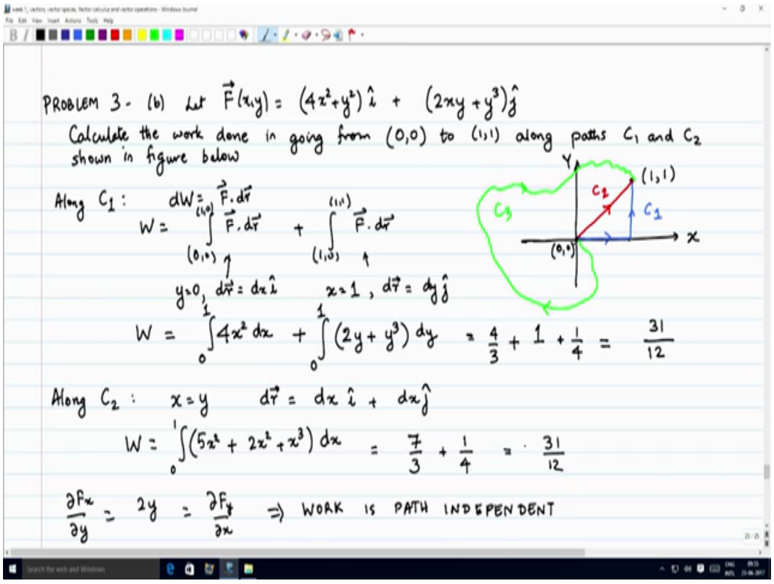

So, the next part of this problem is here. So, suppose your force is given by 4 x square plus y square i and 2 x y plus y cube j. So, this is a force acting on the particle now calculate the work done and going from 0 to 1 1 along path c 1 and c 2 as shown in the figure below. So, what you are doing is you are taking the particle from this point 0 0 to point 1 1 and you are taking along 2 paths - the first path is you go this way and then go up second path you go directly from here to here and what you are asked to do is to calculate the work done in both of these.

Now, now will actually explicitly calculate the work done because that will show you how to do line integrals and then we will we will comment on the path dependence or independence. So, let us calculate work done along c 1. So, suppose you are going along path c 1 the work done can be written and so you should remember that we have dW equal to f dot d r and, so what I can write is that I can write the work done along cone as. So, I will write, I will right in terms of I will break it into 2 pieces - the first is going along the x axis the second is going in the y direction.

So, along the x axis, so what the most important thing in doing this line integrals is to write the path. So, what you are going is you are going from 0 0 to 1 0 F dot d r and then you are going from 1 0 to 1 1 F dot d r. So, this is the path along c 1. Now when you are going from 0 0 to 1 1, so along this path you have, along this path you have y equal to 0. So, in this path you have y equal to 0 and d r equal to d x i. So, it is only x that is changing. Along this path you have x equal to 1, x is fixed at 1 x does not change from 1 it is always 1 along this along this path and you have d r equal to d y j.

So, these are the 2 characteristics of the 2 paths and knowing this now I can easily calculate the work done. So, work done, so along this path. So, what I will do is f dot d r d r is nothing, but d x i. So, if I take f and dot into i, then I will just get 4 x square plus y square d x and along this path you have y equal to 0. So, all you have is 4 x square d x integral and here you are ingraining from x equal to 0 to x equal to 1. So, this is this first path because i put y equal to 0 along.

The second path I have, here I have to put x equal to 1 now d r is just d y times j. So, d y times j means if I take f dot d r i will just get 2 x y plus y cube into j and x equal to 1. So, I have 2 y plus y cube d y and I am taking y from 0 to 1. So, I converted both these integrals to just simple 1 dimensional integrals and so what you will get? You will get 4 by 3. So, 4 x cube by 3 x cube by 3 from 0 to 1 is just 1 by 3 plus, now you have 2 y so you will get y square y square will give me integral y, so y square from 0 to 1 is just 1 and you will have y 4 by 4 that is just 1 by 4 and if you write this. So, you will get 12, 16 plus 12 - 28 plus 31 - 31 by 12.

Now, along c 2, this is the work done along this along the path c 1. Now along c 2 how do you calculate the work done. So, along c 2, now, if you look at this path along this path you have x equal to y. So, d r can be written as d x i plus d x j. So, we can just write it because d x has to be equal to d y and, so along this path you can write d are in this form both components are there. So, r has both an x and a y component d r has both these components, but there they will be equal. So, now, now if I do the integral what i get is W. So, if I just substitute this in this expression. So, F dot d r. So, and then I replace x by I replace y by x. So, I have 4 x square plus x square. So, that is 5 x square and then I will have a d x and then I will have I will have 2 x square plus x cube. So, plus 2 x square plus x cube d x integral and x is going from 0 to 1. So, that is what I had.

So, I substitute at x equal to y and I substituted d x equal to d y and I just went through everything and I got this and you can you can easily verify. So, 5 plus 2 7, so I have, 7 x square that is 7 x cube by 3. So, I just have 7 by 3 and I have 2 x square that is 2 x cube by 3 oh sorry I have x cube, x cube will give me x 4 by 4. So, that is 1 by 4 integrating from 0 to 1 and what I will get is 31 by 12.

So, you notice that work done along both these paths are identical to each other. So, you get the same work done which ever path you go. Now you can actually you could have actually predicted that in this case you could have predicted that the work done would have been the same because if you take dou f x by dou y. So, this gives you 2 y. So, this is the same as dou f y by dou x. So, if you take the derivative of this path with respect to x keeping y constant. So, when you take derivative with respect to x keeping y constant you will just get 2 y. So, in this case work would have been path independent.

So, what that means is whether I went by this path or this path I would get the same work I could have taken some very strange paths. So, for example, I could have taken a path that looks like this, I could have taken this path and c 3. So, even if I take another strange looking path I would do the same amount of work. So, whatever, whichever way I move the particle with this force I will always do the same amount of work. So, that is what it means to say that the work done is path independent.

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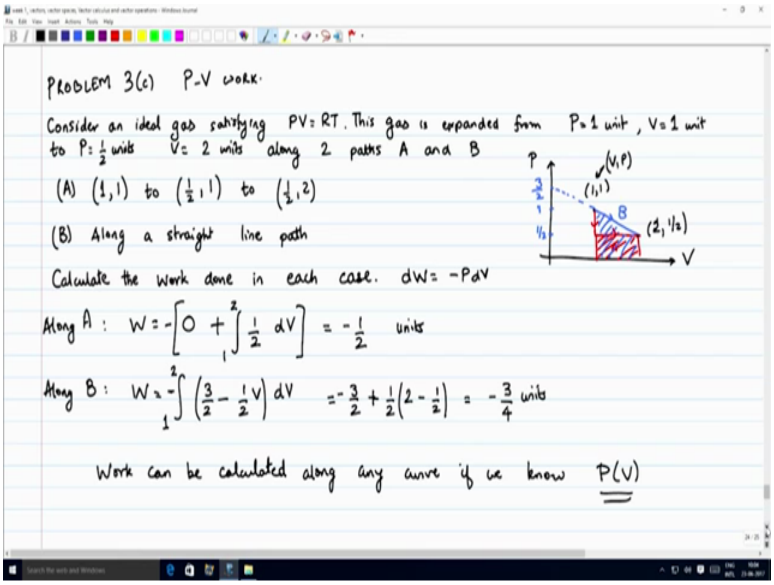

So, next let us let us go to the, let us now look at another case of path independence that you are familiar with this is in thermodynamics. So, this refers to a P-V work and you might have seen this in your elementary thermodynamics course. So, in this problem let us say I consider an ideal gas satisfying p v equal to r t, this gas is expanded from P equal to 1 unit and V equal to 1 unit 2 P equal to half units and V equal to 2 units along 2 paths A and B. So, the first path is you go from P equal to 1 V equal to 1 to P equal to half V equal to 1 and then you go from P equal to half V equal to 1 to P equal to half V equal to 2.

And the second path is a straight line path. So, what will the straight line path look likes? So, let me just show this on a figure. So, if you have let us say V on this axis and P on this axis now you are going from the point let me show it here. So, this is 1 1 and you are going to the point where V equal to 2 and P equal to half. So, in this part V equal to 2, P equal to half. So, here I am showing it as V P here it is shown as P V here, since I have to plot in this way I have plotted P on the x axis P on the y axis and V on the x axis which is what you typically see in thermodynamics.

So, now, you are you are considering 2 parts in the first part you go from P equal to 1 to P equal to half keeping V at 1. So, keep V at 1. So, in path A I will show it in red. So, what you do is, you just go along this path you read this intermediate point and then what you do is you go then you go along this path and you reach here. So, this is your path A and path B what you do is you go you take a straight line path and you are asked to calculate the work done in each case.

So, let us do. So, the work done work done in each case you should know that Dw equal to minus P d V. So, let us look at path A. So, along A W is equal to, now there are 2 paths to the through the path, in the first path your pressure is changing, but your volume is kept fixed. So, in the first part of the path, since the volume is fixed d V is 0 since d V is 0 the work done is 0. In the second part of the path your pressure is kept fixed at half. So, your P equal to half and your volume is changing from, you have integral half d V and V is changing from 1 to 2. So, this is, the total work done will just be half into 1 that is half, half units; I should put a minus sign, I should put a minus sign here. So, the total work done is minus half units. This is the work done along path A.

So, along B how do you calculate W? So, you need if you want to calculate W you need you need to express P in terms of V. So, I need to express P in terms of V. So, now, what I said is it is a straight line and you can easily write down the equation of the straight line, you can easily write down the equation of the straight line if you realize that this point is half this is one. So, if it just goes up here straight line then it will join at 3 by 2. So, I can write the equation of this line in the following form. So, P is 3 by 2 minus now what is the slope of this line. So, in changing by 1 it changes by half.

So, the slope is half half V, this is the equation of the straight line, this is the equation of the straight line, 3 by 2 minus half V, P equal to 3 by 2 minus half V. So, along the straight line I have P equal to 3 by 2 minus half P and I am changing from volume of 1 to volume of 2 and what I will get, I will get. So, the first one will give me 3 by 2 V and 3 by 2 V from 1 to 2 that is 3 by 2 and what you have is 1 by 2 and you have v square by 2, V d V is V square by 2 V square by 2 from 1 to 2. So, will have 1 by 2 when V equal to 2 V square by 2 is 4 by 2, that is 2 4 square by 2 is 2 and when V equal to 1 v square by 2 is 1 by 2.

So, what this works out to be this is 1 minus one-fourth, that is three-fourth and 3 by 2 minus three-fourth is there is a minus sign here and a plus sign here. So, there is an overall minus sign. So, the signs should change, there should be an overall minus sign. So, finally, what you will get is minus 3 by 4 units.

So, in this case we see that the work done in both the 2 paths is different. Now incidentally you might be familiar with the idea that integral P d V is nothing, but the area under this P V curve. So, you could just calculate the work just by looking at the area. So, if you look at area under a this is the work done in the first case and you can clearly see that this area is just half because this height is half, since this point is half and this point is 1 the area is just equal to half half into 1, it is a rectangle and in this case to this you are adding the triangle. So, the area in this case becomes 3 by 4.

So, you can easily see that you know you can calculate the work in this way just by the area or you can do using this line integral. So, this is the fairly well known, you can do this along any other curve, you can calculate, we can calculate work along any other curve along any curve if we know P as a function of V, if we know what this function is. So, you can take any function and you can calculate the work and in general it will be path dependent.

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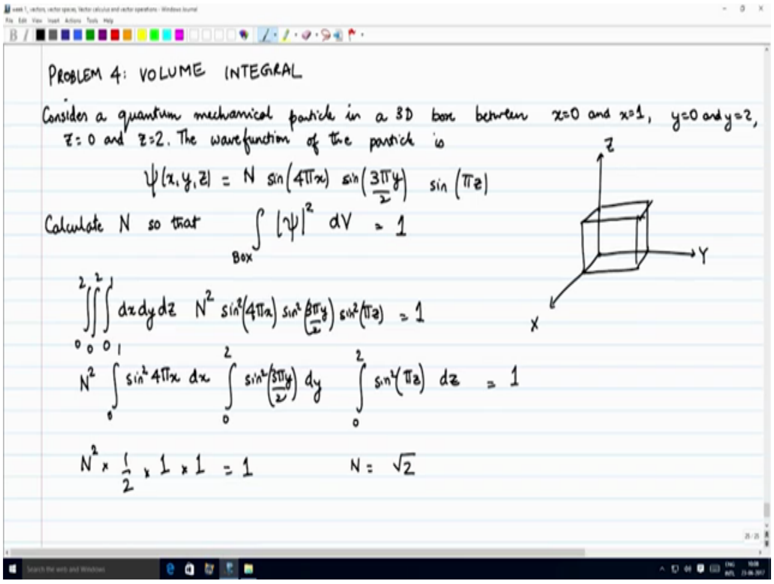

So, now this is about line integral. So, the now the last problem I will do is multi dimensional integral or a volume integral and you know one very common place where this is seen is in quantum mechanics. So, we consider a quantum mechanical particle in a 3 d box between x equal to 0 and x equal to 1, y equal to 0 and y equal to 2, z equal to 0 and z equal to 2. The wave function of the particle is given by in some state. So, the particle is in some state and its wave function is given by this expression.

So, what you are asked to do is to calculate n so that this volume integral of size square over the entire box that is defined by these quantities is equal to 1. So, let me pictorially show the box. So, what you have is something like this. So, this is x this is y this is z then your box goes from x equal to 0 to x equal to 1, y equal to 0 to y equal to 2 and z equal to 0 to z equal to 2. So, this is your box, this is what the box looks like. So, what we are doing is integrating over this entire box. So, the integrating of the volume, so I can easily write that, so this condition is basically integral it is a triple integral over d x, d y, d z and I have to take the square of this function. So, the square of this function is N square sin square 4 pi x sin square 3 pi y by 2 and sin square pi z and my range of integration for x is from 0 to 1, y is from 0 to 2, z is from 0 to 2.

Now, now I can see that this depends only on x and nothing else depends on x. So, I can write this integral. So, this should be equal to 1. So, I can write this as N square, N square I can take outside now the integral over x, integral over x will be integral from 0 to 1 sin square 4 pi x d x and then I have integral from 0 to 2, sin square 3 pi y by 2 d y and then I have integral from 0 to 2 sin square pi z d z and this should be equal to 1.

Now, you can do each of these integrals. So, this integral will just be half, this integral will be equal to 1 and that integral in the third integral will also be equal to 1 you can do these integrals and you can verify. So, what you will get is that this equal to 1 or N equal to square root of 2, N square equal to 2, N equal to square root of 2. This is what you will get and this is a way of doing this volume integral. So, in this case you had a very simple volume integral which you could do. And I encourage you if you have any difficulties in any part you please right on the forum and I will make sure that the question is answered quickly.

Thank you.