Advanced Mathematical Methods for Chemistry
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Module - 03
Lecture - 05
Recap of Module 3, Practice Problems

Today is the fifth lecture which is the last lecture of module 3. In this lecture I will recap what you learnt in module 3, I will make a few points and then I will do a few practice problems.

So, in this module we mainly talked about special functions, we talked about a few special functions that we encounter quite often in various chemistry courses and then I I talked about spherical polar coordinates and cylindrical coordinates. So, now, again these are also things that you will see in your chemistry courses. So, just to get to the details in the first lecture I talked about step functions and Dirac-Delta functions.

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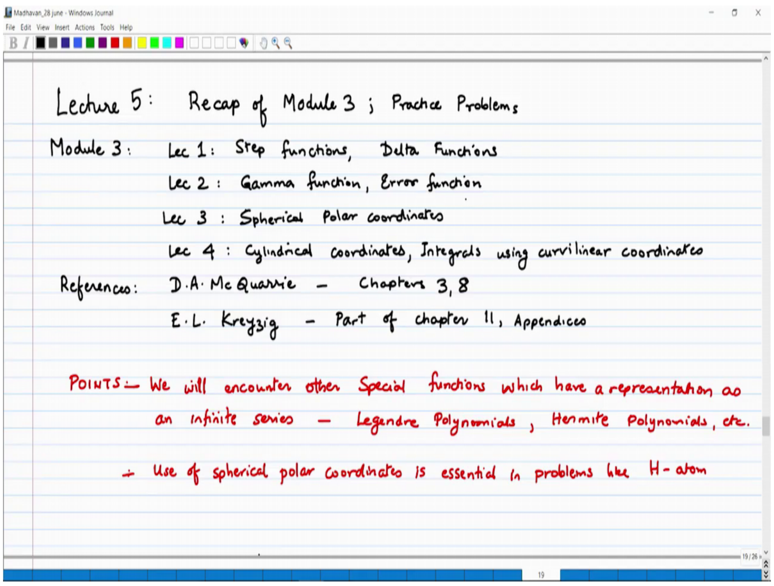

And then in the second lecture I talked about gamma function and the error function. In the third lecture I talked about spherical polar coordinates and in the fourth lecture I talked about cylindrical coordinates and integrals using curvilinear coordinates.

Now, this material is fairly well covered in Mc Quarrie's book in chapters 3 and chapter 8. So, they talk about lot of they talk about lot of other special functions in chapter 3 and they also talk about generalized curvilinear coordinates in chapter 8. The other in Kreyzig this section is not actually covered in any particular place, but there are parts of it in chapter 11 and in some other chapters to they use polar coordinates. So, polar coordinates are described here, delta functions are described where they talk about Fourier transforms and in the appendices they talk about error functions.

Now few points is that you will encounter several other special functions in during your chemistry courses and some of these special functions have a representation as an infinite series. So, these special functions like the gamma function had a representation of an integral, similarly the Dirac-Delta function was a special function that was a discontinuous function which is defined only under the integral, but there are some special functions which have representation as infinite series likely your Legendre Polynomials, Hermite Polynomials, Bessel functions there are many others. And these are things that you will encounter during your during your quantum mechanics courses.

Now, the other point is that use of spherical polar coordinates is essential in problems like the hydrogen atoms. So, the hydrogen atom problem in quantum mechanics you need spherical polar coordinates. So, with this recap I am going to start working out a few problems.

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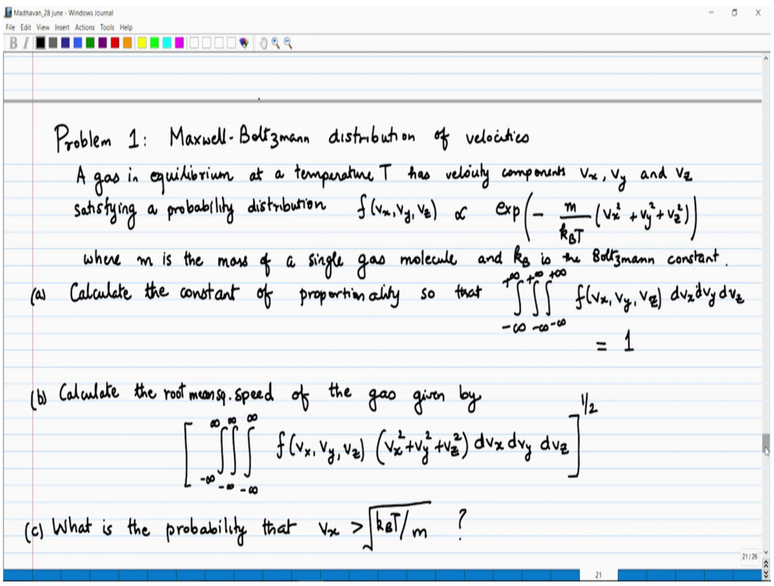

And I encourage you to also practice other problems given in the books because I will just be doing a few problems and hopefully with you know if you are able to work out these problems and also read the book for some practice problems you will be able to work out the assignment.

So, the first problem is has to do with the Maxwell Boltzmann distribution of velocities and when you work out this problem you will see applications of the gamma function and the error function. So, what is the problem? This is a very classic problem that you will encounter in your when you are studying kinetic theory of gases and I am just showing where error functions and gamma functions are used in this problem.

So, the statement of the problem is the following. A gas in equilibrium at a temperature T has velocity components V x, V y and V z satisfying a probability distribution f of V x V y, V z is proportional to exponential of minus m by k B T into V x square plus V y square plus V z square. So, I have chosen to write the exponential function in this form it says because the quantity that I have in the exponent is quite large. Where m is the mass of a single gas molecule and k B is the Boltzmann constant. So, velocity is a vector it has 3 components V x, V y and V z and each of these components can go from minus infinity to plus infinity and you are told that if the gas is an equilibrium then the velocity components have a probability distribution that satisfies this expression.

Now, we will talk about probability distributions in the later part of the course. So, I want expect you to know too much about them, but nevertheless in this problem what you are asked to do is to calculate the constant of proportionality this constant of proportionality that appears before the exponent in the expression for the f such that the integral from minus infinity to plus infinity of f of x, f of V x V y V z, d v x d v y d v z. So, each of the components can go from minus infinity to plus infinity and this integral should be 1. So, that is the first part. So, you calculate this constant of proportionality sometimes it is called a normalization constant. And what you are doing is you are calculating it. So, that the integral over this probability distribution x equal to 1.

Next you are asked to calculate the average speed of the gas that is given by this quantity. So, you have a triple integral of f of V x, V y, V z times V x square plus V y square plus V z square d v x, d v y, d v z and this whole thing raised to the power half. So, this is this is the average speed of the gas. So, the average square speed is, average square of speed is given by this expression and the square root of that we will give you the average speed and then you are asked what is the probability that that the x component of velocity is greater than k B T by m or square root of k B T by m.

So, this problem it looks a little daunting, but when you start working things out then things will become very simple. So, let us work out the first part. So, the first part where you want to calculate this constant of proportionality, so let me go to that.

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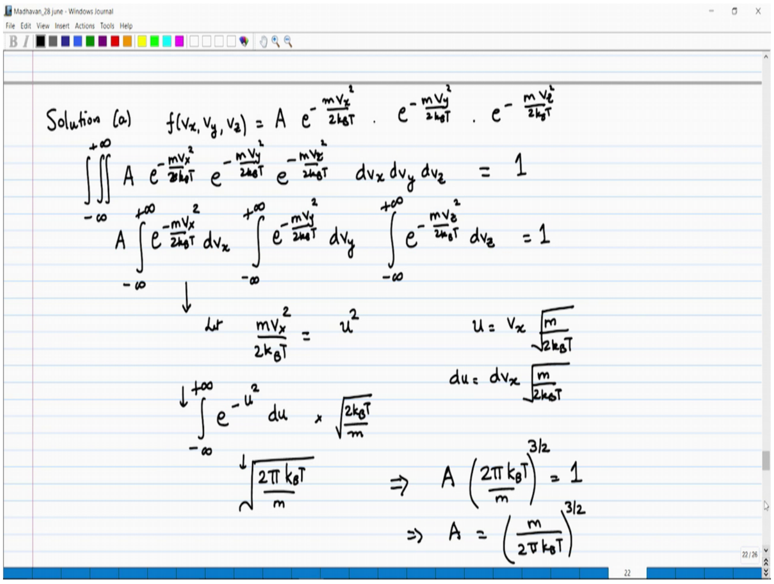

So, so what I would like is I say that f of V x, V y, V z equal to let me call A say A times e to the minus m V x square by 2 k B T times e to the minus m V y square by 2 k B T times A to the minus m V z square by 2 k B T.

So, this is exactly the same expression I just wrote a constant of proportionality and I wrote the exponential as a product of 3 exponential, exponential of the sum as product of 3 exponentials. Now what we would like is that this integral you want this integral to be equal to 1. So, I will write this integral in the following way. So, I will write this as integral, let me write it explicitly. So, you have this triple integral and all of them go from minus infinity to plus infinity and I have a times e to the minus m V x square by 2 k B T e to the minus m V y square by 2 k B T and e to the minus m V z square by 2 k B T, d v x d v y d v z this should be equal to 1.

Now, I can take a outside the integral and I can this the first term depends only on V x, it is independent of V y and V z second term depends only on V y and the third term depends only on V z. So, I can write this as basically 3 integrals integral e to the minus m V x square by 2 k B T d v x times integral e to the minus m V y square by 2 k B T times d v y and e to the minus integral m V z square by 2 k B T times d v z and this should be equal to 1, each of these integrals goes from minus infinity to plus infinity this should be equal to 1.

Now, the first thing you should see you should be immediately be able to realize is that each of these integrals has the same value because here I am integrating over d v x, but I am integrating from minus infinity to infinity here I am integrating over d v y exactly the same function e to the minus m instead of V x I have v y, but e V y is just a dummy variable you are integrating over it. So, it is not. So, the name whether I call it V x V y or V z the integral you will remain the same, all you need to do is to calculate one of these integrals and then you are done.

So, let us just calculate this integral so. So, now, what I will do is I will make a transformation of variables I will say let m V x square by 2 k B T equal to u. Now well I can just call it equal to u square for now I will just call it equal to u square and what you will get by this is that you will get that or. So, I can write u equal to V x times square root of m by 2 k B T and you will get d u equal to d v x times square root of m by 2 k B T. Now the advantage of writing this way is that this integral becomes equal to integral minus infinity to plus infinity e to the minus u square, now d v x is nothing but d u and then you have a you have divided by just constant of proportionality I can take that constant of proportionality outside. So, all I have is this integral multiplied by square root of 2 k B T by m m.

Now, this integral is a very familiar integral we have seen this in the in the earlier part and this is just square root of pi. So, this is an integral that we saw when we did the gamma function. So, what you get is that this is just equal to square root of pi. So, what I can get this whole thing is just 2 pi k B T by m under root and so the first integral was equal to that the second integral, will also have the same value. So, will the third integral and. So, I can write A times this integral, this value this value 2 pi k B T by m raised to 3 or 3 halfs equal to 1. So, a times 2 pi k B T by m raised to 3 by 2 equal to 1 and A is equal to m by 2 pi k B T raised to 3 by 2.

So, this is the, this completes the first part. So, we have found the value of A. So, that your velocity distribution is normalized and we see and we see how the how the gamma function appears very naturally in this calculation.

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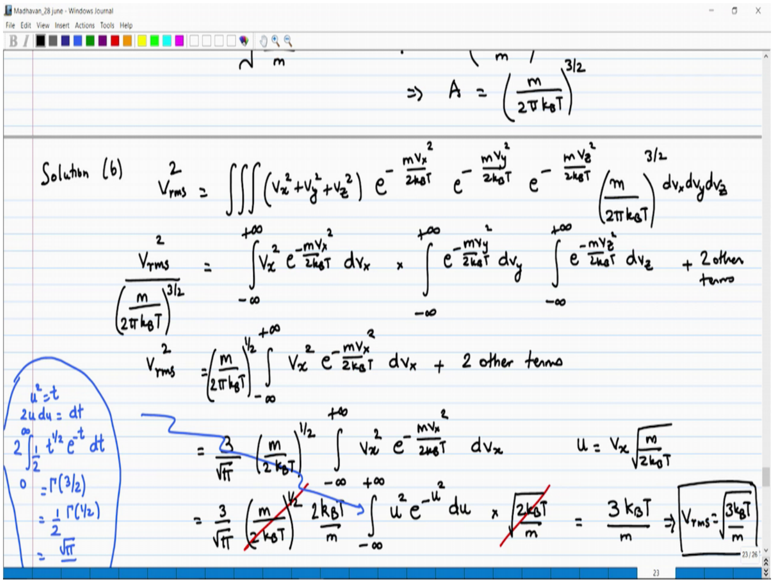

So, the second part second in the in the second part of the problem you are asked to you are asked to calculate the average speed of the gas and we are given the expression for the average speed of the gas. So, the average speed of the gas we are told. So, let me just write V average is equal to this triple integral again. Now, you have V x square plus V y square plus V z square times e to the minus m V x square by 2 k B T e to the minus m V y square by 2 k B T e to the minus m V z square by 2 k B T times now we know the constant of proportionality. So, the constant of proportionality is m by 2 pi k B T raised to 3 by 2, d v x d v y d v z and this is v average square. So, v average square has this expression and now what we are going to do is to actually evaluate this integral.

Now it is not again, again it is not very difficult to do. So, in this case we can see that we can write this as 3 integrals. So, the first integral, I will just write the first integral. You have V x square multiplied by this whole thing

So, let me write v average square divided by m by 2 pi k B T raised to 3 by 2. So, I will just take this m by 2 pi k B T raised to 3 by 2 to the denominator and what I will get is I will just write the first term and things will become clear. So, I have V x square e to the minus m V x square by 2 k B T d v x integral minus infinity to plus infinity. And then I have integral e to the minus m V y square by 2 k B T d v y and I have integral e to the minus m V z square by 2 k B T d v z again from minus infinity to plus infinity.

Now why I wrote it in this way, and I wrote it in this way is because you know each of these integrals this was just 2 pi k B T by m. So, this square root of 2 pi k B T by m this was also equal to square root of 2 pi k B T by m.

So, I can cancel, I can cancel out of these 3 factors 2 of them can be cancelled out. So, I will just write V average square will give me exactly equal to will be exactly equal to, integral minus infinity to plus infinity V x square e to the minus m V x square by 2 k B T d v x and I should mention you have plus 2 other terms it is ok. And now, you have a factor of m by 2 pi k B T raised to half. So, this factor is f. So, the other factor of other 2 factors of m by 2 pi k B T raised to half they cancelled this term.

So, you have this and now the plus the 2 other terms, 2 other terms in the 2 other terms you will find that all that is changing the 2 other terms is V x is replaced by V y and in the third term V x is replaced by v z. So, the 2 other terms will basically have the same value. So, I can write this as a factor of 3 times now what I will do is a I will write I will keep the, I will keep the root pi here and then I will take the m by 2 k B T square root of m by 2 k B T I will take I will take inside the inside the v, inside the d v actually.

So, I can write this as. So, let me let us work it out explicitly. So, I will have m by 2 k B T raised to half and now you have an integral minus infinity to plus infinity V x square e to the minus m V x square by 2 k B T and d v x. So, now you do the transformation that we did the last time. So, u is equal to V x square root of m by 2 k B T. So, V x square, what we will get is 3 by root pi m by 2 k B T raised to half. Now, V x square will be u x square into k B T by m. So, you have a factor of k B T by m and what you have is integral minus infinity to plus infinity u square e to the minus u square and now d v x is d u and there is another factor of 2 k B T over m. So, this should be a 2 k B T over m times square root of 2 k B T over m.

So, what we will happen is that this factor of k B T over m will cancel this factor and what you have here is u square e to the minus u square. Now this can again be expressed in terms of gamma functions. So, to do this we will just do this on one side I will just work out this integral. So, if you want to work out this integral. So, I will just work it out this integral, I will just work it out here. So, I will put u square equal to T and what you will have is 2 u d u equal to d T and also what we have to do is to make this integral because this is an even function. So, this is twice integral from 0 to infinity. So, instead of minus infinity to infinity we will make it twice integral 0 to infinity and when you go from 0 to infinity u and T have the same limits and you can see what you will get, you will get d u will have u d u will be d T by 2. So, we will have a factor of 1 by 2 and you are left with another factor of u, u is square root of T, T raised to half and you have e to the minus T d T. So, this is nothing, but gamma function of 3 halfs, this is nothing but gamma function of 3 by 2. So, this is equal to gamma function of 3 by 2 which is equal to half gamma function of half is equal to root pi by 2.

So, this allows you to do. So, what we did here was to actually evaluate this integral here and. So, and once you know this integral with just root pi by 2 and, finally, what you have is you have a factor of this is just 3 k B T over m. So, this is the root mean squares, this is the mean square speed of the gas. So, I should emphasize this is the mean square speed of the gas and average I should say, average the this is not actually the average speed of the gas, this should be this is actually the root mean square, root mean square speed of the gas. So, this is the root mean square speed of the gas and, so we just this is actually V rms. So, this implies V rms equal to square root of 3 k B T by m. So, this is your answer.

So, that is the root mean square speed of the gas and so here we have worked out the root mean square speed of the gas as square root of 3 k B T by m. I should have I made a small mistake this is what I wrote by this expression is not the average speed, but actually it is call it is the root mean square speed because your taking the average of the squares and then you are taking the root.

Next part of the problem is what is the probability that V x is greater than k B T by m.

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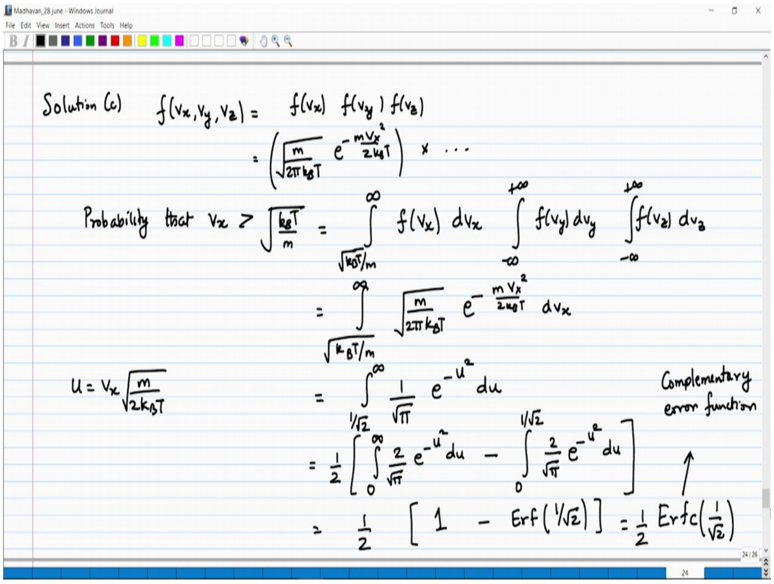

So, by now you should realize that I can write f of V x, V y, V z equal to function of V x times a function of V y times a function of V z and each of these is a, each of this is the normalized probability. So, this is square root of m by 2 pi k B T times e to the minus m V x square by 2 k B t. So, this is the x part and similarly for the y part and the z part.

So, now you are ask what is the probability that V x is greater than square root of k B T by m. So, this probability is given by, it is the integral from square root of k B T by m to infinity. So, these are the values of V that are greater than k B T by m and what you have can do is you can just take f of V x d v x the other integrals if you if you if you look at f of V y d v y and f of V z d v z. So, these go from minus infinity to plus infinity and these integrals will be equal to 1. So, these integrals will be equal to 1. So, you do not need to bother about this. So, all you need to do is to look at this. So, it is integral from square root of k B T by m to infinity now what is f of v x. So, it is square root of m by 2 pi k B T times and you have a factor of e to the minus m V x square by 2 k B T d v x.

Now, again you make the same transformation that we did you said u is equal to v x into square root of m by 2 k B T. When you make this transformation now what you will get is now when V x equal to square root of k B T by m. So, what is the value of u? So, this lower limit, you substitute v as k B T by m then you get u as integral 1 by root 2. So, integral 1 by root 2 when v equal to infinity u equal to infinity. So, you go from 1 by root

2 to infinity and now you can see that d u x equal to d v x into square root of m by k B t. So, I am just left with the factor of 1 by root pi and I have e to the minus u square d u.

Now, I can write this as half times now what I will write it as, I will write it as integral 0 to infinity 2 by root pi e to the minus u square d u minus integral, integral 0 to 1 by root 2 of 2 by root pi e to the minus u square d u. And the reason for writing this in this form is should become obvious because what you have here is nothing but error function of 1 by root 2, this is nothing but the error function of 1 by root 2 and this integral is exactly equal to 1 the this is your usual gamma function. So, this is 1 minus error function of 1 by root 2 into 1 by 2.

So, this is the solution. So, we wrote, we expressed an answer in terms of this error function error function is this incomplete integral it is usually the values of the error function are tabulated. So, you have tables of error functions. Incidentally this term 1 minus error function is sometimes referred to as the complimentary error function. So, then this is written as Erfc of 1 by root 2 this is called the complementary error function.

So, the error function is from 0 to 1 by root 2, the complementary error function is basically 1 by root 2 to infinity, so it is from x to infinity. So, the error function plus the complementary error function they add up to 1. So, this term 1 minus Erf of 1 by root 2 is written as a complimentary error function. So, the solution is just half times the complimentary error function of 1 by root 2. So, we see that you know whenever we deal with these Gaussian functions, the error functions and gamma functions appear very naturally when you are dealing with integrals involving Gaussian function.

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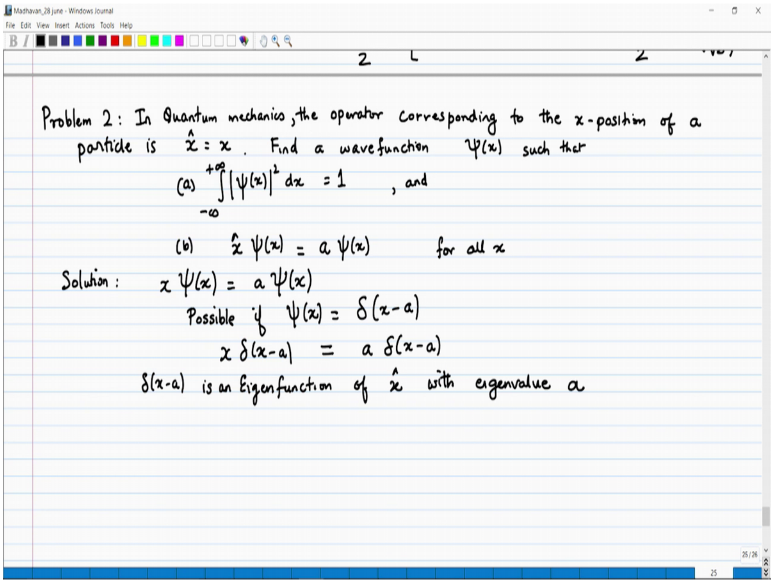

The next problem that I want to do is relates to the Dirac-Delta function. So, here I am just showing 1 very very interesting application of the Dirac-Delta function which is not usually discussed, but nevertheless it is an important point about the Dirac-Delta function. So, the problem statement is in quantum mechanics the operator corresponding to the x position of a particle is x hat equal to x. So, x hat denotes an operator and x hat equal to x; that means, when it operates on a function you just multiply the function by x.

So, now what you are asked to do is to find a wave function psi of x such that the integral of psi of x square d x equal to 1 and x this operator operator on psi of x is the constant times psi of x for all x. So, now, let us look at the second condition. So, the solution, the second condition if you look at is. So, x operated on psi of x is x into psi of x. So, this should be a into psi of x. So, what could be, so you want to find the function such that anytime you multiply the function by x it is as good as multiplying the function by a.

Now, at first you might think that this is not possible how can you have something like this for all x ok. And so the answer is that this is possible if psi of x equal to delta of x minus a; that means, whenever psi of x is not equal to a, whenever psi of x is not equal to a then psi of x is 0 whenever x is not equal to a psi of x equal to 0, so x times 0 equal to a times 0 and this is satisfied. When x equal to a then you have delta of x minus a, so a times delta of x minus a is same as x times delta of x minus a. So, x times is equal to a times delta of x minus a. So, this is the property of the delta function and you can use this property to identify that delta of x minus a is what is called in quantum mechanics and eigenfunction of x operator with eigenvalue a.

So, this is something that you learn in your quantum mechanics course and I just want to show you and application of this. This is not usually discussed in various books, but nevertheless it is a very important idea and you know you can you can physically argue why something like this should be true. So, I want bother with that, but nevertheless you can keep this in mind.

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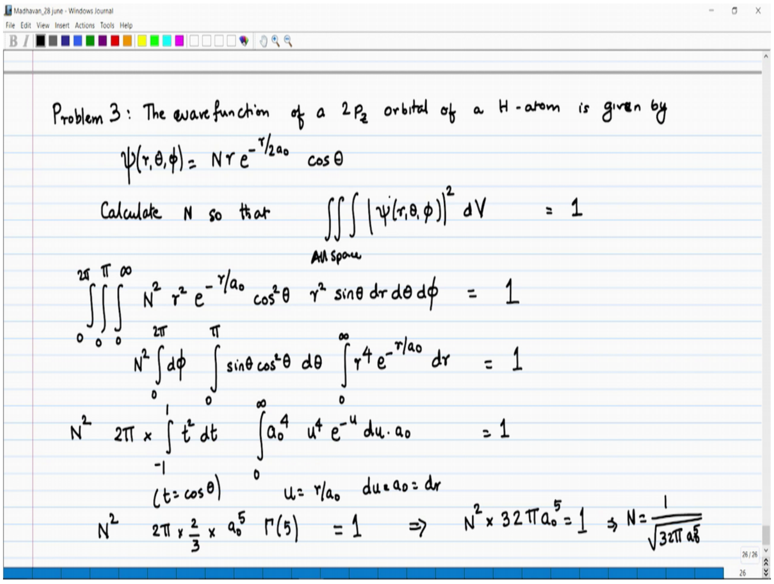

So, the last problem that I want to do has to do with spherical polar coordinates and here we are going to discuss how the spherical polar coordinates which appears naturally in the solution of the quantum mechanical hydrogen atom problem is actually used.

So, the problem statement is the wave function of a 2 p z orbital of a hydrogen atom is given by this quantity. So, psi I have written as a function of r theta and phi. So, usually in the hydrogen atom problem the nucleus is taken as the origin and the location of the electron is expressed in spherical polar coordinates and this wave function is has this fairly compact notation.

Now, what you do, what you have to do. So calculate n so that this integral is equal to 1 and you are integrating over all space all 3D space. So, let us work this out. So, this integral over all 3D space all right the triple integral now you have N square r square e to the minus, now you square this so we will get r by a 0 cos square theta. Now, I should not write d r d v theta I should write d V. So, it is d V. So, the volume integral now the volume integral in spherical polar coordinates is r square sine theta d r d theta d phi. So, you have to do this integral such that this equal to 1 and what are the limits the limits for r, r 0 to infinity, the limits of theta are 0 to pi, the limits of phi are 0 to 2 pi.

So, I can take the N square outside the integral and then the first thing you notice is that this whole integrand is independent of 5. So, I will just get, so I will just get N square times integral 0 to 2 pi d phi times integral now the theta part is basically sin theta cos square theta d theta from 0 to pi and then I have this integral 0 to infinity r square e to the minus r by a 0, r 4 sorry r square into r square. So, there are 4, r 4 e to the minus r by a 0 d r and this should equal to, this should equal 1.

So, now, this the first integral we will just give me a factor of 2 pi, the second integral if you want to do the second integral the easiest way to do it is to put cos theta equal to equal to x or equal to t. So, if I put cos theta equal to T then d T is sin theta d theta, so minus sin theta d theta. So, this becomes integral and when the theta equal to 0 then cos theta is 1. So, it becomes from minus 1 to 1 I am taking the minus factor there and what I will get is T square d T. So, I can write this in this form where I substitute, I substituted T equal to cos theta using that substitution you can get it in this form. And now here, here again you have a very familiar object here. So, suppose I put r by a, suppose I put r by a 0 equal to T, r by a 0 equal to u then r to the 4 is r is u times a 0 so r raised to 4 is a 0 raised to 4 and again the limits remain the same, and I have u raised to 4 e to the minus u, d u and d u times a 0.

So, what did we do in the second integral I put u equal to r by a 0, then d u into a 0 equal to d r. So, that was this last part d u into a 0 and then r by a 0 is u. So, I have e to the minus u and u is r times. So, r raised to 4 will be replaced by u raised to 4 a 0 raised to 4.

Now, this a 0 is the constant, now this integral is T cube by 3. So, T cube by 3 from minus 1 to 1 is 1 by 3 minus plus 1 by 3 that is 2 by 3. So, I have 2 pi into 2 by 3 into a 0 raised to 5, and then now what do we have here? You have integral 0 to infinity u raised to 4 e raised to minus u that is nothing, but gamma function of 5 and gamma function of 5 is equal to 4 factorial and 4 factorial is 24. So, this equal to 1 implies times and N square. Gamma function of 5 is 4 factorial which is 24. So, what this implies is that N square, 4 into 24 is 96 - 96 divided by 3. So, 96 divided by 3 is 32 - 32 pi a 0 raised to 5 equal to 1. So, implies N is equal to 1 by square root of 32 pi a 0 raised to 5.

So, this is the constant of proportionality such that this wave function is normalized. So, this is a very interesting problem in the hydrogen atom where we are using spherical polar coordinates and we are also using gamma functions. So, therefore, I think the tools that we learnt in this module are very useful in various areas especially in quantum mechanics of spherically symmetric problems like the hydrogen atom problem.

Thank you.