Advanced Mathematical Methods for Chemistry
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Module - 11
Lecture - 05
Recap of Module 11, Practice Problems

So, this will be the last lecture of module 11. And in this I will recap all that you have learnt, and then I will also do some practice problems. So, to recap we started in this module we basically talked about error estimates, probability, and probability distributions.

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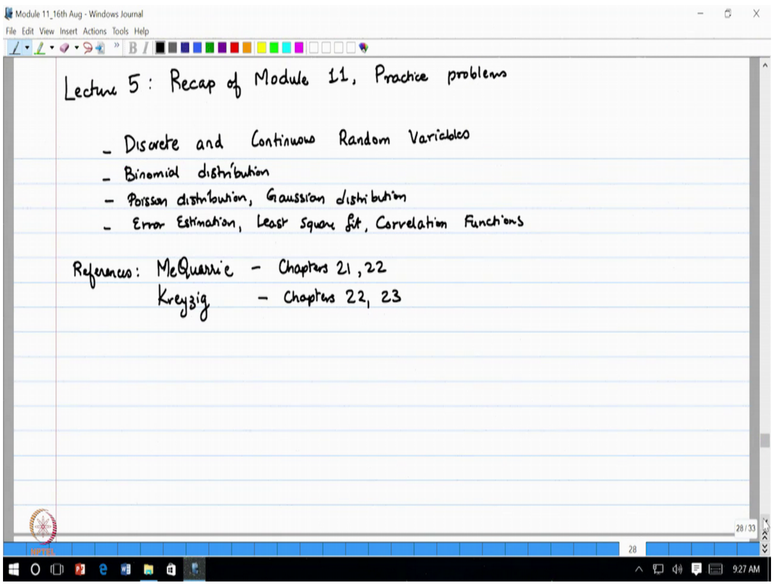

So, we started with talking about discrete and continuous random variables. And we talked about random variables and they are we talked about probabilities and probability distributions here. Then we talked lot about the binomial distribution which is one kind of distribution of discrete random variables. And we talked about Poisson distribution and Gaussian distribution. And then in the last lecture I briefly discussed error estimation, least square fit and correlation functions.

Now this these materials covered very nicely and McQuarrie in chapter 21 and 22, and also Kreyszig chapters 22 and 23. So, now let us do a few practical problems and I should I should say that you know these are tools that we have been using and lot of the mathematics that is involved these things that we already seen before. But in any case let us go and do a few practice problems.

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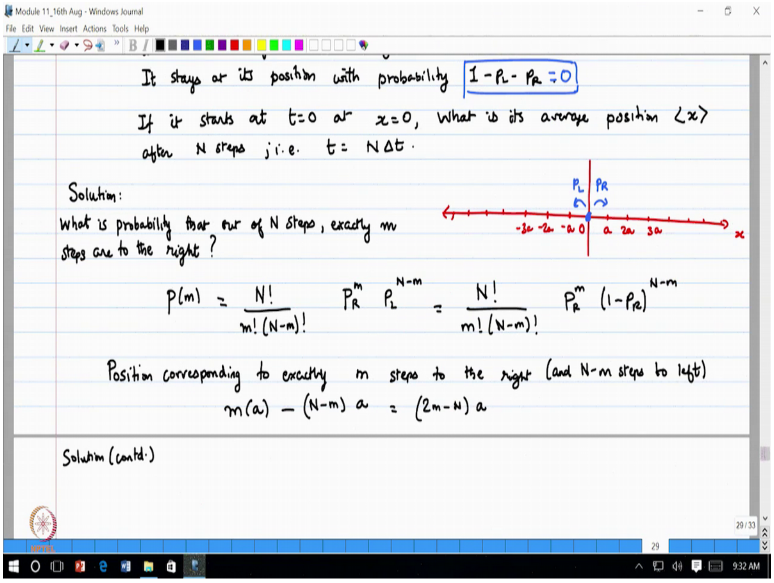

So, the first problem is what is called a one dimensional random walk. So, here a particle is on one d lattice of size a. So, just to clarify I will show you what this looks like. So, you have this is what you mean by a one d lattices, if this is the x axis and then you have various points this is 0, a, 2a, 3a, and so on. This is a lattice one dimension lattice minus 2a, here goes on. And the particle is on this lattice of sized say. And what your particle does is it sits on one of the sites; at time 0 it is on this site. And then it goes to the right with probability P R to the left with probability P L.

Well, for now let me set its states in position with 1 minus P R and let me set this to 0. So, we will set these to 0. So, what it does it; a every step it either most to the left or to the right. And it moves to the left with P R and left with P L and right with P R. And obviously, P L plus P R equal to 1, but they need not be equal to each other. Now what is its average position x after N steps; that is t equal to N delta t.

Now, what you can ask is. So, to solve this we say that what is probability that out of N steps m steps are to the right; exactly m steps. And this is basically your P of m which you write as N factorial divided by m factorial N minus m factorial; P right of m P left of N minus m. And P left is just p right minus. So, I will replace P left by 1 minus P right.

So, now the average position: so if exactly m steps are to the right. Ok let me first say- now, position corresponding to exactly m steps to the right and N minus m steps to left. So, what is the position, so where does it end up? Now you can say that if it makes m to the right it gone m times a, but it has gone N minus m to the left. So, it is m times a minus N minus m times a is equal to 2 m minus N times a. That is where it will end up if it does exactly m step to the right it will end up at 2 m minus N times a. And remember this can be less than 0 also.

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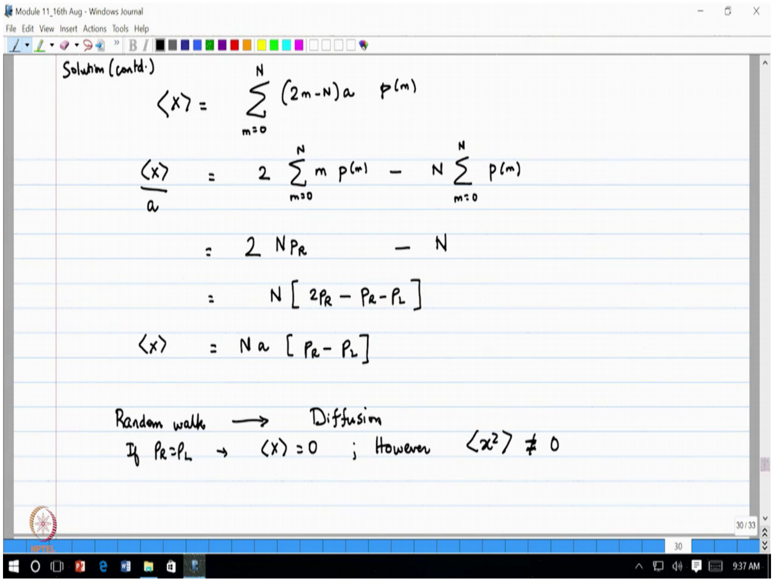

Now, average position is given by 2 m minus N times a times p of m and sum over m equal to 0 to N of this. So, this is equal to twice sum over m equal to 0 to N m times p m and I will divided by a I will take the a outside. So, twice m times p m minus N times sum over m equal to 0 to N p m, ok.

Now, we know the binomial distribution. Since we know that this satisfy the binomial distribution and it is normalized so this is just N. And this is the average value of m corresponding to the binomial distribution. And what we saw binomial distribution with this quantity P r. So, then the average value of m after n trials is just n times P R; N times P r. So, I can write this as N times 2 P R minus 1 and 1 I will write as P R minus P R plus P L is 1. So, average value of x is equal to N times a times P R minus P L. And this makes intuitive sense. This makes sense because in each step this P R chancre it goes to the right and P L chance it goes to the left. So in each step on average it moves this distance and in N steps it will move N a times this distance, but you can formally get this from this argument.

So, this is a use of the binomial distribution. And actually there is an important; there are lots of interesting other connections that you can make. So, the random walk is actually related to diffusion. This is a very important connection between random walks and diffusion. Now what you can see is that if P R equal to P L then average value of x equal to 0. That means, on average it will just be around that. However, average of x square is not equal to 0.

This is what is meant by diffusion, in the sense that on average you have not translated, but the particle is diffusing. So, you imagine that I open a cent bottle; I open a perfume bottle then the perfume does not go straight to its to; its target it sought of randomly hits around and you know executes its Brownian motion and then eventually it spreads out. So, average of x is 0, but average of x square will not be 0 in this case.

So, the point is there is a intimate connection between random walks and diffusion. And you can see this if you calculate the average of x square. The same problem you can take and calculate the average of x square and you will find that it is not equal to 0, even in P R equal to P L. ok.

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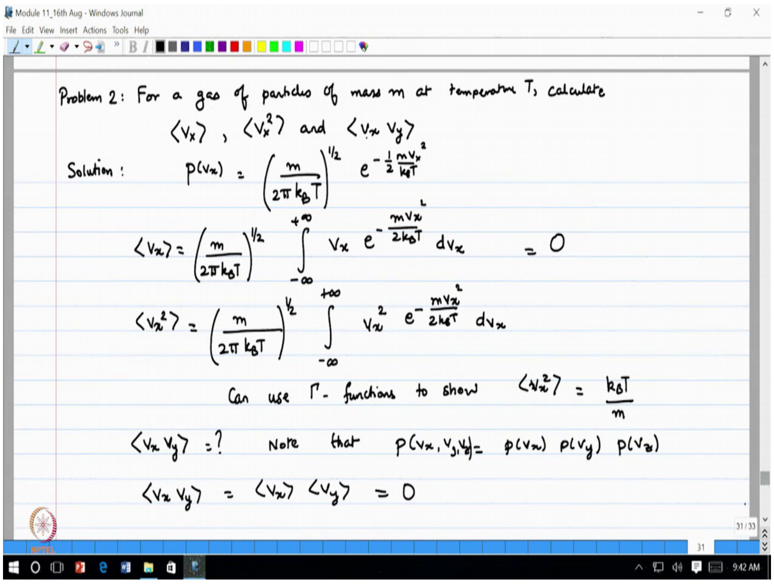

Now the next problem is for a gas of particles of mass m at temperature T calculate average value of V x average value of V x square and V x V y. So, this is a fairly straight forward problem. So, what you will say is that probability distribution of V x is equal to m by 2 pi k B T; you recall the Maxwell Boltzmann distribution raise to half e to the minus half m V x square by k B T. So, this is the probability distribution of V x.

So, you can calculate average of V x is equal to; so m by 2 pi k B T raise to half integral from minus infinity to plus infinity V x e to the minus m V x square by 2 k B T d V x. And now the range of integration is that minus infinity to infinity; the Gaussian function is an even function of V x and V x is an odd function so this is equal to 0. So, we have integral of odd function from minus infinity to plus infinity that is 0.

And if you calculate V x square, this is just m by is to half 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 this can actually be worked out. Again you use your gamma functions; can use functions. So, you can show V x square is equal to k B T by m. You can show this it is not a very difficult thing to show.

Now what about V x times V y: now note that p of V x V y is equal to p of V x into p of V y. So, V x and V y are independent variables. So, for a gas at equilibrium you in fact P of V x V y V z is equal to p of V x p of V y of V z. So, basically V x and V y are independent variables. So, average value of V x times V y is equal to average value of V x times average value of V y and this is equal to 0. Because average value of V x is 0 average value of V y is 0. So, we just used that the idea that they are independent variables to calculate their product of V x and V y; the average of the product of V x and V y.

Now the next problem is from quantum mechanics.

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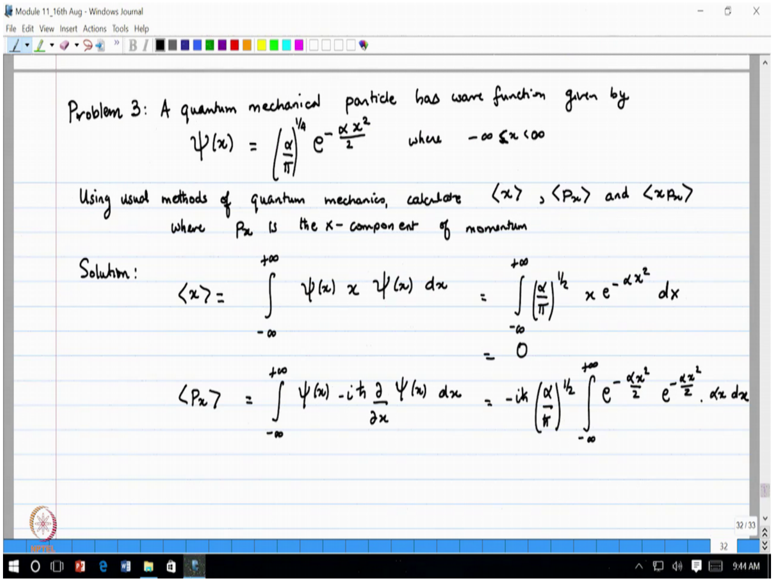

Here, you told that a quantum mechanical particle has a ware function given by this. Using the usual methods of quantum mechanics calculate average value of x P x and x P x. So, what I mean by the usual methods of quantum mechanics is that average value of x is given by integral minus infinity to plus infinity psi of x; now psi of x is the real function, so psi of x x psi of x d x. So, I do not need to write a complex conjugate here.

And this is equal to integral minus infinity to plus infinity alpha by phi raise to half x e to the minus alpha x square. So, I have x square by 2, but I am multiplying twice by itself so I get this. And clearly this is equal to 0. Now average value of P x is integral minus infinity to plus infinity psi of x into i h cross dou by dou x minus minus i h cross dou by dou x of psi of x d x. So, I can write it as minus i h cross integral minus infinity to plus infinity. And let me write this alpha by pi raise to half outside, I have integral minus infinity to plus infinity e to the minus alpha x square by 2.

Now I have to take a derivative of into the e to the minus alpha x square by 2. Now derivative of e to the minus alpha x square by 2 is e to the minus alpha x square by 2 into derivative of alpha x square by 2 which is just alpha x. And you can again see that you have an odd function, you have x times e to the minus alpha x square by 2. Alpha is the constant so I can write this equal to 0.

Now next your asked to calculate the average value of x P x.

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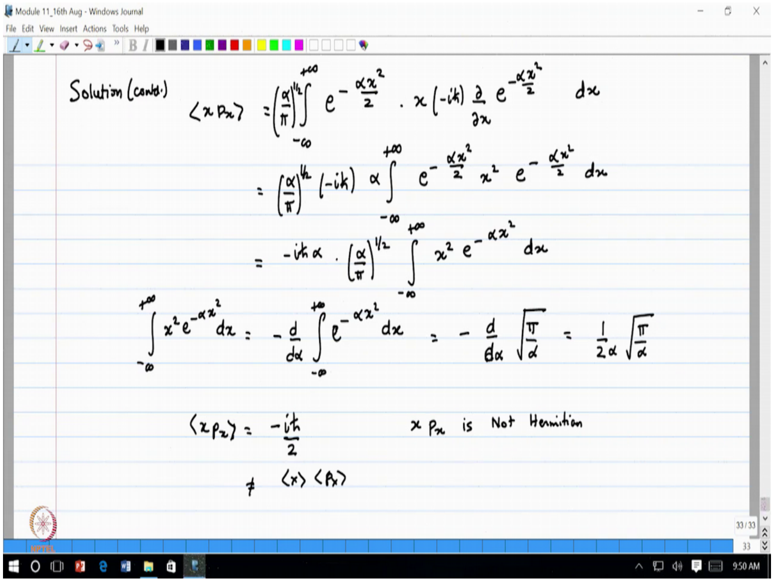

Integral minus infinity to plus infinity, now I will take the alpha by pi raise to half and then what I will have is e to the minus alpha x square by 2 times x into minus i h cross dou by dou x of e to the minus alpha x square by 2 dx.

So now, what I will have is alpha by pi raise to half minus i h cross, and then what I have is integral minus infinity to plus infinity e to the minus alpha x square by 2. And now I just take this so I have alpha, I will take the alpha site now I have alpha alpha x into x. So, x into alpha x that is alpha x square so you take the alpha outside x square e to the minus alpha x square by 2 dx.

So, I can write this as minus i h cross alpha times alpha by pi raise to half integral minus infinity to plus infinity x square e to the minus alpha x square dx. So, I have to evaluate this integral and I can use gamma functions. I will use a little trick evaluate this integral; so little trick to evaluate this integral.

So, we will write integral of minus infinity to plus infinity: x square e to the minus alpha x square d x is equal to minus d by d alpha of integral minus infinity to plus infinity e to the minus alpha x square dx. So, if I do d by d alpha of this then I will get the same thing and then I will have to take the derivative of this that is minus x square. So, I am taking derivative with respect to alpha, so I will get minus x square. And then so I can write as in this way. Now I am taking the minus derivative of that so minus will go away.

So, this is minus d by d alpha square root of pi by alpha is equal to 1 over 2. Now you have square root of pi divided by alpha to the three half. So, I write as 2 alpha square root of pi by alpha, minus sign will cancel that. So, then this integral is just 1 over 2 alpha 2 square root of pi over alpha. So, then what you will get is just minus i h cross now what you have is by 2 that is all you have; minus i h cross by 2, ok.

Now, this seems like a same result that x times P x is this, but you should remember that in quantum mechanics x and P x are not commuting variables. And so you often when you take the product of x and P x you have to anti cemeteries it and then only you get a real variable. So, remember x P x is not hermitian. So, x P x is not is not a hermitian operator in quantum mechanics. So, that is why you even got average value which is complex; we just imaginary in this case.

So, now also notice that average value of x and average value of P x are 0. So, x times P x is not equal to average value of x times average value of P x. So, for this particular problem average value of x P x is not equal to average value of x times average value of P x. In this case you would say that x and P x are actually are correlated in some sense, but we should also keep in mind that you know x times is not a hermitian operator. So, things will be quite different in this case.

So, I will conclude module 11 with this. And we will start module 12 the following week.

Thank you.