Introduction to Molecular Thermodynamics
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Lecture - 09
Microstates of a System (Contd.)

Welcome. Let us continue our discussion on the microstates of a system in equilibrium. We have already looked at how to define the microstates of a given system, if the solution to the Schrodinger wave equation to that system is known. And for this purpose, we have already found how to calculate the number of microstates for N distinguishable non-interacting particles.

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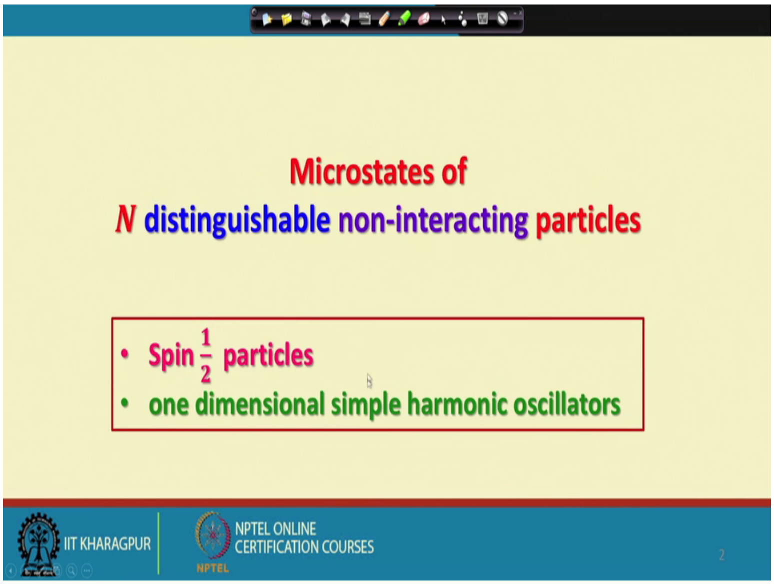

In today is class I am going to focus mainly on spin half particles, and later on we will also see what happens for the similar discussions on one dimensional simple harmonic oscillator.

So, the basic idea that we have already introduced is this that first I am interested in the definition of the microstate for a system in equilibrium, and then I am interested in calculating the number of such microstates. Why I am interested in the number of microstates under a given equilibrium condition? I have not explained that question yet.

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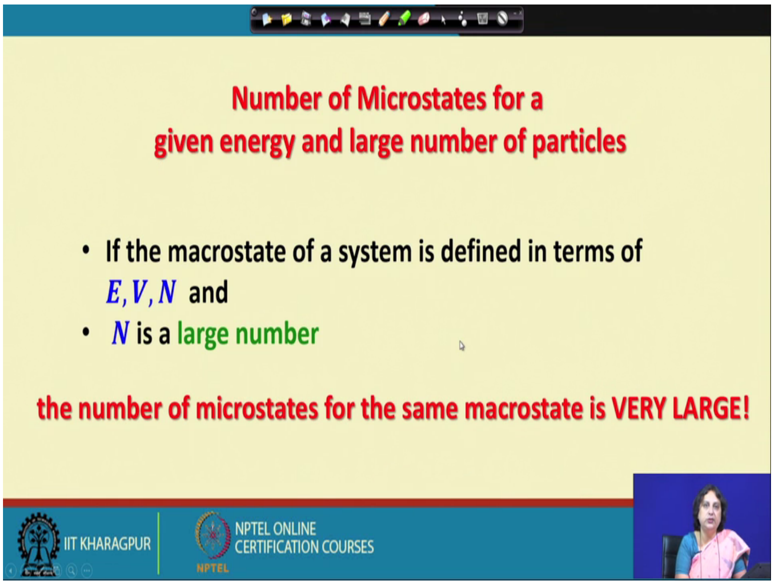

But, what we have done so far is- we have said that if the thermodynamic equilibrium of a system is defined. In terms of the total energy E, the total volume V and the total number of particles N, and if N is a very large number because the kind of values of N that we are interested in are typically of the order of 10 to the power of 23; then we have seen that the number of microstates for the same macro state is a very very large number. This we have already seen.

So, in today is lecture what I will try to demonstrate to you is one step further in this discussion, and the question that I ask is how does the number of microstates change for different values of the total energy.

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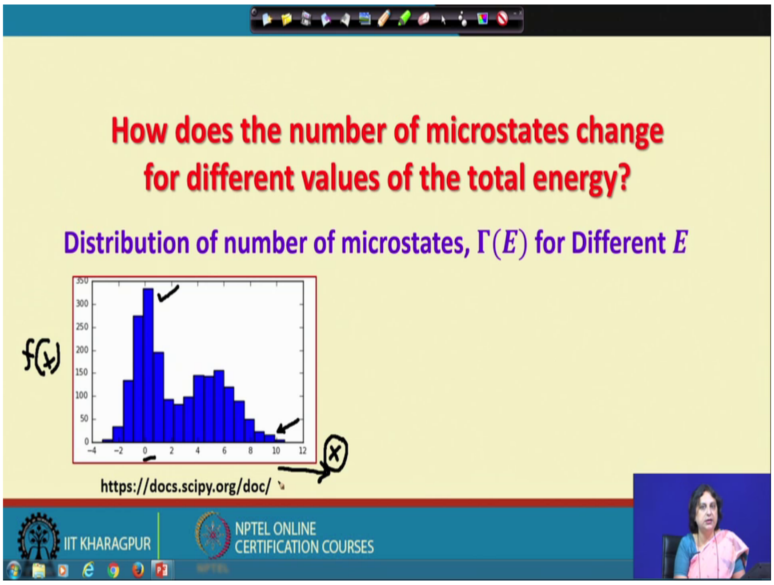

So, in this in answering this question, it is found that it is convenient to talk in terms of distributions. In your introductory courses in probability and statistics you know that if you are carrying out an experiment and the outcome is not certain, and that there may be many different outcomes possible, in that case the experimental results are described in terms of a distribution function. For example, one main present the experimental result using a plot like this, where along the x axis you are plotting the different possible values of measurement of this quantity x. And here you are plotting the frequency or the number of times this particular value of x appears.

So, in this case what I find is that x can take up values from say minus 4 to plus 12, but if I make a very large number of measurements on this system, what is the value of x that I will be getting in most of the times? I find that the number of times I get a value close to 0 and between maybe close to 0 is maximum. If I ask this question how many times shall I get the value its equal to 10, as you see that this comes much less frequently compared to the value x equal to 0. And therefore, the key points over here is that if you make a measurement on the system, x the measurable quantity can take up many possible values and the outcome of your experiment maybe any such value.

So, now if you perform this experiment a very large number of times, in that case you got to start compiling the number of times each value has been recorded, and that gives you the distribution function. So, are there any common forms of the distribution function? Perhaps the most common one is what is known as the Gaussian distribution which looks something like this.

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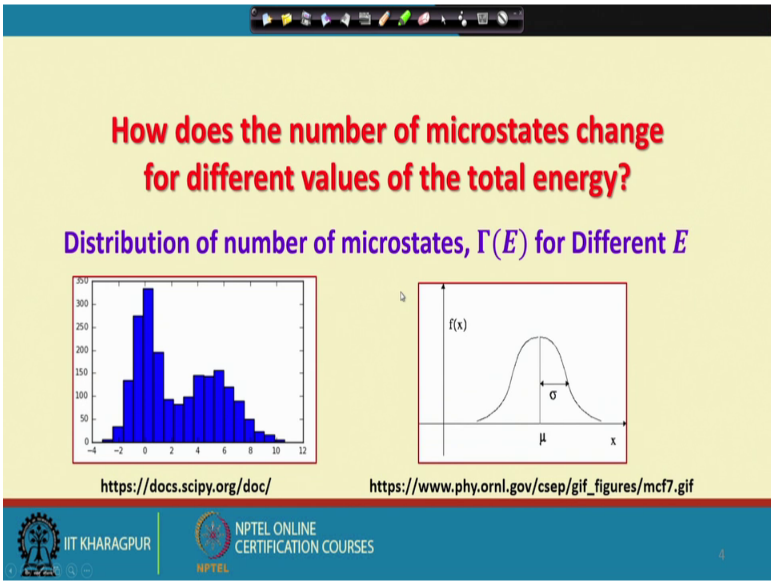

It is symmetric about a mean value, where it exhibits a maximum and then it symmetrically falls off at x deviates from this value x equal to mu.

So, my question is, is it possible to represent the number of microstates in terms of one such distribution function, when I carry out a simple experiment like the measurement of the total magnetic moment of a spin half system. So, this is what we are going to see next.

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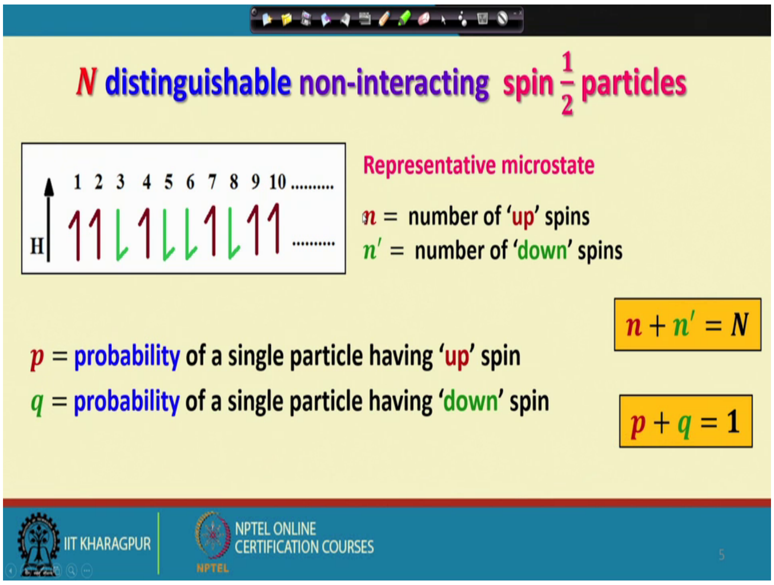

Now, please remind yourself that we are dealing for the sake of simplicity; a very simple system where I have capital N distinguishable non-interacting spin half particles, and correspondingly this is a typical representation of the microscopic state of the system now why do I say that they are distinguishable? That is because each of them carry a different label attached to it. So, how many such spins are present? Capital N such spins are present I have only shown a few. Now where this particular spin depending on the direction of the applied field can have an up spin, or in some other microstate it can have a down spin where it is oriented anti parallel to the applied field.

Now, the question is then how do I represent the microstate of a system which is pictorially represented here. The microscopic state of the system is as we have seen defined in terms of the number of up spins and the number of down spins. So, let us say we adopt this notation that small n is a number of up spins, and small n prime is a number of down spins.

So, in for such a representative microscopic state, the next question that we ask is let us say that the probability of finding a given spin in the up orientation is p. So, that is exactly what I have shown here. So, I am assigning a probability p of a single particle having an up spin, and similarly I am assigning a probability q for that particle having a down spin. Now till now I have not been talking about the probability of having this single particle either in the up spin or in the down spin except that I have said, that there are only two such possibilities allowed by quantum mechanics.

Now, what I find here is if I introduce these two conditions, that a representative microstate must have n up spins and n prime down spins, and the corresponding probabilities are p and q, then I must be having two conditions satisfied. First the number of up spins plus the number of down spins must add up to the total number of particles n.

Similarly since there are only two options for a given spin, I must be having p plus q equal to 1. So, this is the normalization condition. Now you must be wondering regarding I always said that the number of microscopic states is a function of the total energy total volume and that total number of particles.

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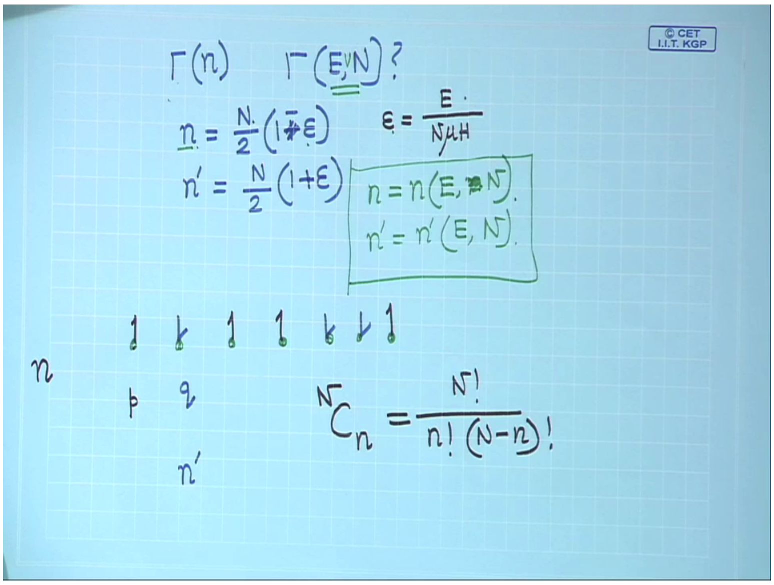

And here I am representing gamma as a function of n.

Now, the question is does it mean that gamma is no longer a function of E and N? Actually in a previous class we have seen that under the given condition small n is equal to capital N by 2 into 1 plus epsilon, and n prime is equal to capital N by 2 into 1minus epsilon. Sorry this is 1 minus epsilon and this is 1 plus epsilon. So, what is epsilon? Epsilon by definition is given by e the total energy divided by capital N mu h.

So, as you can see therefore, if I am representing the microstates in terms of either E,V or N, it is equivalent to say that N is a function of epsilon and N and epsilon is a function of

E therefore, here n is a function of capital E and the total number of spins capital N and n prime is similarly a function of E and N and I am implicitly keeping the volume constant in which this system is present.

Now once I understand this, then the question that we face is what will be the number of microstates associated with the different values of small n that is the number of up spin. You must realize that simply because I have capital N plus n prime equal to capital N between n and n prime only small n can vary as an independent variable. The value of n prime is always capital N minus small n.

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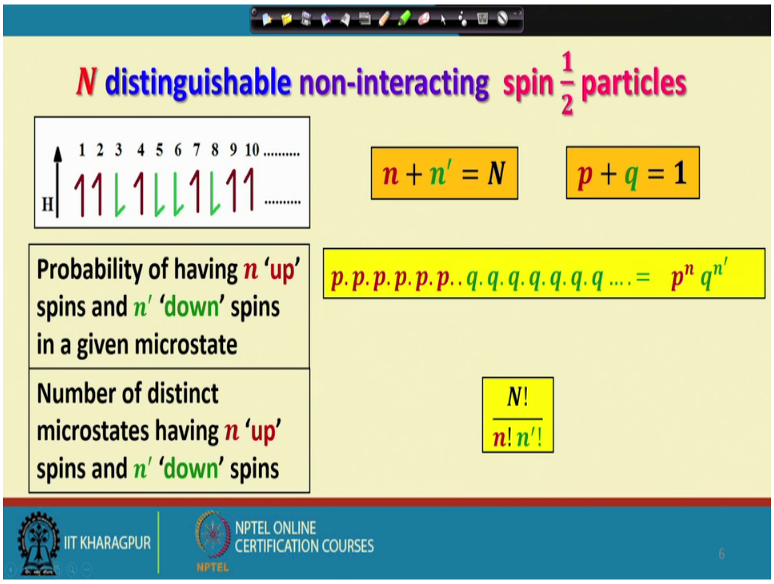

Now with this background in mind, now let us have go and have a look at the kind of distribution that we are talking about for a system like this. Now I asked the question what is the probability of having a microscopic state that has kept small n up spins and small n prime down spins. So, it would be given by a number like this.

So, particle 1 the probability of let us say that particle 1, particle 5, particle 7, etcetera they have up spin and the other particles have down spin. So, if I have small n such sites having up spins. So, let us say that I have a total of say capital N of these sites, some of them are having up spins. This is 1, this is 1, this is maybe 1 this is another one and I also have other sites being occupied by down spins. So, by the definition I know that; what is the probability associated; with this site having an up spin that is p, how many such sites are possible for this particular microstate that is n.

Now, the probability of having a down spin at any given site is q, and how many such q terms are present that is n prime. And since these spins are non-interacting therefore, the probability of whether a particular site has an up spin or a down spin does not depend on what happens, what is happening to the other spins. Therefore, probability associated with having small n up spins and small n down in prime down spins, will be given by small n such terms having probability p multiplied by small n prime such terms having each having probability q. And therefore, this probability will turn out to be small p to the power of n, into small q to the power of n prime.

Now once we know this, then the question that I have here is, I have now the probability of having n up spins and n prime down spins for a given microscopic state, but how many such distinct microscopic states are possible, that will be having small n up spins and n prime down spins, this number can be very easily calculated and this is given by capital N c small n. So, out of an assembly of capital N spins, you are going to choose small n spins with up direction and the rest as a down direction and that is given by N factorial divided by small n factorial and capital N minus small n factorial. So, this is exactly what I have shown over here.

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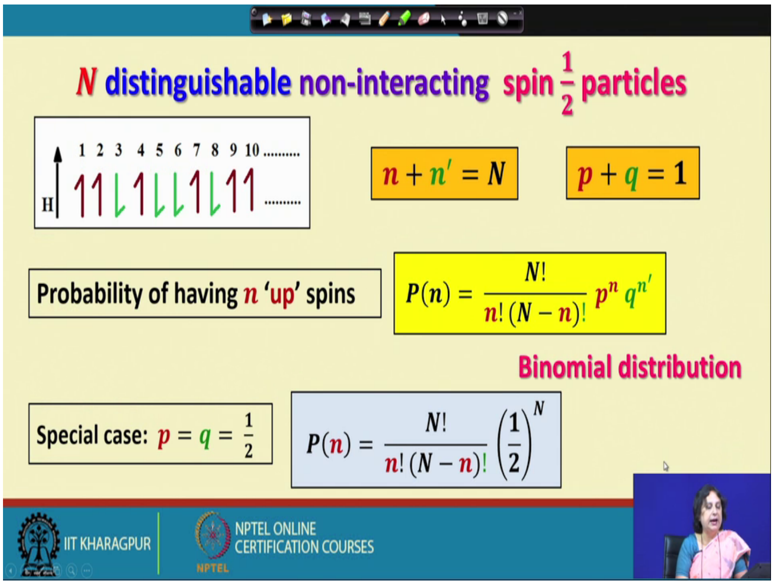

Then for a system like this, I can very easily say that what is the probability of having small n up spins in a system like this?

This is given in terms of this distribution function P n. As you see that p n has two parts; this is the part that corresponds to the probability of a given microstate having small n up spins and n prime down spins, where at each site small p is the probability of having an up spin and small q is the probability of having a down spin. And this part is the contribution of having these many distinct microscopic states associated with small n and capital and n prime.

Once we understand this, then I we can go back and we can say that well this is actually a specific representation of a binomial distribution, and most of the cases we are interested in the special condition where small p is equal to small q equal to half, in that case the binomial distribution takes up the following form, where you have this coefficient and then you have half whole raised to the power of capital N. Now let us have a look at the consequence of having this binomial distribution, and how we can use these concepts in understanding the number of microscopic states. That are possible for a given macro state and what would be the outcome of a measurement, that I make on a system comprised of capital N distinguishable non-interacting spin half particles.

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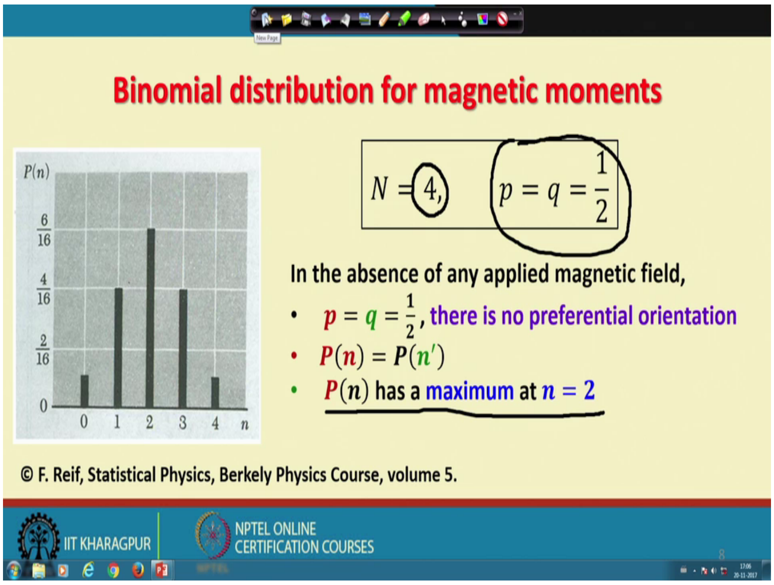

So, let us now have a look at how the binomial distribution looks like for a small number of spin half particles. In this example we have taken capital N equal to 4 and we have also fixed the individual probabilities of having up and down spins equal to half and what does it mean it means? That I am now considering the 4 spin half particles in the absence of any external applied field; as a result there is no similar preference for any given orientation parallel or anti parallel to the field. And as a result of it now p is equal to q and this value can only be equal to half.

Now let us have a look at how the binomial distribution for such a case would look like. So, here what I have is, I have plotted small n the number of up spins along the x axis and p n the probability of observing small n up spins along the y axis.

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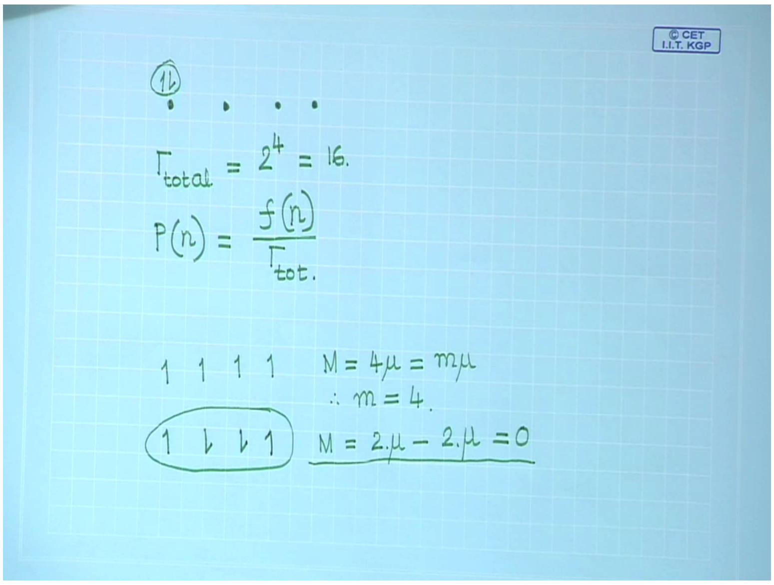

So, here in this example you have how many positions? You have 4 positions; in each position you can have either up spin or down spin. So, what is gamma total? The gamma total will be given by 2 to the power of 4 and that is 16. So, what is the probability of observing one particular event? So, that probability p n will be given by the number of times you have observed the n up spins divided by gamma total. It is very easy to show that if you have n equal to 0 or 1 or 2 3 or 4 the correspondingly f n values are going to be equal to 2 4 6 like that.

So, here what we are plotting is if I make a very large number of measurements on a system like this, what is the probability that I will see small n equal to 3? So, I will I find that that is given by 4 by 16. Similarly if I ask this question what is the probability that small n is equal to 2? I will find that the probability is 6 by 16. So here therefore, the major conclusions from this slide are as follows; in the absence of any magnetic field there would be no preferential orientation. Therefore, the probability of a given spin half particle in having up spin or a down spin will be the same and this value is equal to half.

And the probability associated with the value n is the same as the probability associated with the value n prime, and I also see this very important characteristic that p n has a maximum at small n equal to 2. Please note that under this condition where p is equal to q this value where the maximum appears is actually capital N by 2. We will see the consequence of all these observations later, but now the question that I want to pose is whenever you are studying a system of spin half particles what is it that you measure. We measure the total magnetic moment, and when you measure the total magnetic moment, so, it is not small n that you talk about rather you talk about the value of the total magnetic moment of the system.

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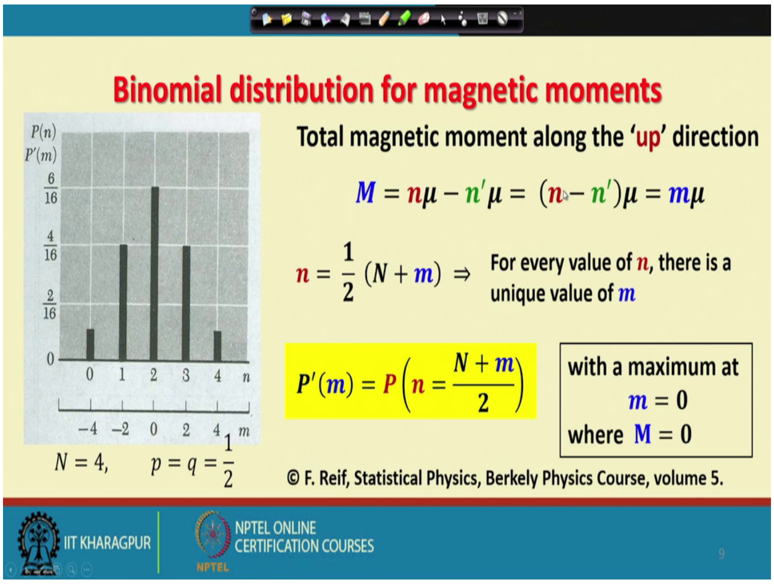

So, it is possible to show that a binomial distribution that is describing P of n can be very easily used to describe the P of n that is a distribution of the magnetic moment. So, let us see how this can be done. So, the total magnetic moment along the up direction by definition is given by the magnetic moment in the up direction, multiplied by the number of such magnetic moments then if I have n prime magnetic moments pointing anti parallel or down, then the associated magnetic moment along the up direction is minus mu. So, this gives the contribution of all the spin half particles that are aligned anti parallel to the up direction.

Therefore, if I combine then it is possible for me to show that this capital M that is the total magnetic moment along the up direction is given by sum numbers small m into mu. So, what is mu? Mu is the intrinsic dipole moment associated intrinsic magnetic moment, associated with each spin half particle. Now it is then possible to do a little bit of algebra, and show that initially we were using small n.

And now I am going to use small m as my independent variable in my binomial distribution and I find that there is a for every value of small n that is a unique value of m which is given by this expression, and that follows from the definition of the total magnetic moment that I have used here. So, basically then I understand that this relationship is valid. The probability distribution associated with the value of m is nothing, but the probability distribution associated with those values of n where small n is equal to capital N plus small m divided by 2.

So, now what will happen is, where do you expect. So, let us have a look at the resultant binomial distribution. So, as you see along the x axis when I plot small n, the value start from 0 and goes all the way up to 4, because I have capital N equal to 4. Now what are the corresponding values of small m?

The corresponding values of small m are given along this direction. As you see when small n is equal to 4, it means that all the 4 spins are pointing up therefore, what is the net magnetic moment of this system? That is equal to 4 into mu and I know that this is equal to small m into mu therefore; it says that small m is equal to 4. Now if I consider the case where this particular case, where I have small n is equal to 1. In this case I must be having a typical macroscopic state as this is that so, no this will give you capital M.

That is equal to 2 up spins with mu, minus 2 down spins with mu that is equal to 0. And therefore, I would say that this microscopic state is associated with capital M equal to 0 now therefore, small n is equal to 1 a small n is equal to 2 is associated with small m equal to 0. And this way one can map the original p of n onto p prime of m and they exhibit the same behaviour whereas, there is a maximum and now the maximum is located at small m equal to 0 where the net magnetic moment vanishes.

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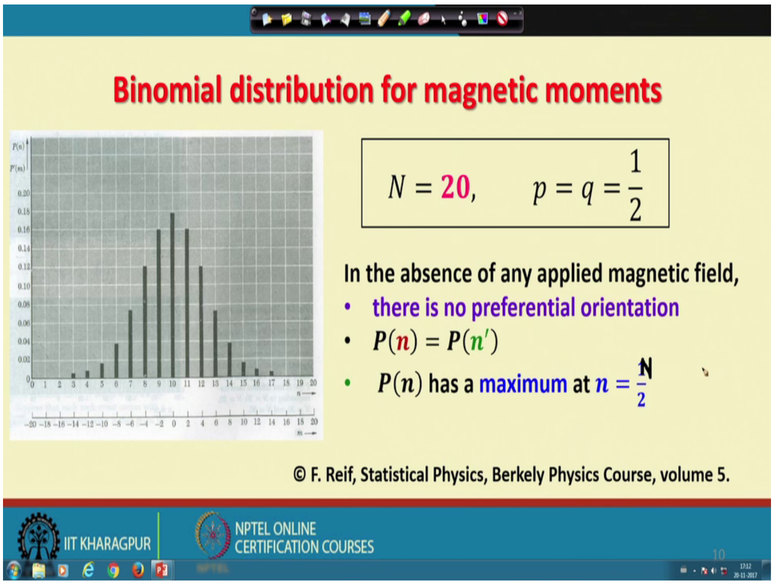

Now, in the next slide let us still have no applied field in the system, but we have a larger number of spin half particles. And in this example we have taken the total number of particles equal to 20, and as you see here because of capital N equal to 20 small n can now vary from 0 to plus 20, when small n is equal to 0 all the spins are pointing downwards when small n equal to 20 then all the spins are pointing upward. And here the conclusions are very similar to what we have got for capital N equal to 20. So, in the absence of any applied magnetic field. Once again there is no preferential orientation P n is equal to P n prime and P n has a maximum, once again at capital N as a maximum at capital N divided by 2.

So, we will conclude this particular lecture by summarizing, we have shown that if there is no external applied field, it is possible to associate a discrete distribution to the number of microstates possible for each value of an observable. In this case the observable is the magnetic moment of the system, and we have shown that how a binomial distribution can be used to show the distribution of a small number of spin half particles, and where each spin has only two possible orientations up state and down state.

Thank you.