Chemical Principles II
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Calculation with Multi-Level Systems with Fixed Energy
Part - 02

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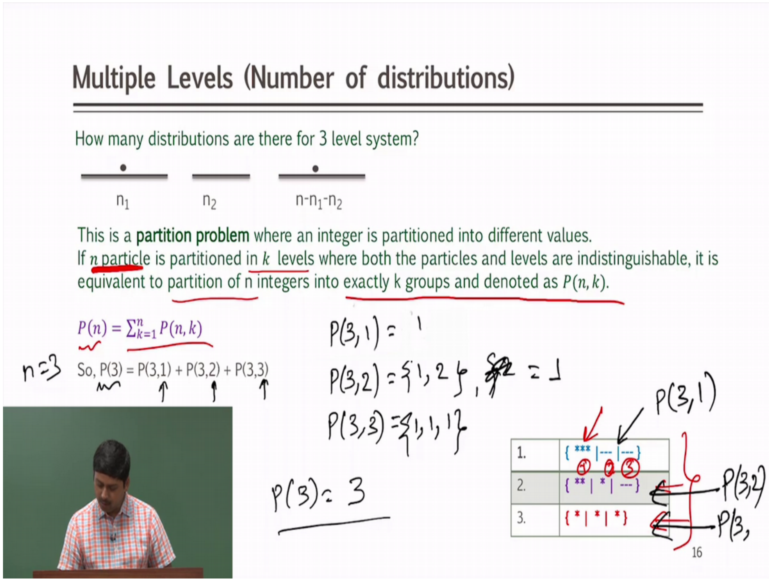

So now how many distributions are there when there are, you know 3 levels or how many distributions are there for a 3 level system, how many distributions? We saw that it is 3 distribution A, B and C, but you get a number because we can get a number when we try to calculate indistinguishable particles in distinguishable cells, remember we discussed about that before, stars like indistinguishable particles and these are boxes, box number 1 box number 2 and box number 3.

So it is an indistinguishable particles in indistinguishable box problem, I think if you are not confused with, now all this indistinguishability and distinguishability, then there are only 3 things that is possible, particles are distinguishable, levels are distinguishable that is one particles are indistinguishable, levels are distinguishable, that is another and both are indistinguishable, so we are talking about a both are indistinguishable, the reason is that, since the levels are also indistinguishable this 3 stars does not matter which box it belongs to, it will give you the same value. 2 star, 1 star boxes are indistinguishable does not matter and of course in this case anyway, it has to be in all the 3 different boxes.

So this problem where we need to figure out that how many possible distributions are there, when of course there is no energy constrain or anything, it is a problem of partitioning an integer number, for example if we have N particle which is partitioned into K levels where both the particles and the levels are indistinguishable, it is equivalent to partition of N integers into exactly K groups and that is denoted by PNK.

For example I will give you some example that and total number of partitions of course to the will be sum over K equal to 1 to N, let me give you an example if how many ways I can partition my 5, 5 is an integer, how many ways I can partition, so I have already have an example, so I will just go with that, I will go with that, so let say I want to partition number 3, so N equal to 3 here and K can be 1, can be 2 and can be 3. Okay.

In order to get that how many ways I can separate my 3 into one part, only one way that is 3 because there is only one way, I am breaking 3 into only one way, how many ways, so P-3 is nothing but 1, how many ways I can break 3 into 2 parts 1, 2 and 2,1,1, 1,2 is the same. Okay 2, 1 and 1,2 are same because they are indistinguishable boxes as well, so 3, 2 also can be only one way and how many ways I can distribute 3 into 3 parts only one way 1, 1 and 1.

So you see P-3 then is sum of all that 1+1+1, so it is only 3 okay, so as you can see that P-3 equal to 3, so I am partitioning my 3 into 3 different possibilities and it is denoted here, you see this distribution is nothing but P-3 into only one, 3, 1 this is nothing but P-3, 2 I am breaking it into 2 parts and this is nothing but P-3, 3.

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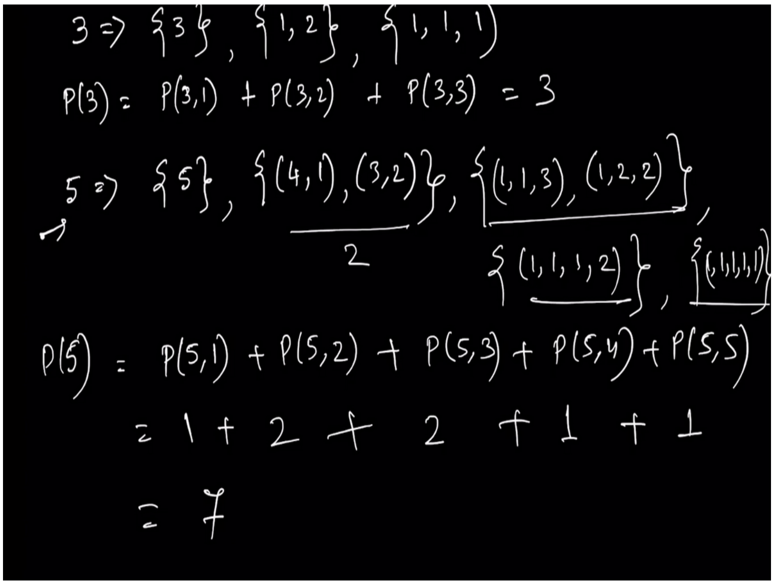

So first I give you the example and then we will write, so let say I want to partition, so we have seen that if I want to partition my 3 into different levels. I can do, I can partition into only one group which is 3, I can partitioning into two groups as 1, 2 because 2, one are equivalent and I can partition into three groups as 1, 1 and 1, now this one is typically called 3, 1, P-3, 1, this will be called P-3, 2 because I am dividing 3 into two parts and this will be called P-3, 3 because I am dividing 3 into three parts.

So in general I am getting P-3 as the sum of all of that as 3 okay, so now let us do same for 5, now 5 can be divided into one group as just one way 5, 5 can be divided into two groups as 4, 1 or 3, 2, 1, 4 the same 2, 3 is same and is there any other way no, so 5 can be divided into two groups as only these two possible ways, 5 can be divided into three groups as 1, 1, 1, 1, 2 +3, 1, 1, 3 one way 1, 2, 2 other way, is there any other way I can divided it no, so that is possibility.

Now 5 can be divided into four groups as 1, 1, 1, 2 and no other way and 5 can be divided into five groups as only one way 1, 1, 1, 1, 1, so now which means that I can write P5 as some sum 5, 1 +5, 2 +5, 3 +5, 4 +5, 5, now 5, 1 I got as 1, 5, 2 I got as 2, 5, 3 I got 2, 5, 4 as I got 1 and 5, 5 I got as 1, so 2+1, 3, 5, 6, 7, so be 5 that means 5 integer can be partitioned into all possible ways in the 7 possible ways max, which is then equivalently saying is that 5 particles can give rise to 7 possible distributions, if I do not constrain my energy.

If there is no energy constrain is their then I can get 7 possible distribution, so just like from 3 we got 3 distributions, from 5 I can get 7 distributions, now how do I know for general number, do I have to write like this or is there any better formula available.

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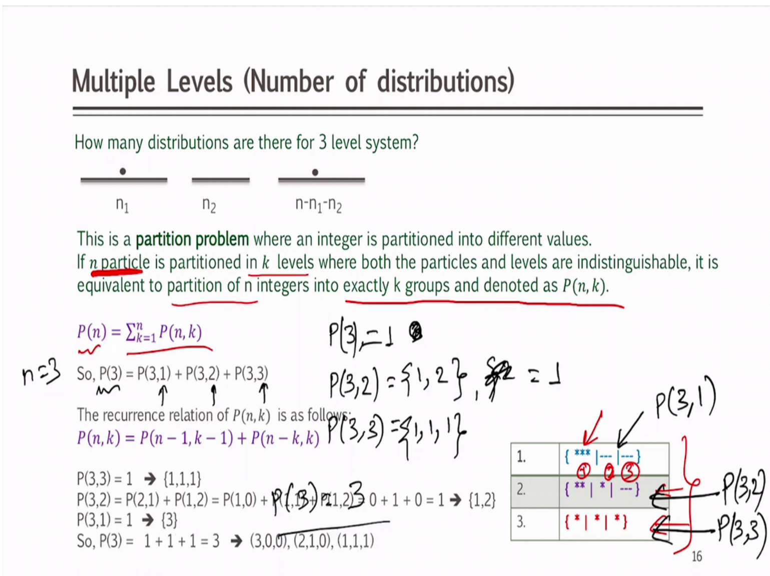

Distributions increases with number of levels

So, P(5) = P(5,1) + P(5,2) + P(5,3) + P(5,4) + P(5,3) + P(5,2) + P(5,1)

P(5,1) = 1
P(5,2) = P(4,1) + P(3,2) = 1 + P(2,1) + P(1,2) = 1 + 1 + 0 = 2
P(5,3) = P(4,2) + P (2,3) = P(3,1) + P(2,2) + 0 = 1 + 1 = 2
P(5,4) = P(4,3) + P(1,4) = P(3,2) + P(1,3) + 0 = P(2,1) + 0 = 1
P(5,5) = 1

So, P(5) = 1 + 2 + 2 + 1 + 1 = 7

(Verify with mathematica)

For large n, $P(n) \sim \frac{1}{4n\sqrt{3}} Exp\left(\pi\sqrt{\frac{2n}{3}}\right)$

$$P(n,k) = P(n-1,k-1) + P(n-k,k)$$

$$P(11,3) = P(10,2) + P(8,3)$$
$$= P(9,1) + P(8,2) + P(8,3)$$
$$= 1 + P(7,1) + P(6,2) + P(7,2) + P(5,3)$$
$$= 1 + 1 + P(5,1) + P(4,2) + P(6,1) + P(5,2) + P(5,3)$$
$$= 3 + 1 + P(3,1) + P(2,2) + P(4,1) + P(3,2) + P(4,2) + P(2,3)$$
$$= 9 + P(4,2)$$
$$= 9 + P(3,1) + P(2,2) = 11$$

Distributions increases with number of levels

So, P(5) = P(5,1) + P(5,2) + P(5,3) + P(5,4) + P(5,3) + P(5,2) + P(5,1)

P(5,1) = 1
P(5,2) = P(4,1) + P(3,2) = 1 + P(2,1) + P(1,2) = 1 + 1 + 0 = 2
P(5,3) = P(4,2) + P (2,3) = P(3,1) + P(2,2) + 0 = 1 + 1 = 2
P(5,4) = P(4,3) + P(1,4) = P(3,2) + P(1,3) + 0 = P(2,1) + 0 = 1
P(5,5) = 1

So, P(5) = 1 + 2 + 2 + 1 + 1 = 7

$P(11,3) = 11$

(Verify with mathematica)

For large n, $P(n) \sim \frac{1}{4n\sqrt{3}} Exp\left(\pi\sqrt{\frac{2n}{3}}\right)$

So let us see that, so skip this part, so this part. I have just shown you, just now, so as I said that for 5 it will be 7, now what is a general formula, so that general formula for large N is very complicated, we are going to show you in mathematic just now, general formula is very large, it is exponential it will increase but there is a recurrence relation that one can use and that is PN, K is PN -1, K -1 plus PN minus K, K this is a recurrence relation one can use that.

By the way, this part is, you know outside the syllabus, you know, this is if you are curious only then only you can look at it, otherwise the best way to do is just to look and see how you can partition that and we will not use in the exam much higher number of N or K, but this is just for the curiosity for curious student, if you want to understand how it can be done this is subject call partitions in number theory and using his recurrence relation we can get that.

For example if I take an arbitrary N and K, I want to try out 11 particles into 3, how many possible ways I can do that, so if I want to do that I have to do same formula N -1, K -1 which will give me 10, 2 plus P 8, 3, now 10, 2 can give me 9,1 + 8, 2 N -K, K plus I have 8, 3, now 9, 1 or anything 1, when K equal to 1, there is only one way of doing it, so I have to divide by integer into one possible ways that will give me always 1, now 8, 2 again 7, 1 + 6, 2 and 8, 3 can be 7, 2 + 5, 3.

So 1+7, 1 can give me only one way, whenever there is K equal to 1 that is only one way 6, 2 I can write as 5, 1 + 4, 2 + 7, 2 can be written as 6, 1 + 5, 2 + P 5, 3 is already there, so P 6, 1 can be written in also one way, so I have got 3 already plus this one can also be written in one way 3+1 4, 4, 2 can be written as 3, 1 + 2, 2, now 5, 2 can be written as 4, 1 + 3, 2 and 5, 3 can be written as 4, 2 + 2, 3, now that will be interesting, now you see 3, 1 is also 1, 2, 2, that means integer 2 dividing into two parts that is only one way, so this also gives me 1, 4, 1 will also give me 1, 3, 2 dividing 3 into two parts only one possible way 1 and 2, 3 into two parts.

There is only one possible way, that also give me 1, so now I have 3+1 4+1 5+1 6, 7, 8, 9 I got already 9 there plus I have to still break P 4, 2 and P 2, 3, now whenever N becomes less than K, less than 3 that means how can I divide 2 into three groups, minimum I need 1, so this is going to be 0, now what is 4, 2, 4, 2 is again I can do, 3, 1 + 2, 2, now you know 3, 1 is also 1 and 2, 2 is 1, so I am getting 11, 9+3, 1 is 10 + 2, 2 is 11, so I am getting 11 as a number, you can verify this, so we got P 11, 3 as 11 and you can verify that it mathematica.

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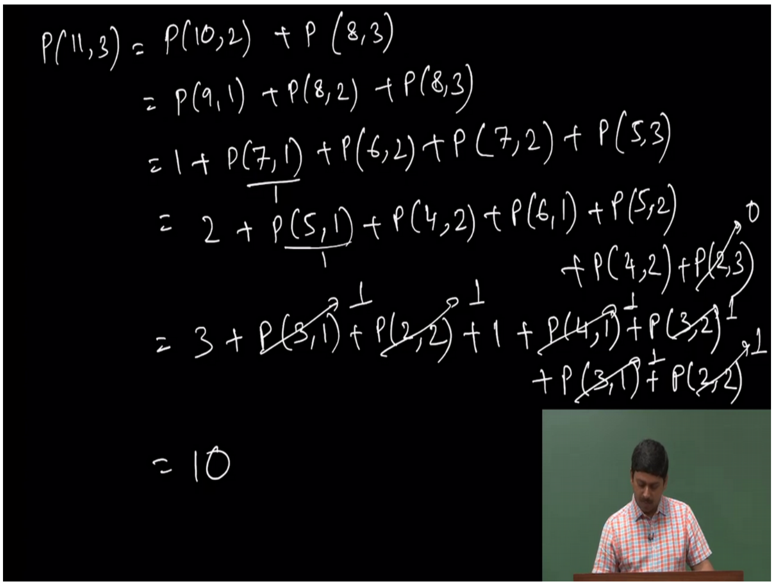

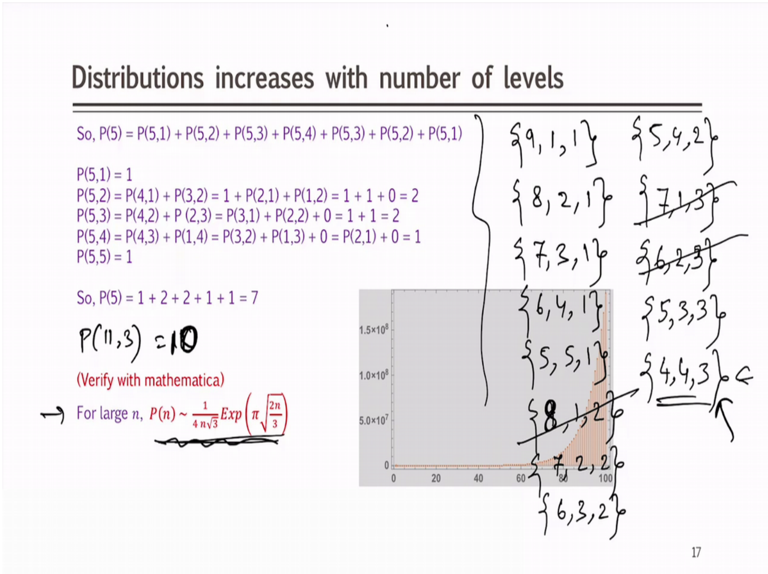

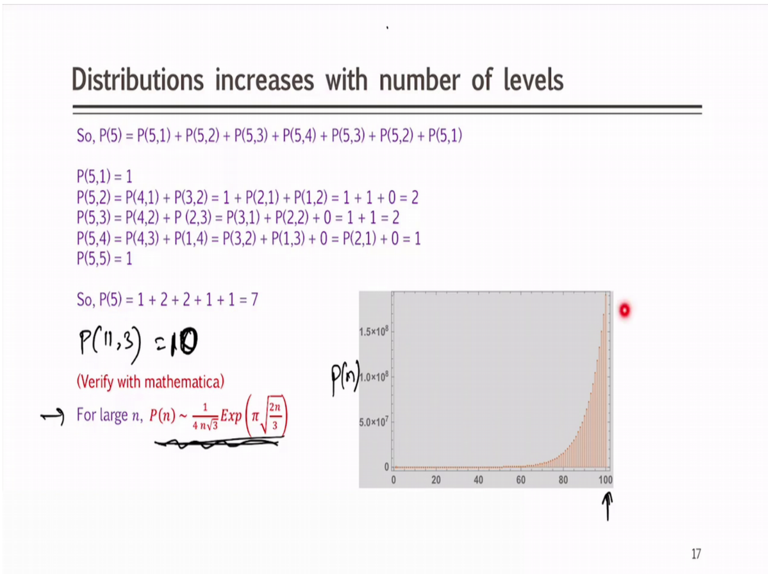

I will just do one more time just to check, so P 11, 3 is P 10, 2 plus P 8, 3 equal to P 9, 1 plus P 8, 2 plus P 8, 3 equal to 1 plus P 7, 1 plus P 6, 2 plus P 8, 3 is 7, 2 plus P 5, 3 equal to 1+1 2 plus P 5, 1 plus P 4, 2 plus P 6, 1 plus P 5, 2 plus P 4, 2 plus P 2, 3, 2, 3 is going to give me 0, 5, 1 is going to give me 1, so 3 + P 4, 2 can be 3, 1 + 2, 2, 6, 1 is giving me 1, 5, 2 can be 4, 1 plus P 3, 2, 4, 2 can be 3, 1 + P 2, 2, so now 3, 1 is giving me 1, 2, 2 is going to give me 1, I have already 1 available here 4, 1 which going to give me on 1, 3, 1 is going to give me 1 and 3, 2 is also giving me 1 and 2, 2 is also giving me 1, so I do not have to do any more, so this is 3+1 4 +1 5 +1 6, 7, 8, 9 and 10, so I am going to get 10.

So P 11 divided into 3 is giving me 10, 10 possible ways I can do that as you can see, so it is 10, P 11, 3, so how do I do that, so actually I say P 11, 3 means maximum up to 3 in fact we, no P 11, 3 is like all, only 3 possible divisions, which in mathematica as I can show is that there are like few possibilities will write, one is that 9, 1, 1 is one possible ways to break it, 8, 2, 1 is another possible way, 7, 3, 1 is another possible way, 6, 4, 1 is another possible way, 5, 5, 1 is another possible way and 4, 6, 1 will repeat as 6, 4, 1 so will not do, now 1 we have to change, now I can see 8, 1, 2 is one possible way, 7, 2, 2 is another possible way, 6, 3, 2 is another possible way, 5, 4, 2 is another possible way is it 5, 4, 2.

Now, 4, 5, 2 will repeat, so now instead of 2 we are going to 3, so if we start with 7, 1, 3, 6, 2, 3, 5, 3, 3, 4, 4, 3. Okay, now we have to go to 4 which is going to match, now let us see how many are their 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 okay 8, 2, 1 and 8, 1, 2 are same, and then any other same 7, 3, 1 and 7, 1, 3 which is allowed 6, 2, 3 and 6, 3, 2 great, so that is give me 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, so these are the 10 possible ways that 11 can be broken into 3.

So you can see that I am going to get from 11 particle and 3 levels in which all the levels are same energy I can get this many possibilities and each of them, however will give rise to a number of microstates and doing much calculations I can say that this will give is most probable distribution because we have to check it is like should be close, so 11 divided into 4, 4, 3 will be the equal possible divisions actually ideally 4, 4, 4 is the if for 12 particle will be the equal division, but it is close to the equal division possible into 3 groups, so that, this one will give us the most probable distribution.

So now we will see that how we can get distributions, now with the number of particles, the number of partitions will increase exponentially as you can see with this formula which is only true by the way for only large number and not for the small numbers, so you can need not use that for N equal to 11 or 12, you have to use like huge number to show that, so I show here the plot of number of partitions like P, N as a function of N, so I just clear it out for you to check the figure and you can see that when the number goes to 100 this P, N goes to more than 10 to the per 8 as you can see, in goes more than 10 to the, so number of partitions becomes huge, just for you to see that how a number of microstates actually is going to change in the number of particles enormous.

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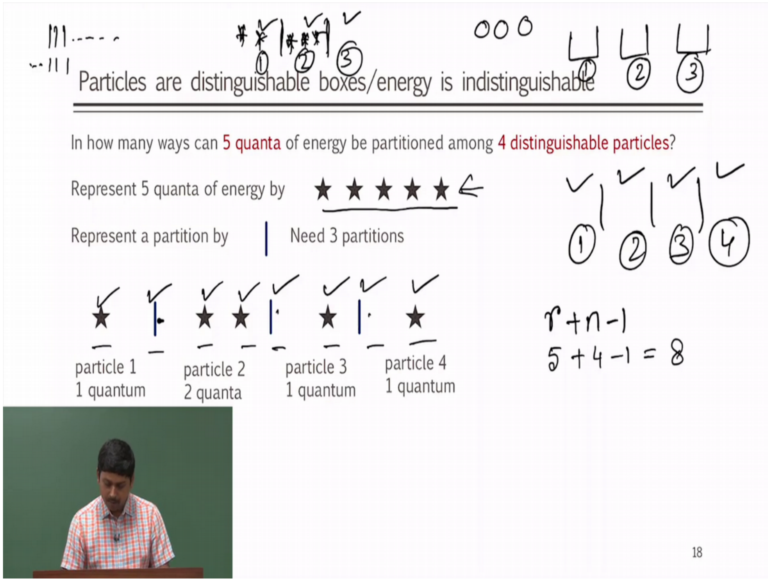

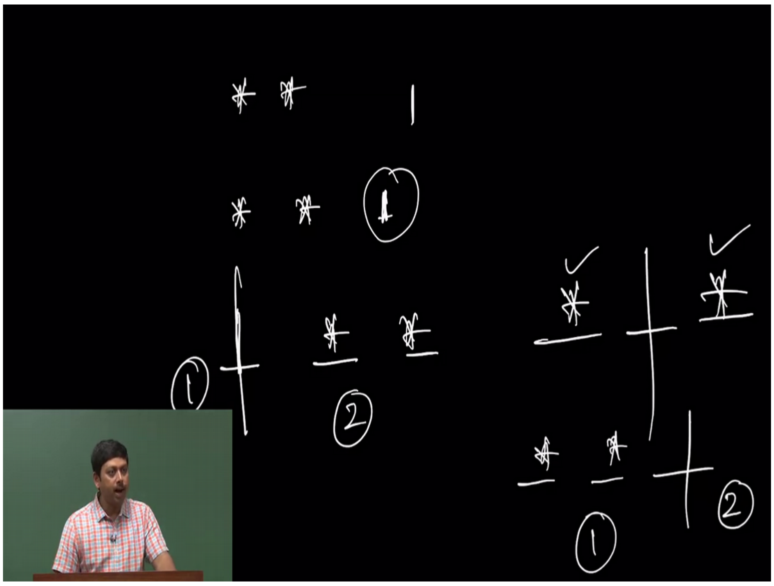

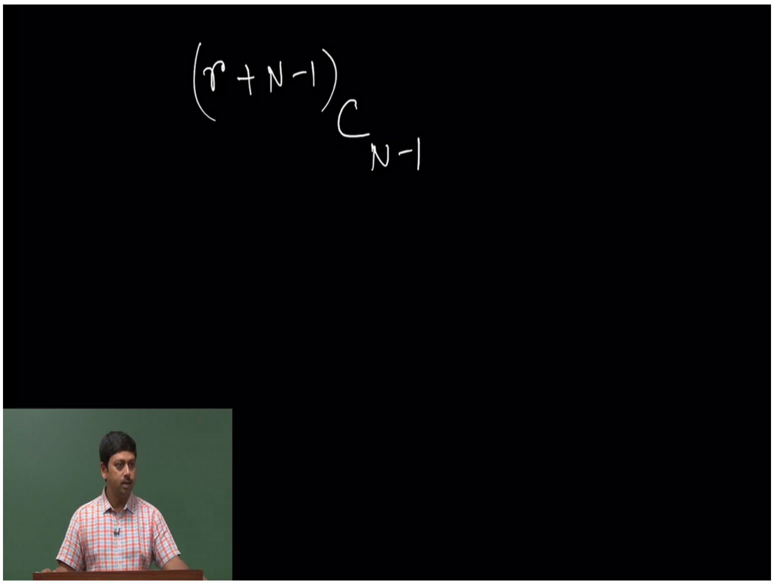

So now coming back that to the fact that, we talked about indistinguishable particles and indistinguishable boxes, now we are going to talk about indistinguishable particles and distinguishable boxes and the reason is that we are going to put energy into particles and we know that energies are indistinguishable, so this problem is typically called star bar problem, so here the question is that many ways I can distribute 5 quanta of energy into 4 distinguishable particles, now 5 quanta of an energy is denoted by 5 stars, stars are indistinguishable, energies are indistinguishable, so just a different way, you know you have to think, so earlier we are talking about indistinguishable particles in distinguishable boxes with this examples right, this is indistinguishable particles and these are distinguishable boxes.

I was saying, describing this varied but now the boxes will be distinguishable based on the bars, so whenever I put 2 bar I essentially have 3 boxes and we can call those boxes as 1, 2 and 3, now if I have in box number 1, 2 units of energy. I will put 2 stars, if I have 3 units of energy in box number 2, I will put 3 stars here, so like that, I will divide you know, 5 stars into 4 boxes, now you know that for 4 boxes how many bars we need? We need 3 bars for 4 boxes right, see 1, 2, 3 and 4, I get 4, with 3 bars I can make 4 boxes, so that means, now I have all total, 1, 2, 3, 4, 5, 6, 7 and 8 things which is number of stars which I can call it as R plus number of boxes -1 because that is going to give me the number of elements now.

Now you see in this elements, so that is the number of spaces that I have 1, 2, 3, 4, 5, 6, 7 and 8, I have 8 spaces why? Because my number of stars is 5, number of distinguishable particles is 4 and -1 that gives me 8, so you can see that why I am getting N -1? Because N -1 bar will give me N boxes and that is the reason I am getting N -1, star are just 5, so I kept as 5, now what I am saying is that I have now 8 spaces left and in 8 spaces I can put my this 3 bars in whichever way I want to, I can put them consecutively 3, I can put them all at the same time, then all my stars will be here, that means in 1 box only the stars are there and other box are empty or I can put all the stars on the 1st box itself.

So if there is no, I just explain it little bit here, so let us see I have let say 2 star and 1 bar, 1 bar essentially means there are 2 boxes, so I have now these 3 items, star, star and bar, so I have basically 3 spaces, I can put my bar wherever I want to, let say I put my bar here, my star here, that means 1 box is empty, this box number 1 is empty and box number 2 is having 2 particles or 2 units of energy, similarly I can put my bar here, then each box will have some units of energy or you can say that if stars are unit of energy, then particle number 1 has one unit, particle number 2 has another unit of energy. Okay.

And let us see if I put my bar here, than this particle number 1 will have 2 units of energy, particle number 2 will have 0 units of energy, so you see that in 3 spaces wherever I put my bar accordingly that will work, so now the thing is that I have, therefore, R number of stars plus N -1 number of bars, this many spaces I have in which N -1 number of bars I can put wherever I want to and that will distinguish the particles or energy levels into different distinguishable particles or you can see indistinguishable particles into different boxes, whichever way you can think of.

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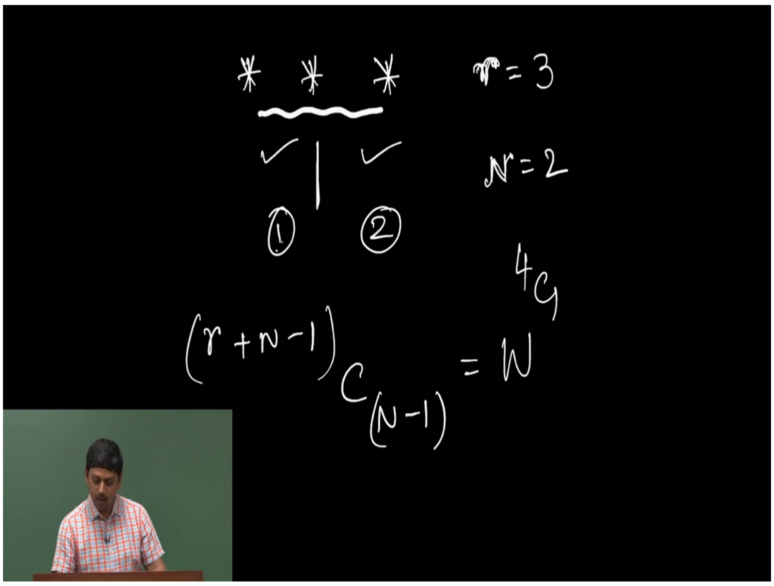

So imagine that you have 3 particles or 3 units of energy and 2 boxes, so 3 units of energy are equal to 3, 2 boxes is N equal to 2, now 2 box can be obtained by 1 bar, left-hand side of the bar will be a box and right inside of the bar will be another box, let say call it box number 1 and number 2 or we could stick to according to the problem that a bar will give us 2 particles, particle 1 and particle 2 and the stars are energy levels, so I have 3 units of energy and I have 2 particles. Okay, so now what I am going to do is that essentially I have 4 elements now 1, 2, 3 and 4 elements.

Now just imagine them as elements, I have these 4 elements, this 4 elements out of this 4 elements I can put this bar in any of the 4 places, so since I have 4 elements I have to keep all this 4 elements let say somewhere, so this 4 elements can be put into this four places, now how many ways I can put my bar, I can put my bar in any of the four places, I have 4 things and I have to choose one out of that, so I can do it in 4C1 ways, how many ways I can choose my bar? That is fine right, how many ways I can choose my bar?

Meaning whenever you choose something you basically decide where you are going to place because there are 4 things you have to keep all the 4 things on the floor right, now you can put let see you have a bar and 3 stars, you can put the bar front and 3 stars or you can put the bar 2^{nd} place or 3^{rd} place.

Student: (())(25:46).

Prof Arnab: Correct, correct, so depending on the position of the bar the stars will be divided, earlier like the boxes were fixed because star, bar are imaginary things, stars are nothing but a units of energy, if one box has 2 star means that particle has 2 units of energy, is another box has 3 stars that particles has 3 units of energy, so particles are distinguished by the boxes, and stars are just units of energy, so in general, I have R plus N -1 number of items star, bar included from which I choose N -1 bar and that is the statistics, W for indistinguishable particles in distinguishable boxes or indistinguishable energies in distinguishable particles, whichever way you want to think okay.

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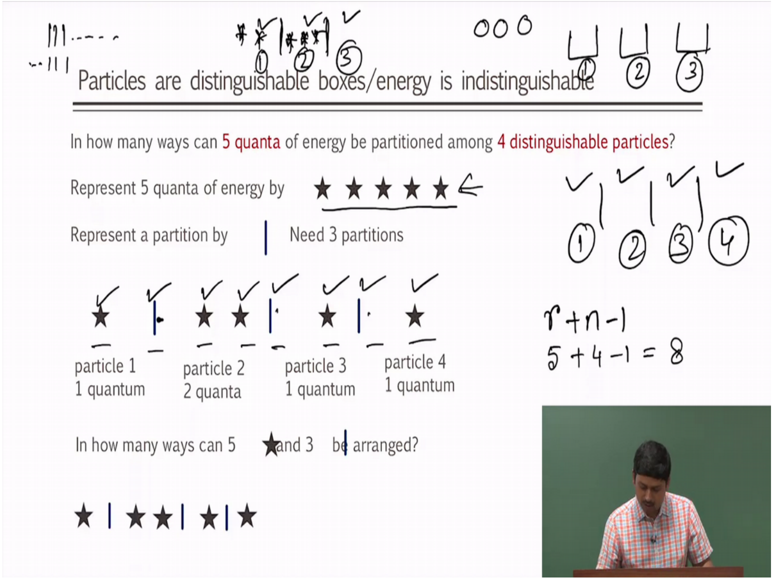

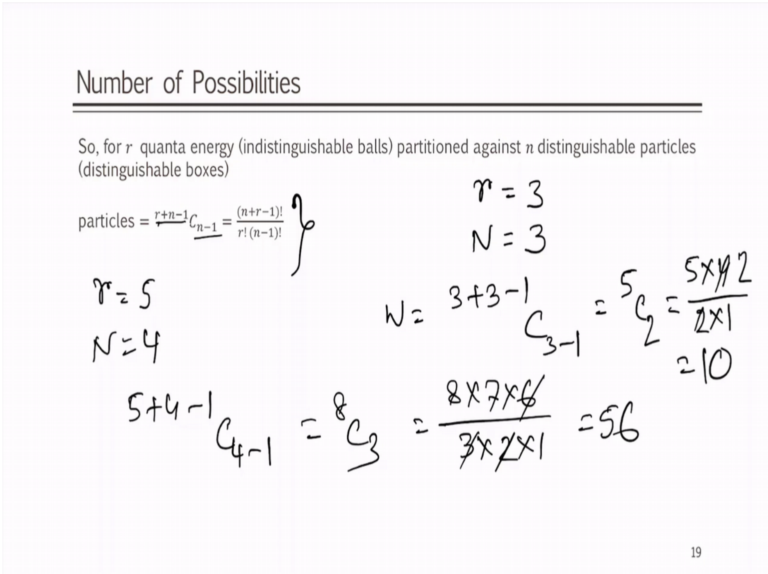

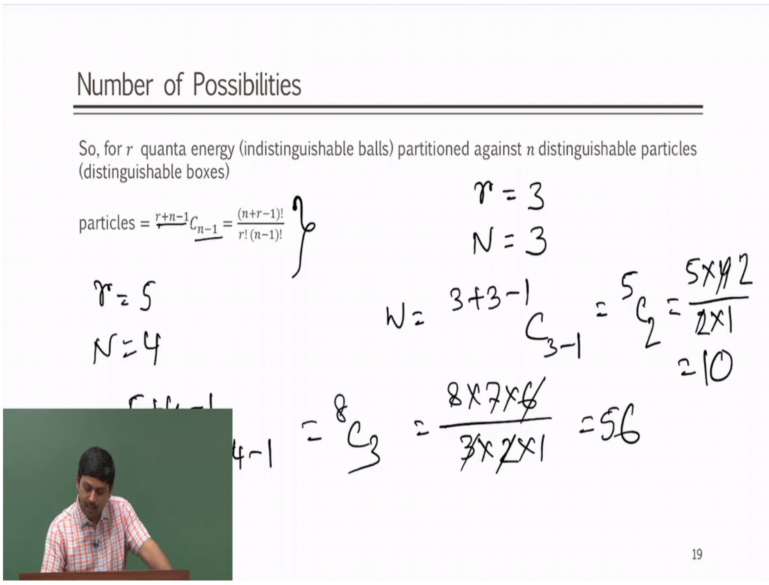

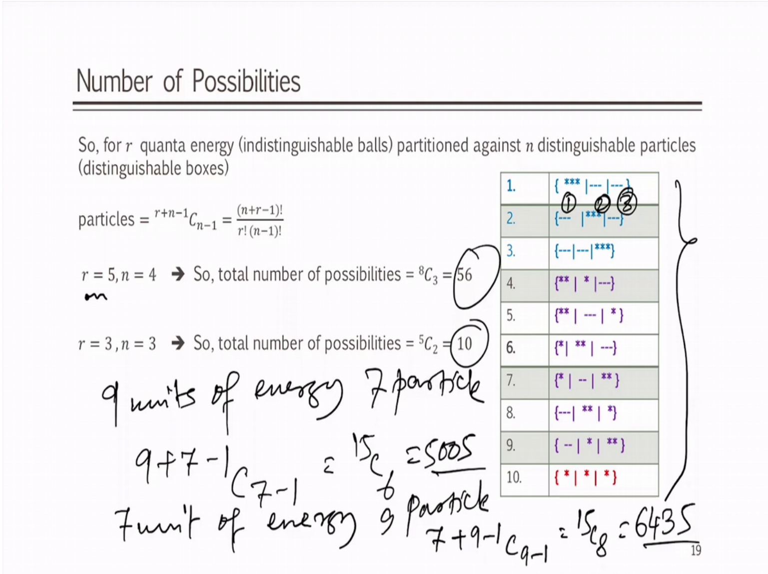

Now let us go back and see that is not working or not, so this is the formula that I showed R plus N -1, C N -1 and that is this formula, now imagine this problem of 3 particle and 3 boxes, so 3 particle and 3 boxes is 3 units of energy and 3 particles sorry, 3 units of energy means R equal to 3 and 3 boxes, 3 particles means N equal to 3, so number of ways is 3+3-1 choose 3-1 which is 5 C2 and what is 5 C2? 5 into 4 by 2 into 1, it giving me 10 and 10 was a total number of possibilities obtained when 3 units of energy were distributed in particles, remember that right.

So if I distribute 5 units of energy, if I use 5 units of energy, so R equal to 5 into 4 particles that means N equals to 4, how many will get 5+4-1 C4 -1 which is 8 C3 which is 8 into 7 into 6 by 3 into 2 into 1, 3 and 2, 6, 56, so you will get 56 total number of possibilities of distributing 5 units of energies into 4 particles, is that clear. Okay, so which situation I am doing that where particles are indistinguishable and boxes are distinguishable, I am doing that or I can think of as a distributing some units of energy into distinguishable particles, same thing I am saying, one is indistinguishable another is distinguishable, not both are distinguishable, not both are indistinguishable either.

If both are indistinguishable will go to partitions, if both are the distinguishable be either we go to N to the power R or we go to permutation combination thing we go to the N factorial by, N1 factorial into factorial and all that, this is where we talk about indistinguishable particles and distinguishable boxes but in our problem we will be merely concentrate indistinguishable energy units to distinguishable particles because classical particles as I said are distinguishable and with their we are putting the energies, we will see later on indistinguishable particles, distinguishable boxes or energy levels would be important for

Boson and Fermions quantum statistics because Boson and Fermions are all indistinguishable but the boxes where you put it that distinguishable, so Boson and Fermions this statistics will become important.

Whereas the other one where he said their all particles are distinguishable boxes at distinguishable in that case, the Maxwell Boltzmann statistics are important. Okay, so here we are getting an handle of that total number of possibilities how one can get, I just clear this marking and then 56 we got it here as you can see 10 we got it here, as you can see and these are the 10 values, remember here particles are indistinguishable, the stars, here I am talking about not energy only, I am talking about actual particle, actual ball or you can think of that as energy units, whichever way and the boxes are distinguishable 1, 2 and 3 or you can thing of them as particle.

So let say this is particle number 1, this particle number 2, this particle number 3 and the stars are energy units and you see these other 10 possible ways that you can add in, these are all total 10 possibilities, in which, however we have 3 different distributions and each distribution has different possibilities like A, B and C, so A has 3 possibilities, B has 6 possibilities and C had only 1 possibility, so this gives me this formula N plus R -1 C N -1 gives me the all total possibilities, all possible distributions they give me, they do not give me just, you know 1 distribution, they give me all possible distributions.

So if I have 9 units of energy and 7 particle how many we should get? 9 units of energy, 7 particles, so 9+ 7 -1, C7 -1 which is 15 C6 and you know what 15 C6 is? But if I do the opposite 7 units of energy into 9 particle how many we get? Now it is 7 units of energy, the 7 +9-1 choose 9-1, so it will be 15 C8, not 15 C6 anymore and that will give you 6435, you are not getting the same thing because one is indistinguishable and another is distinguishable. That is why you are not getting the same thing, you see in one case 9 units of energy and 7 particle, in another case 7 units of energy and 9 particle.

Now energy units are indistinguishable, particles are distinguishable. That is why you are ending up with two different statistics okay, so now this fact that R equal to 5, that means 5 units of energy into 4 possibilities giving us 56, how do we get that 56? That we are going to talk about now.

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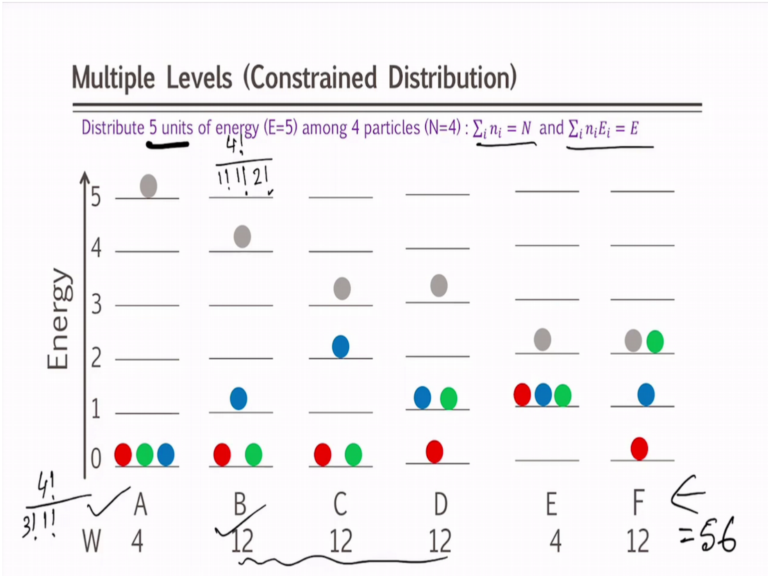

Multiple levels and constrained distribution, why do I say constrained distributions? Because my number of particles is fixed and my energy is also fixed, my energy is what which? 5 unit and what is my number of particle? 4 particle, there are all both are fixed, how can I do that? I can do that by drawing the labels, simple labels and distributing them, for example, my units of energy is 5, so I put one particle in 5 and I put 3 particle here, so I have 4 particle right, this is one possible distribution, I can now have another possible distribution as this one, I can have another possible distribution, so now it is 4 and 1, now it is 3 and 2, now it is 3 and 1, 1, now it is 2 and 1, 1, 1 and now it is 2 and 1 and 0, 2, 2, 2, 2, 1 and each of them has now different Ws.

So now I got 6 possible distributions A,B,C,D,E,F, I do not know whether you can get anymore, you can check that, 6 possible distributions, now how do I get W equal to 4, it is there are 4 particles, so factorial 4 divided by factorial 3, 3 particles in one box right, factorial 3, factorial 1 and all are zeros, that will give you the 4, how do you get 12 here, you have to do again the same thing, factorial 4 by factorial 1, factorial 1 and factorial 2, this will give you for factorial is how much? 24, 24 x 2 is 12, so you will get 12 here, this is the same as is formula, this is same as this formula, this same as this formula, this is 3, 1 distribution is same as this formula and this is same as the 1st formula.

So as you see the total number when you add them up is 12+12, there are how many 12? 12, 12, 12, 12, four 12, so 48, 48+4 is 52, 52+4 is 56, so there are total 56 possibilities, which we already got from R plus N -1 C N -1 you already got 56 right and this is how the 56 is breaking into 6 possible distributions and then what is the most possible distribution, there is not a one that is single most possible distribution, all B,C,D are, you know and F are all most possible distribution because we are really cannot, they are all equal and that is, the situation is coming because of this, smaller number of particles, smaller units of energy, it is basically not come when there are huge number of variations are there, but this will give you an idea that how one can distribute energies into particles.