Chemical Principles II
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Calculation with Multi-Level Systems with Fixed Energy Part - 01

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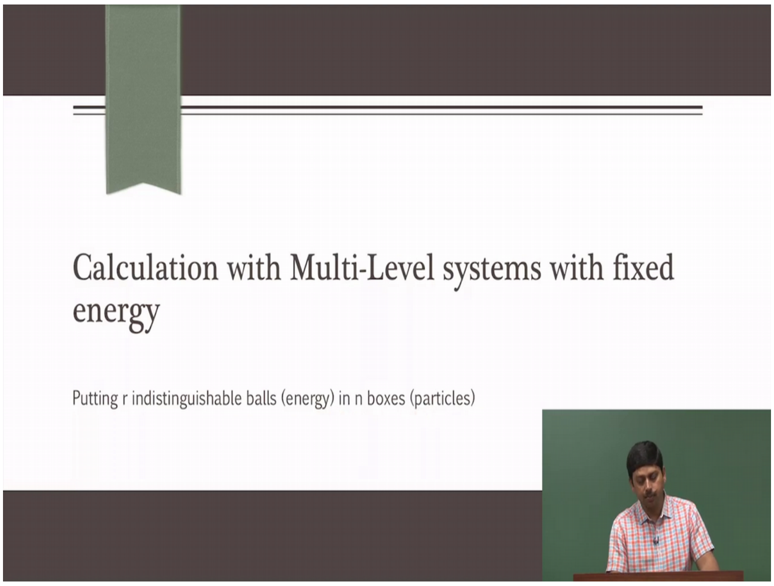

We are going to now calculate that multilevel systems with fixed energy, now that is another constraint that we are adding, earlier the constraint was that total number of particle is N, I divide into 3 levels, 4 levels, 5 levels and find it that, now I have an additional constraint that I have a fixed amount of energy, earlier all energy levels were all, you know equal now I can have different energy levels, some higher-level, some lower-level and in that case, how we can address those problems, so those problems are similar to putting R indistinguishable particles or balls into N boxes, so R indistinguishable balls which are like will see that as energy in N boxes which are particles, we will come back to that.

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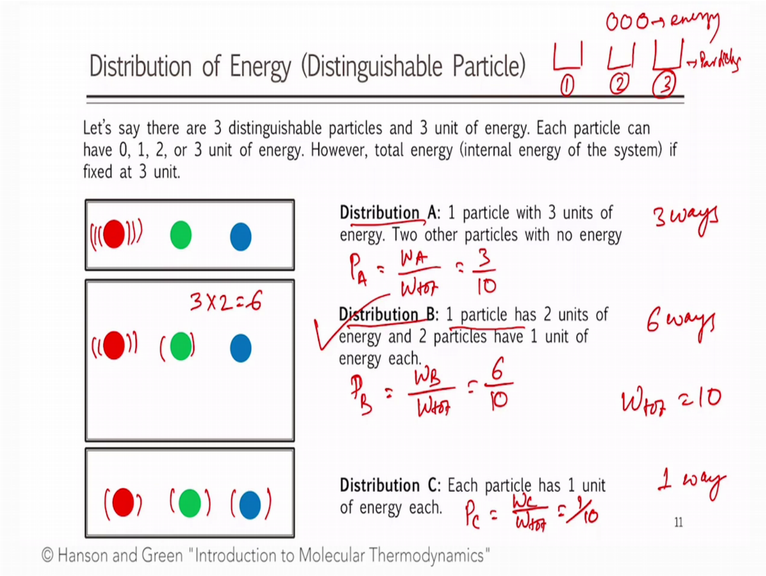

So now we are talking about distribution of energy, energy are indistinguishable by the way. Okay, because energy is just unit of energy, we cannot associate this energy is green energy or a blue energy or things like that, energy are indistinguishable, so let's a I have 3 distinguishable particles and 3 units of energy, which are indistinguishable, so this problem is, as I discussed before putting indistinguishable particles in distinguishable boxes, I just remind you it is like you have 3 distinguishable boxes and you are putting 3 indistinguishable articles, I did not color them, they are indistinguishable.

So here I am saying that this is our energy and this is our particle why? Because particles are distinguishable and energies are not, that is why we have arranged that, so in probability we can take any possible choice as we like, since our energy are indistinguishable we have considered energies as the indistinguishable particles and since our particles are distinguishable we considered them as distinguishable boxes, then it boils down to putting indistinguishable particles indistinguishable boxes, the same statistics we can apply.

So, I will show you that, for example, let us say 3 distinguishable particles are there and we need to put energies into that, so how many ways we can do that, I will just show you in a moment, so let say I put 1 particle with 3 units of energy, so I can put the 3 units of energies, so this line denotes energy, so I can put 3 units of energy around only 1 particle, so I can put that around red particle, I can put that around green particle, I can put at around blue particle, so of course I have 3 ways of doing so right, now my distribution B in which I put 1 particle with 2 units of energy and another particle with 1 units of energy, how many ways I can do that, my 2 units of energy. I could have chosen for any of the 3 particles, then rest I could have chosen for any of the other 2 particles, so I have 6 ways of doing so is it clear.

Now the last distribution is this particle is one unit of energy, can I do in any other way than 1 I can do only one way so you see, I have now 3 possible distributions with the constraints that total number of particles are 3, total number of particles is 3, total energy is 3, I could get 3 distributions and I could get a total of 10 possible ways, so my W tot is 10, so my W, my probability of this distribution A is WA by W tot, which is 3 x 10, probability of distribution B is WB by W tot is 6 x 10, probability of C, which is WC by W tot's 1 x 10.

So which is most probable distribution? Distribution B is the most probable distribution because it has the highest probability. That is why it is more probable distribution, so if you have 3 units of energy and 3 distinguishable particles than most likely what will happen is that 1 particles will get 2 units of energy and another particle we get 1 unit of energy, another particle will not have any energy with it, so again, this is figured relatively speaking, because again, you see probability are not that widely differences with 6 x 10 and 3 x 10, one is double of the other, another is 6 times of the other or 3 times of the other.

However, as you know with more and more particles are more and more energy of units the number of distributions will increase and most probable distribution will be much, much more probable than the other distributions.

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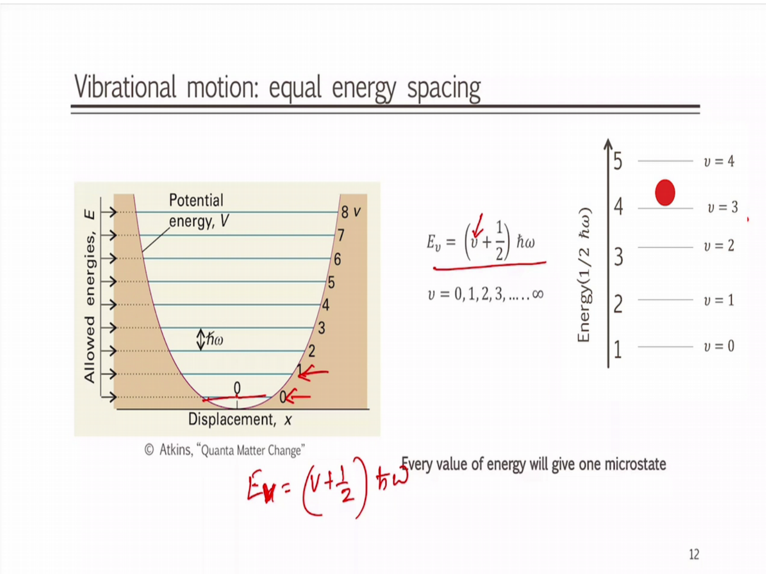

So I will give you a realistic example of different possible energy gibe aloes in a realistic situations where a particle can be in addition different possible energy values and one of the classic example is vibrational motions or known as like quantum harmonic oscillator, so I know in our classical, you know that in your classical oscillator your is like a spring that string is an expands under a potential okay, so same kind of potential use to solve Schrodingers equation, then you will get a solution in which the energy values will be spaced equally is that the energy of one particular level is or one particular level EV will be V plus half H new or H cut omega.

So again, so that is shown here, so these are quantum levels, so you know in chemical principles one we discussed about that, you know how one can get quantised energy that the potential energy is important in order to get different effects and quantum harmonic oscillator that is solution, where the potential V is half K axis square, where it is bound is like a spring where it is found on one side, so one side is held and another side will move, so also you can think of the distance between the proton and electron is described by a condom harmonic oscillator thing, but although it is not exact with the case because the potential is actually different but one can get this similar idea that why there will be different levels.

So in quantum harmonic oscillator case it is just half K axis square is the potential and then you get different levels of equal spacing, so which means that if you are in the ground level you have some energy values and you move like little bit from here you can move this much but in the 1st excited level, you know you move farther apart with higher energy, 3rd level you move further apart with higher energy, the bottom line is this is an example, right now we are just reading at an example of different energy levels in which a particle.

So what you mean by a particle? You can say a quantum state, you know the state of the system is now in one of the level okay, you can think about that way or when you solve or an electron under the harmonic potential it is just 1 particle the potential and it can be in a different, so this is an example of 1 particle in different energy levels, so we are talking about multiple energy levels but with 1 particle.

So N equals to 1, this, you know shown here, so this V zeros, so this V0, V1, V2 and V3 are different vibrational levels and the particle can be in any of them, so you talking about what, so remember we discussed about 1 particle in a box and I can be said only one possible ways to do it that because the box has 1 level of energy, the accessible states were only one, so your we are showing that particle number less but many more accessible states which will give rise to more entropy because now same particles can be in any different states, for example in earlier, we talked about N equal to 210 particles 3 boxes, so accessible states were 3 number were huge, even if we had 1 particle, 1 particle could have been in any of those boxes.

So there are 3 possibilities could have come here, there are infinite possibilities because the particles can be in any of this levels okay, infinite possibilities with just one particle, however we see that and an each one will give you 1 microstate right, whether it is in 4 or 5 or it is in 3 will give you in 1 micro-state right, but if we say that energy is fixed, let say if I say that okay, what is the number of microstate for 1 particle in the harmonic oscillator and the energy is 4, than there is only one possible ways to do that right, we cannot have multiple possible in this way, the fact that we are getting more number of microstates because more access a states are there, then there is no constrain.

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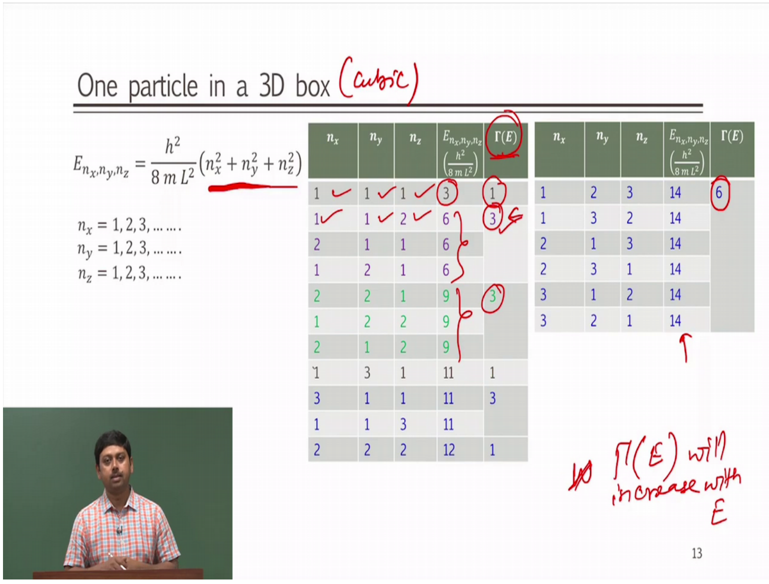

So now I will show you the similar situation where accessible states are more even for 1 particle and the example is particle in a 3-D box, so particle in a 1 3-D box again had the similar energy, you know different energy levels like harmonic oscillator, similarly particle in a 3-D box also energy levels are not equally space but we are giving you an example where 1 particle that have or accessible states and therefore more degeneracy even when the energy is fixed, so harmonic oscillator case what we see 1 particle the energy is fixed, then can have only one possible ways, 1 particle nothing fixed, no energy is fixed then there are infinite possible ways one can do that for harmonic oscillator.

But particle in a 3-D box interestingly you will see that, so you can write that energy as NX square plus NY square plus NZ square, H square by 8 ML square, where L is, so we are talking about 3-D box which is cubic, cubic box where all the 3 lengths are same, H is a constant, M is let say electrons, so it is constant, L is let say fixed, even than you have this quantum numbers in NX, NY and NZ, so it is dimension, so we are now increase the dimension of the system from one dimensional harmonic oscillator to three-dimensional box and here an interesting things happens that.

So you know that NX, NY and NZ they can go from 12345 all integers number they can take starting from 1, it cannot have 0, though, unlike the harmonic oscillator and it was 0 is also possible, so if you put those values you are going to get different energies, so let us put 1, 1 and 1 will get energy as 3, unit is H square by 8 ML square, we get 3, how many possible ways we can do that? Only one possible way, now let us put 1, 1 and 2, so energy become 6 and there are 3 possible ways to get that.

So again, if I now 1 particle system, energy value fixed, earlier for harmonic oscillator for 1 dimensional harmonic oscillator you would get only 1 microstate why? Because 1 dimension, 1 particle, 1 energy level, here 1 particle, 1 energy level, but 3 dimension and we are getting more number of possibilities, we are getting 3 possibilities and the energy is 6, again 3 possibilities an energy is 9 and we are getting 6 possibilities that energy is 14 and many more, probably you will get more possibilities when energy increases.

So the point here is that either the dimension or the number of particles or the accessible states, if any of them changes than that give rise to more possibilities, more number of microstates and this quantity denotes the number of microstates for a given energy and you can see that number of microstates for a given energy also increases, so W will increase, no so the number of microstates for a given energy will increase with E, that is very interesting find that it come back later on that for a given value of energy, the number of microstate that we calculate will increase with the value of energy, which means that since the number of microstate is increasing which means that the entropy is increasing.

So entropy will increase with energy and that is also taken as a postulate when the postulate diathermic dynamics is used and you will see that it is reedit with the temperature, yes so it is reedit to the 1 by temperature, so the number of microstates energy is here.

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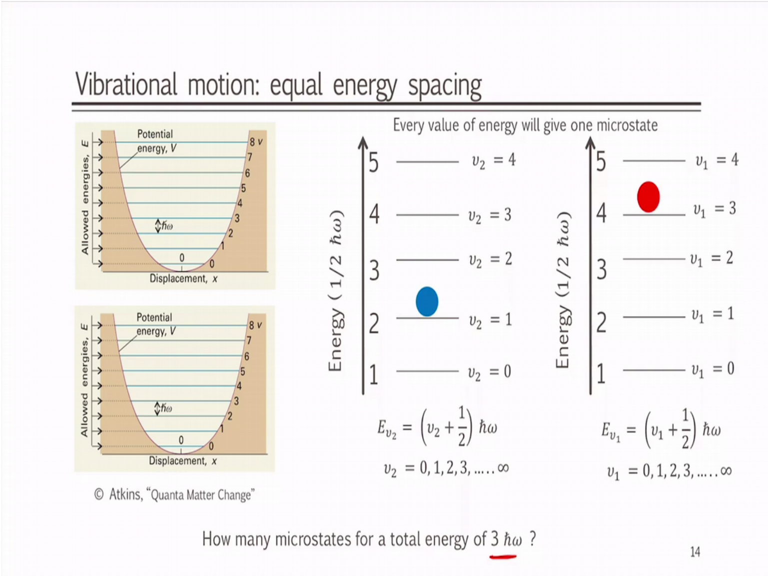

So now let us talk about 2 harmonic oscillator like 2 particles, each harmonic oscillator has equal spacing just like we had discussed before and that time, what happened is that if the energy level is fixed then number of microstates was just 1 but now I have just increased the number of particles to 2 and a number of harmonic oscillator to 2 as well, just like a situation where one harmonic oscillator has is equal spacing in which the blue particle is sitting at some level V2 equal to 1 and I have another harmonic oscillator in which red particle is sitting at some level giving this, so this number.

Now ideally this red particle can be anywhere here and the blue particle can be anywhere here but I give a constrain that how many microstates are there for total energy of 3 H cut omega, now in order to get that, let us right down the number.

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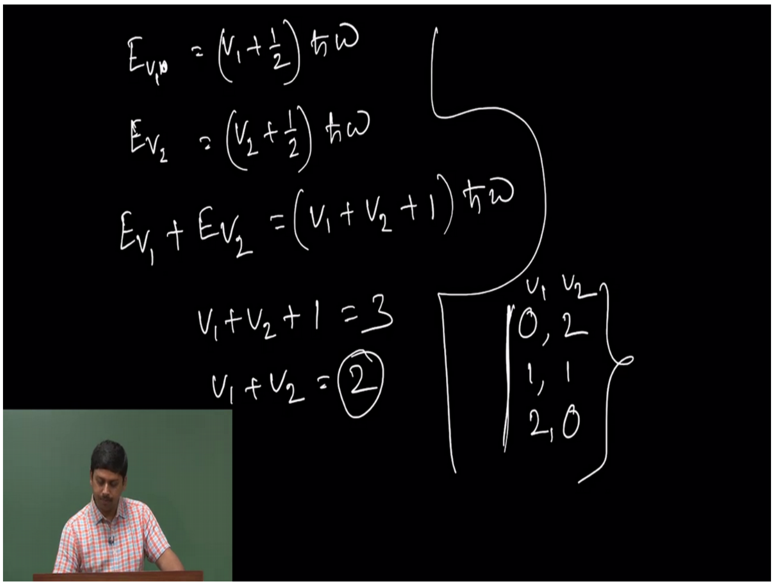

So V1 gives me V1 plus half H cut omega and V2 gives me V2 plus half H cut omega, so the total energy is V1 plus V2 giving me V1 plus V2 plus 1 H cut omega, now I need to get V1 plus V2 +1 equal to 3 therefore V1 plus V2 I need to get as 2, so once I do that, so that is means, now I have to see that one can give me 2, so 0, 2 can give me 2, 1, 1 can give me a 2, 2, 0 can give me a 2, so now I can actually 3 different ways to get the total energy 3 H cut omega I can obtain by using this particular rule.

So basically have to kind of a partition my number, integer number 2 into 2 different levels, exactly 2 different levels a partition my number, so when I talk about partition a number, so I have said that my total number is 2 and then I have to see that 2 is divided into 2 parts, I can be 0 to 1, 1 or 2, 0, so this will me 3 different possibilities.

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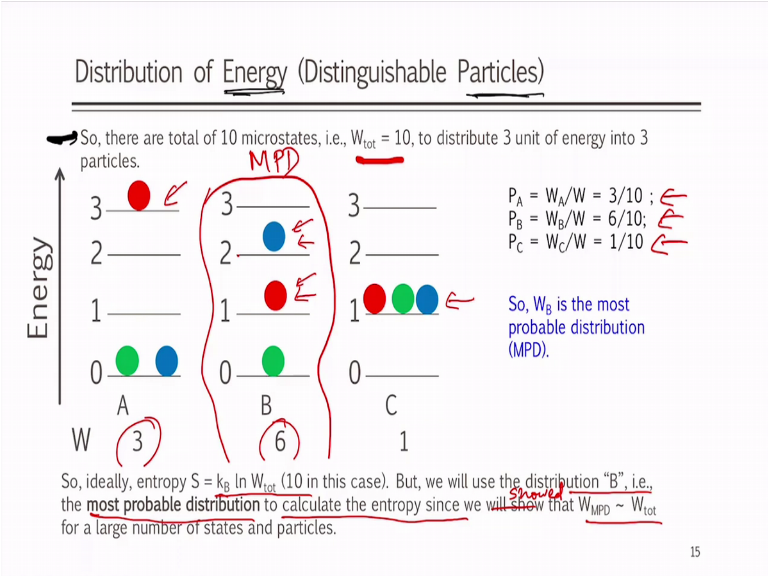

So now let us talk about that distribution of energy and distribution of energy into in a boxes, so remember I said that distribution of indistinguishable particles to distinguishable boxes we discussed about that, here the indistinguishable particles is energy and distinguishable boxes are particles because the particles are distinguishable be consider as box now and because energy is indistinguishable we considered that as a particle now that is a whole idea. Okay.

The idea is that you put indistinguishable things into distinguishable things. Okay, so there will be a how many possibilities, so we will come to that, so this particular part will come to that, so we are back to the same problem, remember that we said that 3 units of energy and 3 particle, same situation we came back, but now instead of drawing with lines we are drawing with energy levels, so let say there are, you know 4 energy levels available 0, 1, 2 and 3 and there are 3 distinguishable particles with 3 colors, how can we do that?

You see, I can put 2 particles in 0 level and 1 particle in level III that will satisfy my total energy, total particle is satisfied and total number of states are also satisfied, second possibilities that I can put 1 particle in level II and another particle in level I that will give me a total of 3 units of energy or I can put all the 3 particles in level I itself, that will also give me total energy 3, so here we are talking about distribution when the total energy is constrain, that is the idea, distribution of distinguishable particles in different energy levels when the total energy is constant and that is what we are trying to do.

Of course, as you can see that I can put at this level and 3 of the particle and that gives me 3, at this level II I can put any 3 of the particle for which I can put any 2 particle here and that gives me 6 and have no choice but to put all the particles in this level and therefore I have only one choice, so this is our earlier distribution A, distribution B and distribution C that we discussed before and the corresponding probabilities that we talked about before giving me this is my MPD, most probable distribution.

You see interestingly, notice one thing the most probable distribution is the one where particles are all in different, different levels and we will see later on that particles would like to be in all different, different levels to increase the entropy, unless they are constrained by something else to be somewhere, then it will change, but if you have no constrain than particle to be in all different levels because that will increase the number of microstates and therefore entropy of the system, so this is the same thing that I discussed that, I just clear this part, so that you can see that ideally we will say that the total number of distribution is 10 as I say W tot is 10 because you can add them and the most probably submission is 6, so I really we should right, the entropy as KB LN W tot, but we will use distribution B only which is most probably distribution to calculate the entropy since will show that W MPD equal to W tot for, we already have shown that for two-level systems, it is true for multilevel systems as well, we are already shown that, so it is not that we will show, so basically be already showed before by showing that.