Introduction to Molecular Thermodynamics
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Lecture - 13
Microstates of a system (Contd.)

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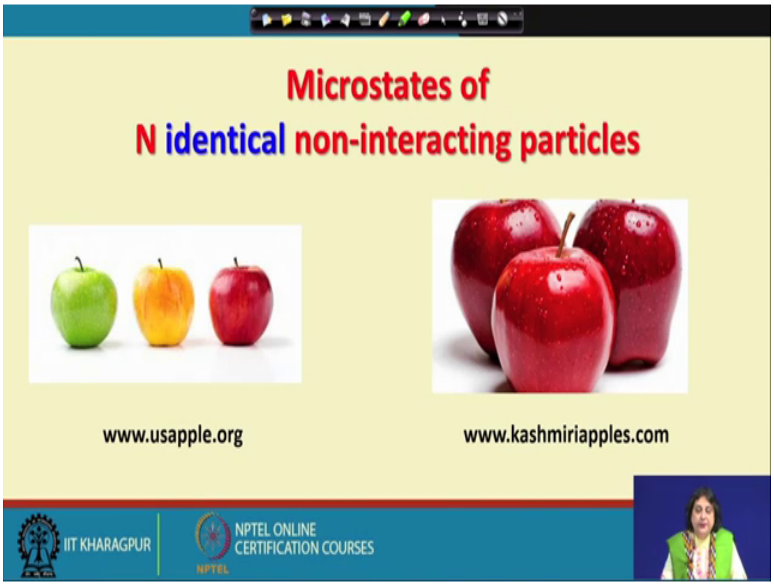

Welcome back today we are going to talk about a topic, which is very closely related to what we have been discussing so far, but there is a little difference. So, in continuation of our discussion on microstate of a system in equilibrium today we are going to talk about the microstates of a system which is comprised of N non-interacting particles as before, but now we have taken up the problem of using N identical non-interacting particles.

So, let us go ahead and see what we can do with these identical non-interacting particles and therefore, unlike the previous discussion where we had each particle comprising the system to be different and distinguishable from each other. Now, all the particles that we are going to deal with at the microscopic level are going to be exactly the same and you cannot tell the difference of one particle from another one.

So, now the chemists deal with certain types of systems, and there are certain system, the certain particles that they are always thinking about. So, let us try and have a look at the kind of identical particles that are of interest to practicing chemists. Of course, the first choice that comes to your mind, other electrons.

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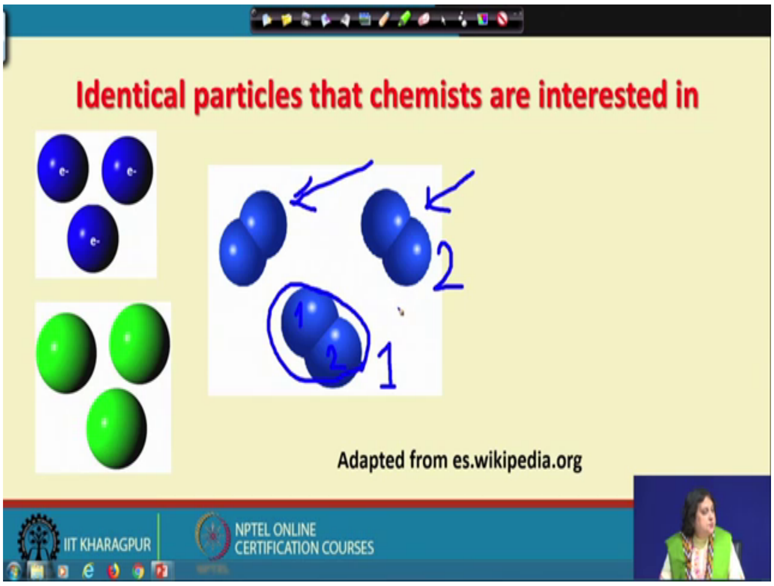

Chemists work with electrons and this is the cartoon representation of electrons where I have represented by this fears the typical electronic cloud asymmetric typical electronic cloud probably characteristic of one is electron it may. So, happen that the system that the chemists is interacting with is comprised not only of electrons, but it is basically comprised of a set of atoms. For example, I can talk about the setup atoms as this is a typical microscopic picture of a cluster of three argon atoms.

Now, is there way where I can say I can distinguish between this atom from this atom or this atom from this atom, the idea is none of them are distinguishable as far as all the measurement processes that I have available with us. Then of course, at the chemists we deal with molecular system. So, this is the typical microscopic snapshot of same nitrogen gas as you see that each molecule now is comprised of two atoms atom one and atom two. Now, these two atoms give me one particular molecule.

Now, if I look let me label this as molecule one. Now, if I pick up another molecule like this; and if I put a label to it as number two is there any difference between number one and number two, the answer is no. Therefore, for all practical purposes if I go on considering each and every molecule present in a nitrogen gas; I must say that all of them are identical. Therefore, if I am looking at the property of these systems, then I must realise that the microscopic state of the system is going to be characterised by a set of identical particles.

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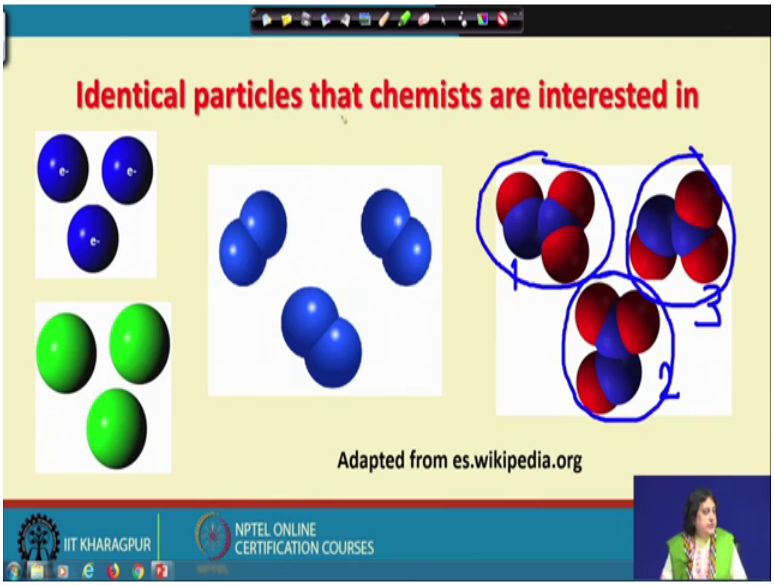

And there is another example where I have a much more complicated molecule. So, what I am showing here is look at this particular molecule. This molecule is comprised of 1, 2, 3, 4, 5. T t has 5 atoms and does not matter which molecule of the system I pick up I have the same atomic arrangement, and I cannot distinguish between molecule one from molecule two or between molecule 2 and 3. As a result, I would say that in most of the systems that the chemists deal with we are dealing with identical particles. Therefore, in continuation to the previous discussion on how do I characterise and count the number of microscopic states for a given thermodynamic condition, today we are going to pick up this problem of counting the number of microscopic states in the identical particles.

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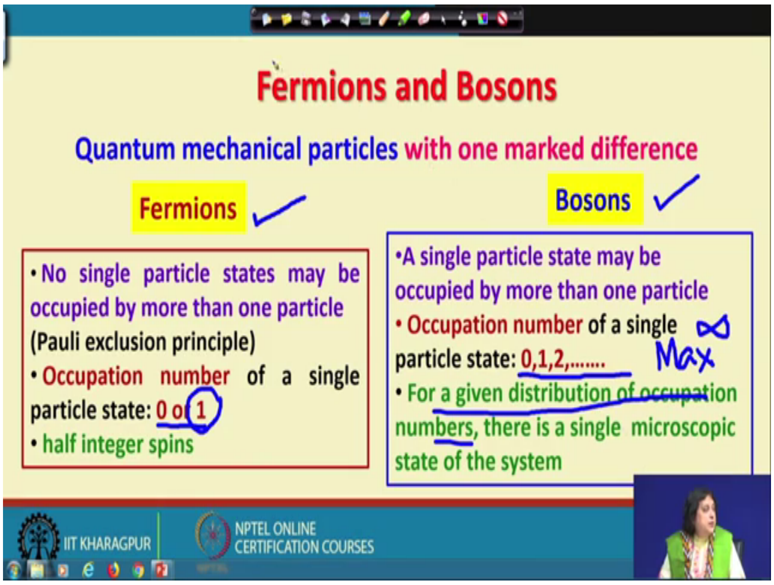

So, in this case there is a generic description that is found to be extremely useful. Now, as I said that one class of the particles that we are interested in are electrons. Similarly, there are several other quantum particles that we know about that can be broadly categorised into two different classes. One class we call them fermions and the other class we call them bosons. Now, let us see, what is the difference between these two classes of quantum particles. The first one fermions which is said that, if you have a system comprised of fermions, then no single particles state may be occupied by more than one particle I will explain to you what each of these terms in this definition mean, but at present it seems to imply that if you have a single particle state then the occupation number of the single particle state can be either zero or one. And fermions are usually characterised by half integer spins.

Now if I look at the contrasting definition of what I have as bosons then what I find is that here also we will talk about the single particle states. And the difference between the fermions and bosons is that the single particle state can be occupied by an under restricted number of bosons. Now, if I look back, in the case of fermions the single particle state has only two possibilities; either it is empty that is occupation number is zero or it is singly occupied which means that this particular state has only associated with only one particle. On the other hand, in the case of bosons you see that for a given single particle state you can have a very large number of particles associated with it, so that the occupation number can start from zero which is an empty single particle state then singly occupied state, doubly occupied states and so on and so forth.

So, what is the maximum number of occupancy over here? It is understandable that by this definition that the maximum occupancy is going to be infinity. If I have an infinite number of particles associated with the system that I am understanding, I will come back to this distribution of occupation numbers, this concept later on and how to characterise the microscopic state of the system with that it.

But for the time being, it will suffice to know that fermions are characterised by two things. Single particle states as well as the occupation number and the limited choice for an occupation numbers. And the bosons, they are characterised by a single particle state where the occupation number can be anything starting from zero to infinity.

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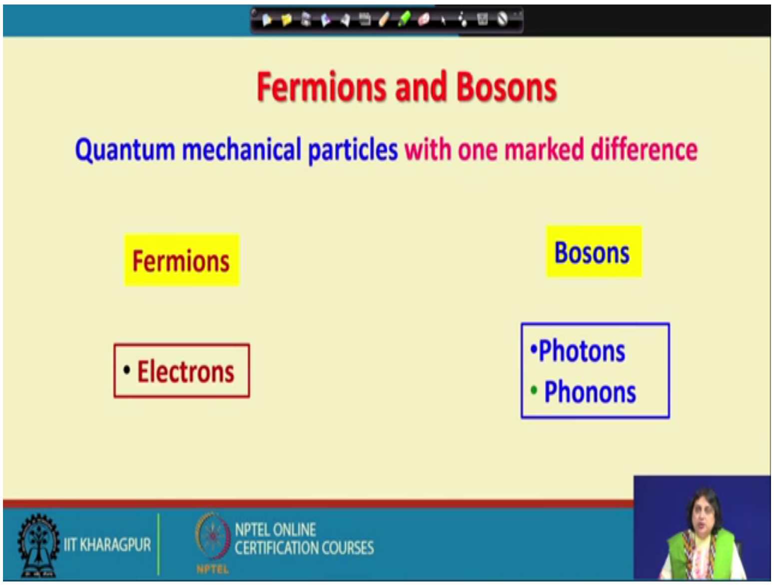

Now, let us go back and now try and check what are the examples. A typical example of a fermions is an electron on the other hand a typical example for a boson is a photon or a phonon. So, let us now take up one by one what I mean by the single particle state and why for example electrons work as a fermions.

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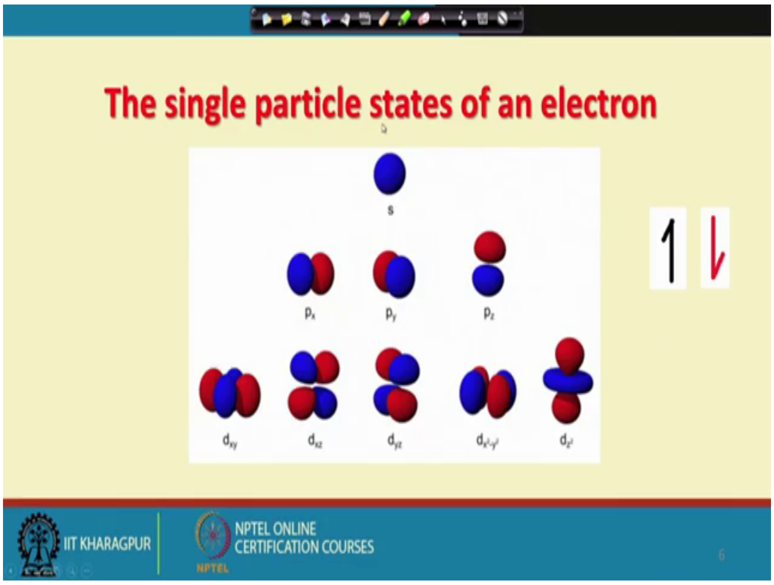

So, the if I want to derive the single particle state of an electron it means that I shall be solving the Schrodinger equation at the microscopic level that is the equation that we solve to obtain the quantum mechanically allowed states of the system. Now, I have said a single particle state, which means that for an electron, I will solve the electronic Schrodinger equation when only one electron is present in the system.

So, can you tell me which system gives me this an example of just one electron present, where I can solve the electronic Schrodinger equation analytically. I am sure you have learned in your quantum mechanics or quantum chemistry class that the Schrodinger equation of a hydrogen atom can be solved analytically and these are the allowed solutions that we have known.

So, first we have the lowest line Eigen state which we call as the s orbital. So, this is a single particle state of the electron where we have plotted the this is three-dimensional plot for the probability of finding an electron around the nucleus of the atom with say 95 percent probability this is called an ISO surface. So, basically I am connecting all the regions around the nucleus, where the probability of finding the electron is 90 for at least 90 percent. So, for the s electron what I find is that this is the small spherical region, and there is one thing that you note that this has been coloured using a single colour.

So, this is the single particle state of the electron in an hydrogen atom. And this is the simplest representation of a single particle state of an electron that we know of from our study of hydrogen atoms. There of course, are other known possible single particle states, but the difference between s and p etcetera is that that if I am talking about only the lowest energy state it has to be 1 s.

And then you will have to go for higher energy state associated with n equal to 2, and then you can have 2 s and 3 ps. And as you can see that when you have the p orbital and using two different colours, why is that? So, that is because the solution of the Schrodinger equation is the solution to a wave equation and therefore, the solution of the wave equation actually has a phase factor which says that the wave function is positive in some regions of the solution and negative in some other regions.

Now, since I am plotting the probability and actually looking at the square of this wave function and that is addressed with some other factors that the moment you squared it then you have lost where the wave function was showing a positive sign and where it was showing a negative sign. Now, this has actually a lot of importance as far as these overlap of these orbitals are concerned. And therefore, it is found extremely useful if you use two colour codes.

For example, here in this case this part of the single particle state that is the p x orbital originally had the say the positive sign underlying associated with the wave function and this portion had a negative sign. And therefore, these two are coloured differently although each of them signifying the probability of finding the electron in this area either here or here with typically 90 to 95 percent probability

Now, the basic point here is not our concern about what these things mean, but the candidature of the solution of Schrodinger equation to give us single particle states of an electron. So, if I assume that the single particle state of an electron is given by this hydrogenic atomic orbitals. Then I can start by thinking of attaching one electron to one of this states, now then the microscopic state of the electron will be having two parts; one is the orbital part to tell us whether it is present in an s orbital or a p orbital or even in a d orbital. So, let us have this time being concentrate on placing one electron in an s orbital.

Then the orbital part of the electronic wave function is given by the 1 s orbital. Now, this electron in addition to its orbital properties will also have another property which is spin. Now, the spin may be an up spin or down spin, but we do not know simply because we have not applied any external field it is only in the presence of an external field that the difference between the two spins will become apparent.

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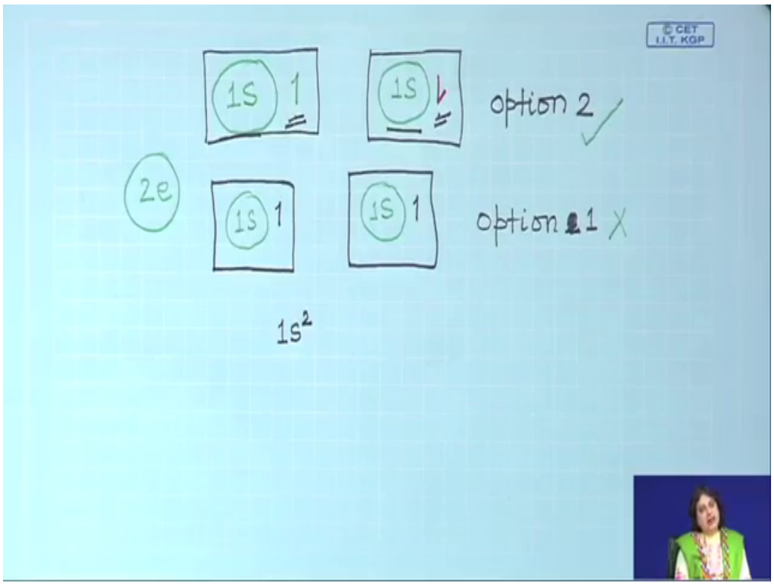

And therefore, the single particle state of this electron that I am talking about this is given by 1 s, this is the orbital part and this is the spin part. So, this is one possibility the other possibility is the same orbital part, but the spin part is different that is it has so called down spin. Now, in the absence of a field these two are two different two possible single particle states. Now, what happens if I bring in another electron, and the second electron is also capable of occupying any of this single particle states. The second electron also has an in its wave function and orbital part and the spin part.

Now, the question is when the two electrons are together in my system my system it is comprised of two electron in that case the question is it possible to have both the electrons having say the 1 s orbital wave function and both up spins. So, the question that we are opposing here is as follows. I now have two electrons. When I have two electrons, then I am assuming that both of them are occupying the 1 s orbital. So, now there is one part of their single particle state missing and that is there spin part.

Now, we are asking this question is it possible that electron one is going to have a single particle state like this; and at the same time in my system, there is the second electron which is going to have a single particle state like this. So, this is my option one for the two electron system sorry option one. The other option; obviously, is what I have drawn on the top, so the first electron and the second electron both of them have the has the orbital wave function the 1 s orbital, but one of them is having an up spin and the other one is having a down spin.

So, let us say that this is my option two. Now, from our knowledge of atomic structure, we know that well this option is not valid, but this is the valid option as put forward by the Pauli exclusion principle. And therefore, we would say that using the Pauli exclusion principle, the single particle state for two electrons are going to be like this that the orbital parts can be the same, but there spin parts are going to be different.

And that is why we always write the electronic configuration of a system where there are two electrons like this which means that I have hydrogenic 1 s orbitals the first electron is occupying the hydrogenic orbital with let us say an off spin. And the second one if it is having the same hydrogenic orbital 1 s, it is going to occupy, it is going to have a down spin wave function. Now, that we have talked about the microscopic states of an electron the possible microscopic states in terms of the single particle states.

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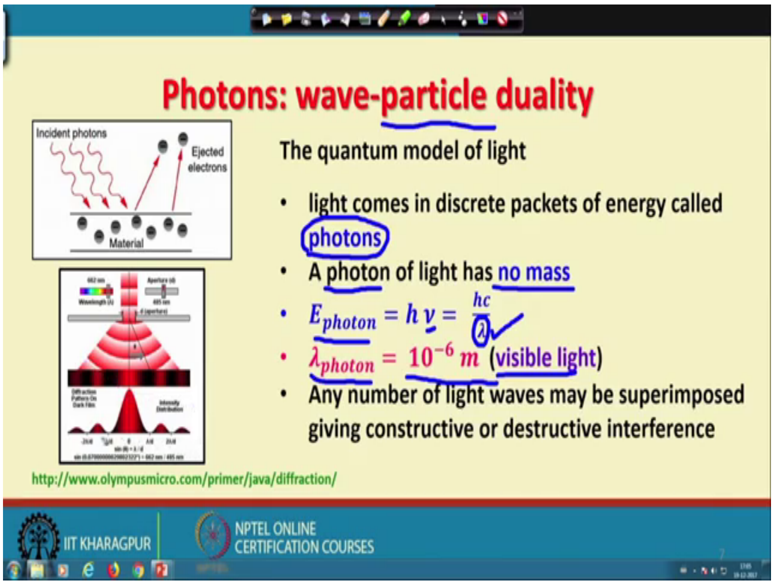

Let us now move over and talk about the wave particle duality, but may be before that let me go back and once again emphasize the fact in summary of this slide, we can say that an electron is the fermions, because it has two single particle states accessible to it. What is given single electron one is 1 s up spin, the other one is 1 s down spin. And therefore, one electron can either occupy one of them or not. So, these are ideal cases of the fermions. Now, let us look at what happens in the case of photons. We know that light when it shines on any surface or any matter, we generally understand light has an electromagnetic radiation, which is associated with wave nature.

So, it came as a big surprise almost 100 years back that the particle nature of light was proposed and the quantum model of light then said that light comes in discrete packets of energy and not in a continuous fashion. And these discrete packets of energies are called photons. And do you know the kind of evidence that was put forward in support of this theory, yes, Crompton effect, photoelectric effect; these are the different experiments which came in the beginning of the twentieth century for which Einstein developed his theory of the quantum nature of light. And this photon was proposed to be package of energy having no mass.

So, how do you define the microscopic state of a photon? You say that if you have a light of certain wavelength lambda, then the you can associated with it a frequency nu this is the frequency nu which will tell you about the energy of the single photon. And the single photon energy is then given by h nu, where h is the Planck's constant. And you can replace nu by c by lambda, therefore relating the energy of the single photon to the wavelength of the light.

So, if I look at the visible light it is very easy to show that the wavelength associated with the photon is about ten to the power minus 6 meter. Now, as a result of having this wave particle duality, you must appreciate that I am having a stream of discrete packets of energy impinging on whatever matter I am looking at.

And this impinging train of packets they also behave like waves that is because if you allow the light to go through some kind of slit as you may have performed some slit experiment, you see that there are certain diffraction pattern formed which are typical of the wave behaviour. And simply because any number of wave can be superimposed to give you either constructive or destructive interference, you see that light passing through this aperture gives you an intensity diffraction pattern which has varying intensity has been recorded in this picture.

Therefore, the conclusion from here is yes the microscopic state is of light is comprised of quantum units called photons which have definite energy values, which do not have any mass. And if I want to think of the number of photons that I can associated in a given single particle state, there is no restriction. And therefore, I will say that a photon is a boson by definition.

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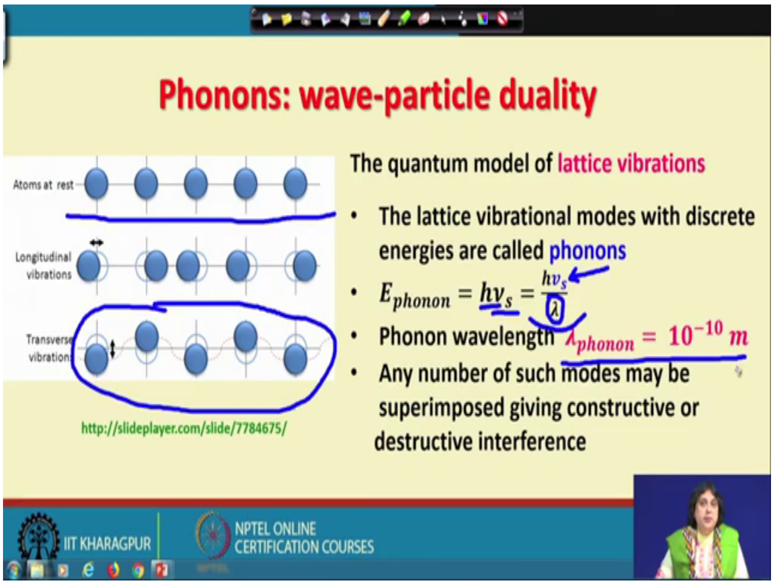

Similarly, one can think of the lattice vibrations in a solid as bosons. Now, I will just introduce the name phonons here by saying that when you have a solid this is a simple one dimensional representation of a periodic solid these are the different lattice point that we can see here and there are atoms at rest. But in real world you do not have the atoms at rest, but they are capable of executing small vibrational motion about their mean position at the lattice points, and this would generate some kind of displacement along this direction along which we are periodically seeing the placement of the atoms. So, these are known as the longitudinal vibrations.

But in may so happen that if you have a 2D lattice, two-dimensional lattice there may be displacements in the directions perpendicular to the longitudinal direction of longitudinal vibration, and these vibrations are called transverse vibrations. Now, it has been proposed that this vibrational modes that are generated by coupled vibrations of the different atoms in these lattices these are quantised and this quantised modes of vibration of a solid is known as a phonon.

Now, if you look at the energy of a phonon mode, then it is once again given by the Planck's constant multiplied by the frequency of the phonon mode. And in this case, you can related to the wavelength of the phonon because these vibrational motion that has been shown here generates a wave like nature of the vibration that propagates through the medium. And therefore, here you can talk about the wavelength of vibration as well as the velocity of the phonon that determines what the energy of the phonon is. The other thing that I would like you to note is that the wavelength of a phonon is 10 to the power minus 10 meter what was the wavelength of a photon, it was 10 to the power minus 6 meter. And therefore, all the both photon and phonons are bosons they have very, very different energies that when we consider them in detail. So, in both the cases of phonons and bosons what we find is they are it is possible to accommodate them in the same single particle state.

So, the next question that we will ask is can we now count the number of microscopic states possible for these identical particles, this is what we will see next.