**Introduction to Molecular Thermodynamics**
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**Lecture - 05**
**Microstates of a System**

Welcome. In today is lecture we are going to look for a description of the microscopic state of a system that we are interested in. So, the title of today's lecture is Macro and Micro States of a System in Equilibrium.

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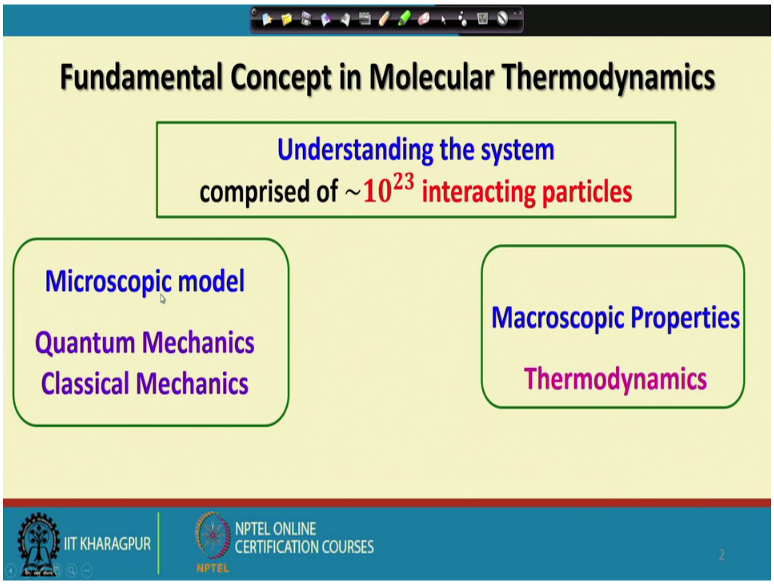


We have already seen this slide which basically summarizes the fundamental concept in molecular thermodynamics. It says that if you were trying to understand the properties of a system that is comprised typically of 10 to the power of 23 interacting particles. First as, we have already seen that we will be we have already discussed how thermodynamics can be used to understand the macroscopic properties of the system. And here, in today is class we will be interested more in understanding the microscopic model of the systems that we are interested in.

And as we have mentioned before, in general most of the systems are modelled in terms of quantum mechanics. For example, if you are interested in molecular systems, in that case you are going to use quantum mechanics without fail. But there are certain cases where the description of classical mechanics to develop the macroscopic model, is also found to be extremely useful. But in today is class what we are going to do is, we are going to concentrate on developing the microscopic model of a system, in terms of quantum mechanics. And in the third part of this course we will see how statistical mechanics connects these two extreme descriptions.

So, let me just remind you of what we have learnt regarding the macro state of a system. Or in other words how to characterize the equilibrium state of a system that can be experimented on in the macroscopic scale.

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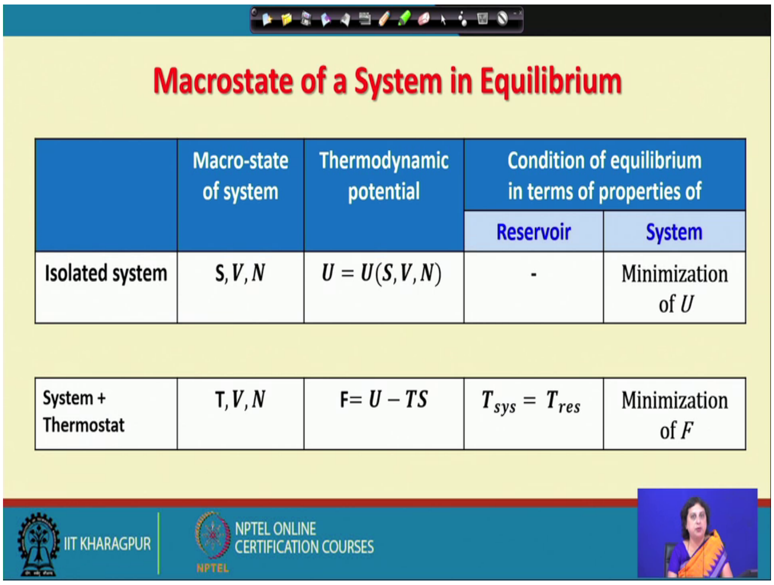


So, we have already seen that if I have an isolated system, in that case I require only three thermodynamic variables, entropy volume and number of particles to describe a given equilibrium state of the system. And in those scales we found that that is a quantity called thermodynamic potential which uses these three variables as natural variables, and the condition of equilibrium is determined in terms of minimization of the internal energy.

We have also seen if I couple the system with a thermostat and allow it to interact with the reservoir in a certain way, then for example in this case you will use these three variables, temperature volume and the number of particles to describe the equilibrium property of the system. The corresponding thermodynamic potential is the Helmholtz free energy and the condition of equilibrium is given by equality of temperature between the system, and the reservoir as well as the minimization of the Helmholtz free energy.

Now, with this idea of description of the macro state in mind, now we go and look for how do I define the microscopic state of a system.

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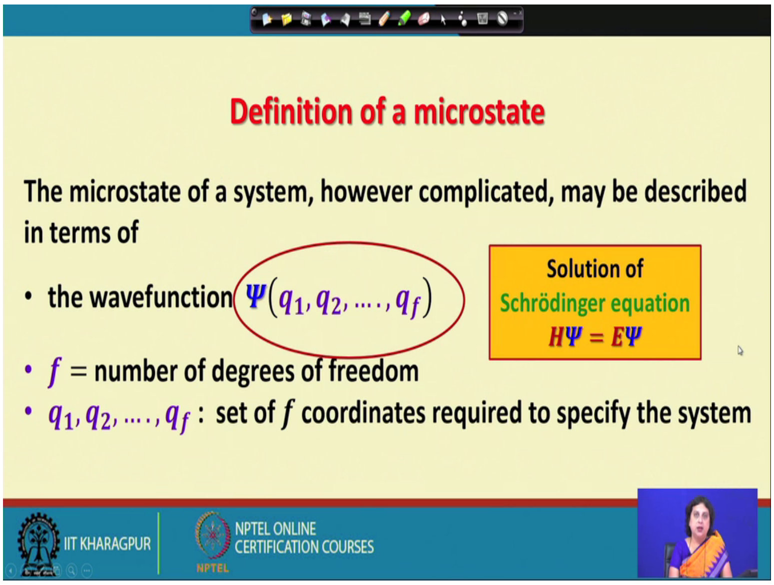


So, once again your system is the same, it may be a box full of gas or completely sealed bottle of some liquid, it does not matter however complicated.

Your system may be what we are looking for is the most general description of the microscopic state of the system. So, a state that described the microscopic length scale configuration as well as interactions. So, let us have a look at what quantum mechanics tells us about the microstate of a system in this extreme regime. It says that the microstate of the system can be defined or may be described in terms of a wave function. So, here psi the wave function and let us say I have these variables q one q two etcetera up to q f; these f variables which decide what the value of this wave function going to be.

So, once we know this, then the question is how much information regarding the wave function do I require. So, it before I try to explain that, let me explain that f here is a number of degrees of freedom in the system, and the independent variables q one q two etcetera this is a set of f coordinates that is required to specify the system completely.

So, once again coming back is it possible to understand or obtain complete information regarding psi for a very complicated system. The answer is well it may be possible for simple systems, but it is not possible for very complicated systems. But it still does not prevent us from defining a microscopic state and this is how we are going to do it.

The information regarding the psi the wave function psi is obtained as a solution of the Schrodinger equation. So, we are going to look at the solutions of the Schrodinger equation for simple model systems and try and understand what these microscopic states are and how we can count the number of possible microscopic states. So, let us look at the renewed definition of the microstate.

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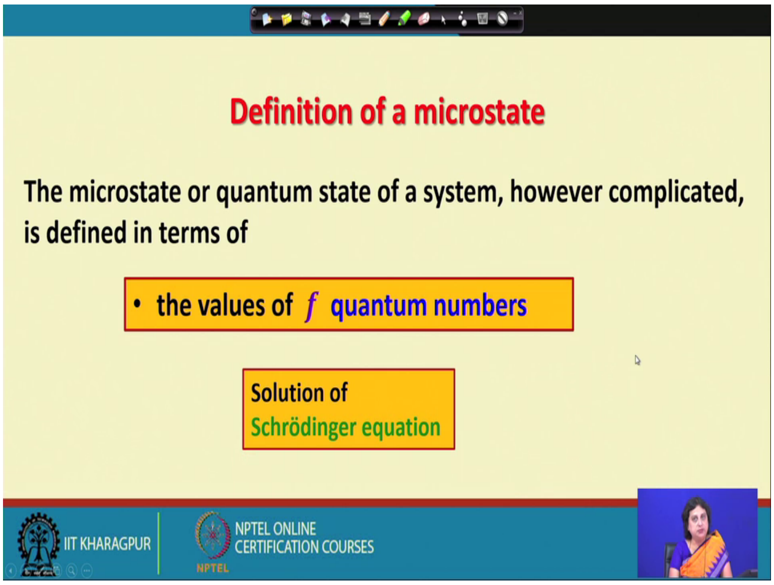


We would say the microstate or a quantum state of a system does not matter. However, complicated is, can always be defined in terms of f quantum numbers; and these f quantum numbers; obviously, will ask me the question where do I get them from; obviously, you would get it from the solution of the Schrodinger equation and they these quantum numbers tell us how many solutions are possible which will obey the Schrodinger equation.

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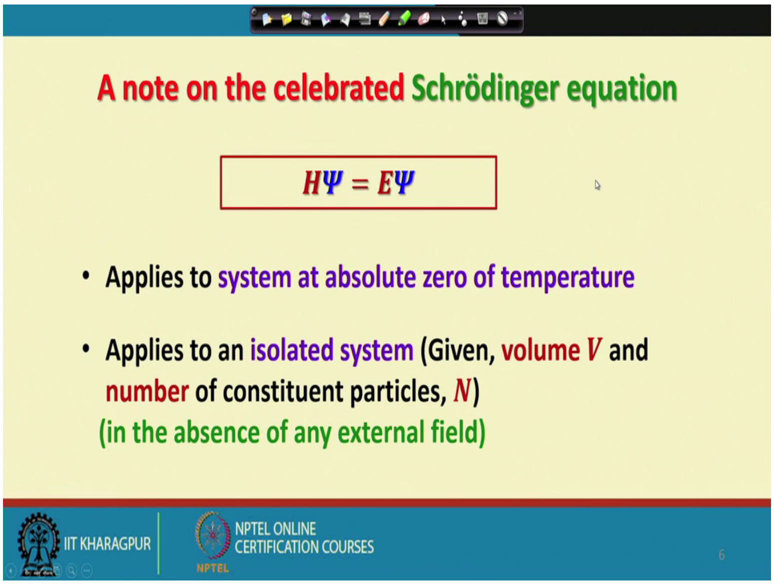


Now before I proceed further, I would like to point out there whenever you are using the Schrodinger equation, you must be very careful in the sense that the Schrodinger equation at the microscopic level, when it describes the properties of the system, it solves the one solves the Schrodinger equation at absolute 0 of the temperature.

If you look at the specific functional form of the Hamiltonian operator that operates on the wave function side do you find any temperature there? No because the wave function because the Hamiltonian is a summation of the kinetic energy operator plus the potential energy operator and temperature does not appear anywhere. So, basically you are looking for the microscopic state of the system at absolute 0 of temperature. You should also remember that whenever you are solving the Schrodinger equation, you are actually specifying the volume of the system and also the number of constituent particles. And then you are looking for solutions of the Schrodinger equation for various allowed values of the energy Eigen state.

So, for one energy Eigen state the total energy of the system is constant, the volume is given and then the number of particles is fixed. And therefore, I would say that the solution applies to an isolated system, which is not interacting with the surrounding. Of course, this has to be the case when you are in the absence of any external field. Now with this background in mind let us go and have a look at some of the examples as to how these solutions can be used to describe the microscopic states of a system.

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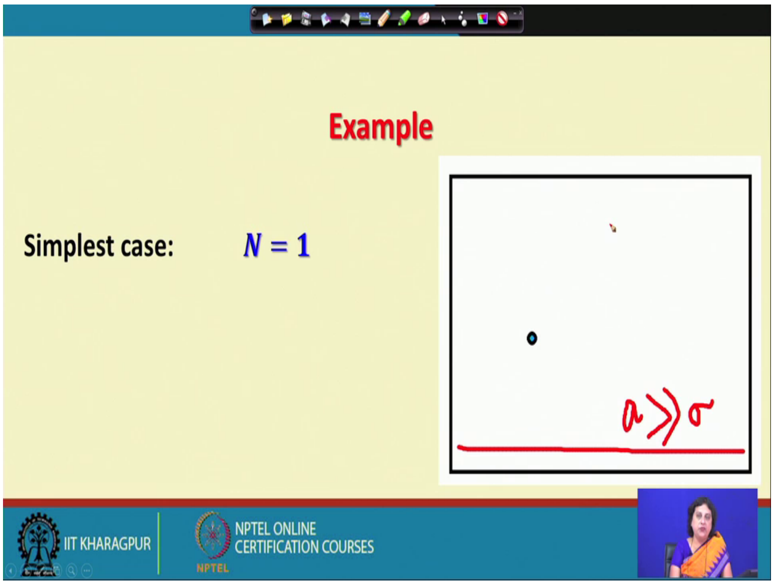


We will start with the simplest case where there is only one particle present in the system. So, typically this would look like this picture, you have a huge system and there is probably one particle present in it and why can I see this single particle with naked eyes the answer is no.

Therefore, any such picture tells you that you are now modelling the system at the microscopic length scale, and then the dimensions of the box as shown here in a small scale this must be if let us say that this is a, then this must be much much greater than the size of this particle which typically is taken in terms of sigma. And I would say that therefore, this is a typical representation of the microscopic snapshot of the system which we are trying to investigate now.

So, the first example that we take is a very simple one.

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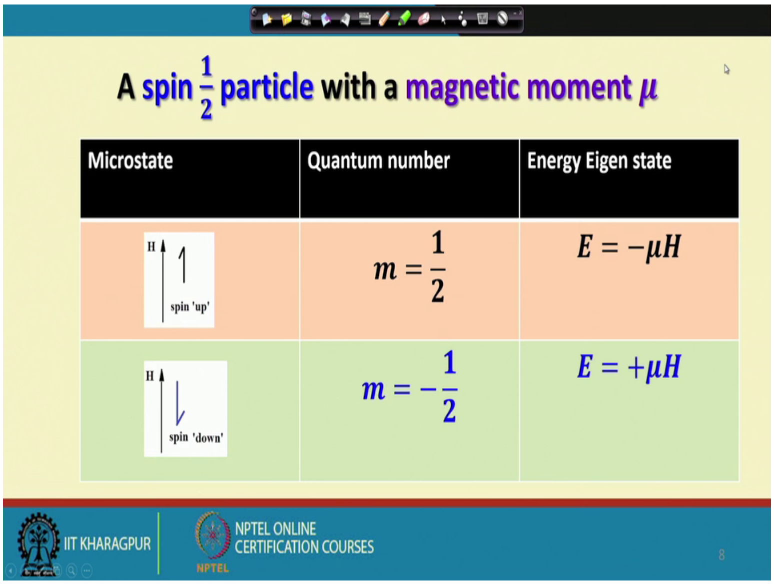


It is a spin half particle with a magnetic moment mu. Now what is a spin half particle? This is a particle whose spin angular momentum can take up only two allowed values, when it is present in the presence of an external field.

So, typically solution of the Schrodinger equation tells you that the spin angular momentum under such cases, will be either plus half or minus half of the basic spin angular momentum. So, here a typical microscopic state of the system would look like this. So, if this is the direction of the applied field, this would be corresponding to the spin up state, where the spinners aligned parallel to the direction of the field.

And in that case the associated quantum number would be such that you will have the m value equal to plus half, and the energy Eigen state will have the value of minus mu into H. On the other hand there is another possibility allowed by the rules of quantum mechanics and that is the spin down state, where the single spin half particle that we are considering, is now directed opposite to the direction of the applied field and accordingly its energy is e is equal to plus mu H. So, what do we learn from this particular slide we learn that I have a system where n is equal to 1 and let us say the volume is fixed at v.

Now here capital n is equal to 1. So, for this given microstate of the system this is a typical snapshot of the microscopic state of the system, this is another possible snapshot of the microscopic state of the system. If I now fix the value of the total energy of the system, at this value there is only one microscopic state which is this. If I fix the total energy of the system at this value then; what is the possible microscopic state, this is the only possible microscopic state as allowed by the rules of quantum mechanics.

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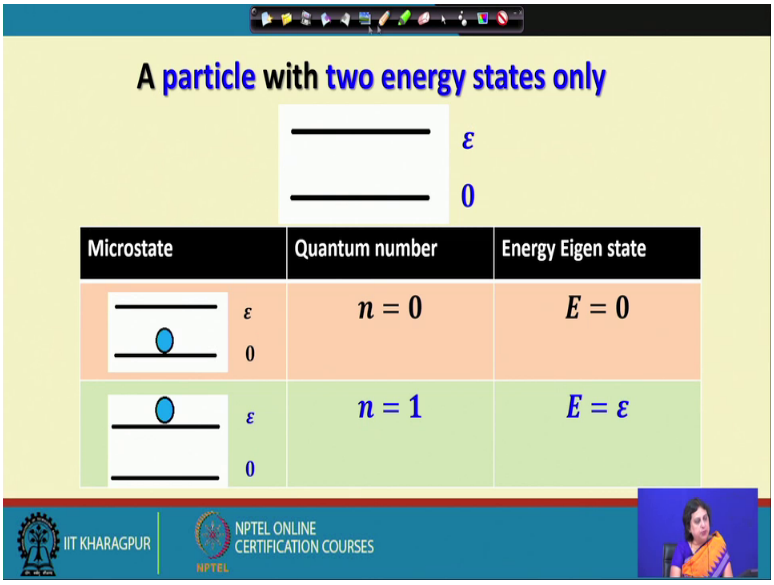


Now there can be other situations as well and in general this is one of the simplest situations.

That you can have let us say you have a single particle present in a constant volume, and solution of the Schrodinger equation for this particle gives you only two energy states. The lower energy state is the 0 of the energy which I designate as epsilon equal to 0. And the upper energy state which is higher than the 0 energy state is associated with some energy value epsilon. If I use a quantum number in that case I will say that let us say that this quantum number is n. So, how many quantum numbers can I find here associated with these two possible solutions? Of course, there will be two quantum numbers associated with these two values. So, typically let us say that the first value allowed value of the quantum number is n equal to 0.

Correspondingly the energy Eigen state as shown here will be equal to 0, and this is going to be a typical representation of the microscopic state of the system. So, by using this ball all I am trying to say is the system now occupies the lower energy Eigen state, Now when the quantum number n is equal to 1. So, it has taken up its second possible value then the energy of the system would be equal to epsilon, and then this is going to be a typical representation of the microscopic state. So, it says that there are two energy states available to the system, given a chance it can either be here or be here when the system is in the first microstate.

The total energy of the system comprised of the single particle is E equal to 0, but when the system is comprised of this microstate, the total energy is equal to 0. Now can you answer this question which microstate will be possible for this system if the total energy is epsilon; of course only this system is possible. Now let us once again see some more examples so that we understand how the quantum numbers are being used.

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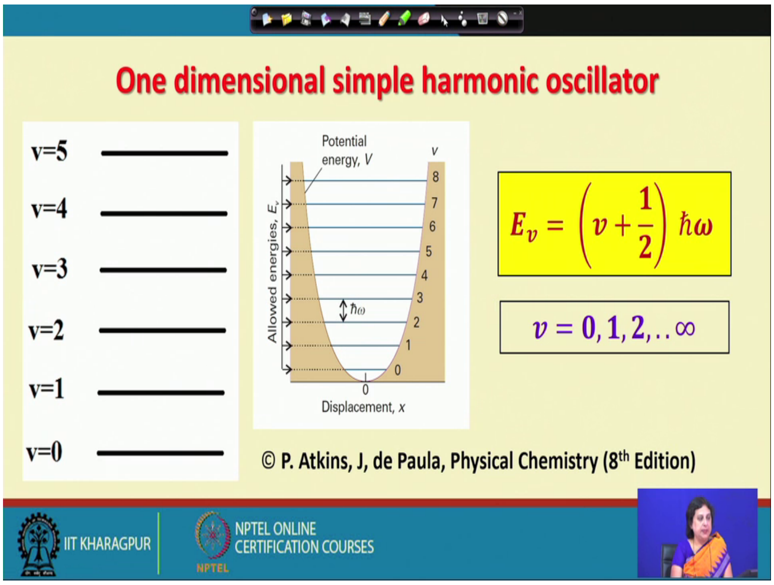


Now, we take up this one dimensional simple harmonic oscillator. So, as all of us know that the solution to the Schrodinger equation to define the microscopic state of a system.

For any such system is characterized by a single vibrational quantum number or a simple quantum number v and the discrete values of energy that are obtained by the solution of the Schrodinger equation is given by Ev, that is h cross omega multiplied by v plus half. Now what is omega in this case omega is the intrinsic angular frequency of the simple harmonic oscillator; h cross is h by 2 pi where h is the plan constant and this will be used all throughout our discussion. So, here are different possible values of E varies from each other in terms of this quantum number v. So, the question is what are the different values of v does quantum mechanics allow; it is possible to show that we can take a values from 0 1 2 and so on and so forth up to infinity.

So, what do we learn from this kind of result, we understand that if I have a simple harmonic oscillator that is present in a one dimension in that case how many microscopic states for the system are possible? The answer is infinitel; how do I know that there infinite that is because v can take up an infinite number of different values. Now let us have a more pictorial representation of these microscopic states and they are as follows. So, if I plot the different energy values possible for different values of the quantum number v, this is the energy value for v equal to 0, this is the energy value for v equal to 1 v equal to 2, v equal to 3, v equal to 4 and so on and so forth.

The interesting thing to note here is that, the difference in energy values between any two pair of energy states is the same independent of whether you are looking at the energy difference between v equal to 0 and v equal to 1 states or v equal to 3 and v equal to 2 states it does not matter, all these energy gaps are the same. Now when I understand this, then I should also be able to visualize where this energy states came from. In the original Hamiltonian one used a potential energy function v, which is given by this solid line and told me that as the system undergoes a displacement from its mean position there is a potential nonzero potential energy that tries to restore it back to its position.

And the solution of the Schrodinger equation has now given you these discrete energy values, which are possible which are allowed for the system according to quantum mechanics. And we understand that many such energy states are possible even if you have a single particle and this particle is present in just one dimension.

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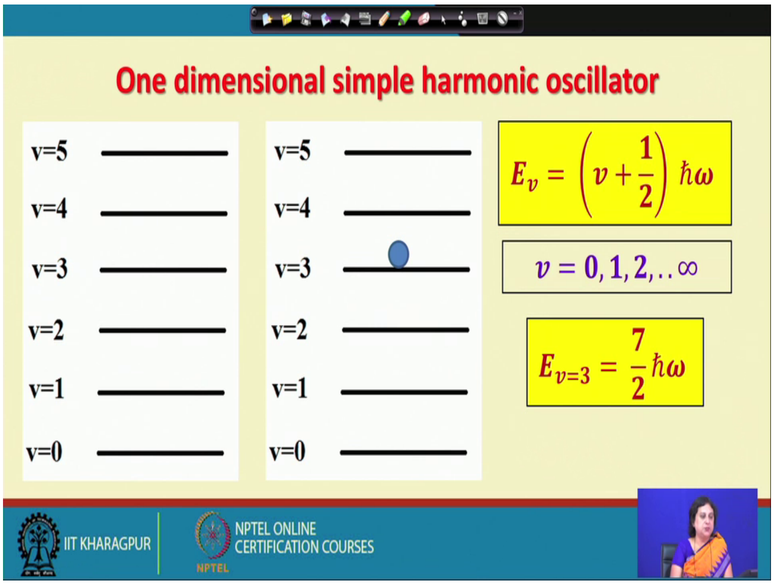


So, let us next have a look at what these microscopic states are. So, as before I have these level levels with me and this is typically how I am going to represent a microscopic state where the system is present the single particle is present in the lowest energy Eigen state corresponding to the lowest value of the quantum number v.

So, that is v equal to 0 therefore, what would be the energy of this system if I put v equal to 0 in this expression, this is what I get its half h cross omega and you are quite aware of the fact that this is the 0 point energy of the one dimensional simple harmonic oscillator. Now I can also go back and represent the situation when this single particle is occupying the energy Eigen state with v equal to 1, then the energy of the system is going to be 3 by 2 h cross omega corresponding to the value, that I obtained by putting v is equal to 1 here. I can also have another microscopic state which is corresponding to v equal to 3.

Where the system is placed high up in one of these are energy Eigen states and the corresponding energy is 7 by 2 h cross omega. So, what does it tell us it tells us that even if I have a single particle and I have this particle in just one dimension even in that case depending on what are the energy of the system is the system can have many many different microscopic states, and that I can either represent pictorially or I can in general say that depending on what are the value of the quantum number v is, I can describe the corresponding microscopic state of a simple harmonic oscillator present in one dimension.

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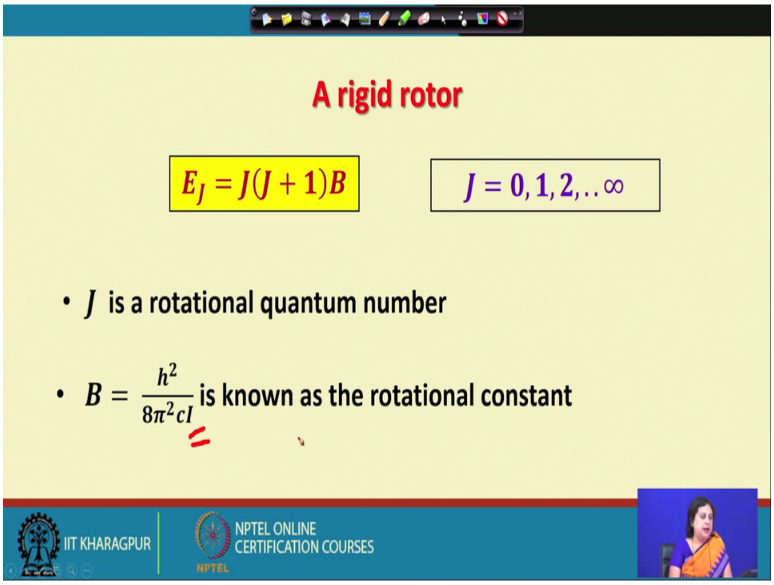


The next system that I will just touch upon is a rigid rotor; and it is known from quantum mechanics that the discrete energy values that are allowed for a rigid rotor is given by this expression where it is characterized by this rotational quantum number J and it is shown that E J is given by J into J plus 1 into v, where J can take up discrete integer values starting from 0 1 2 and so on up to infinity. So, what are the possible E J values that you can think of? You can think of an infinite number of possibilities, in this case there is another quantity that appears and this quantity is B. So, what does B represent? B represents the rotational constant and it is a characteristic property of the system that you are studying.

Because it depends on the moment of an inertia of this rigid rotor, and that is the information of the specific system that is carried by B. So, once again we have a system, where I have a single particle which is a rigid rotor and there are infinite number of values possible for the quantum number J, with which I associate the discrete energy values E J therefore, the different microscopic states are going to be characterized by different values of J. Now once I have some ideas about these simple very simple systems, let me now go back and pick up a little different idea but still in the one dimension.

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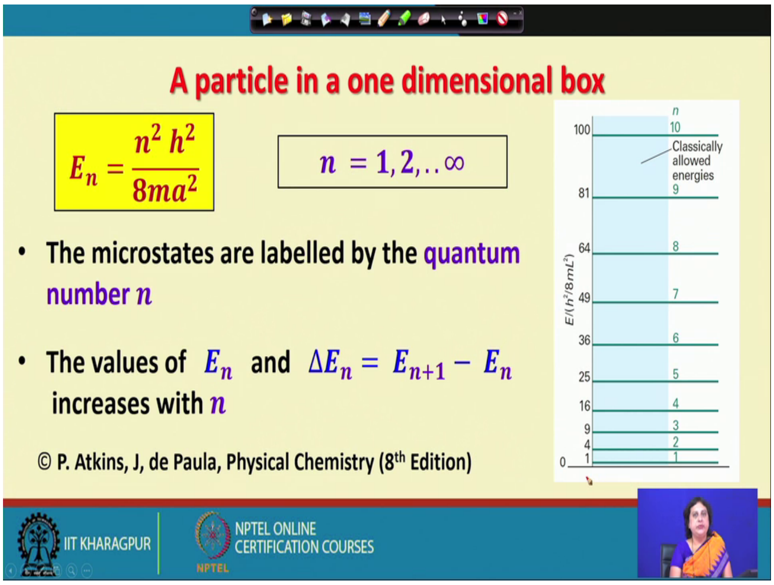


And in your introductory courses on quantum mechanics or quantum chemistry, you have come across this situation where a particle is confined within a one dimensional box, and if this length of confinement is a and if the particle has a mass m, then the discrete energy values that are possible for the system are given by E n, that depends on the mass m the length a of the direction in which it is confined and it also depends on one particular quantum number which is represented as n. An n can take a values from 1 2 3 to infinity. And therefore, I understand that for a particle in a one dimensional box, once again we are faced with the situation that an infinite number of microscopic states is possible and for each value of n I have an associated value of E n, which gives the value of energy Eigen state of my system.

Now if I want to have a closer look here. So, this is how the energy states vary with the quantum number. So, here this represents the energy value with respect to n equal to 1, this represents the energy value with respect to n equal to 2 3 4 and so on and so forth. So, what I can see is quantum mechanics once again has predicted a discrete set of energy values, corresponding to each value of the quantum number n, and then I can basically generate different microscopic states by using this quantum number n, and I also understand here this particular example is different from my previous example; in the sense that here I have energy values as before increasing with n.

So, for n equal to 1 the energy value is h square by 8 m a square, let us divide e n by this h square divided by 8 m n square a square. So, what I am left with this n square. So, as you see for n equal to 1 the scaled value of E that is 1, for n equal to 2 the value is four and so on and so forth. Now have a look at this, if I am in this region then the energy difference between two successive energy states is small, but as I go higher and higher up this value goes on increasing. So, as I would say that this is a very different set of microscopic states from what we have seen in the previous case of simple harmonic oscillator.

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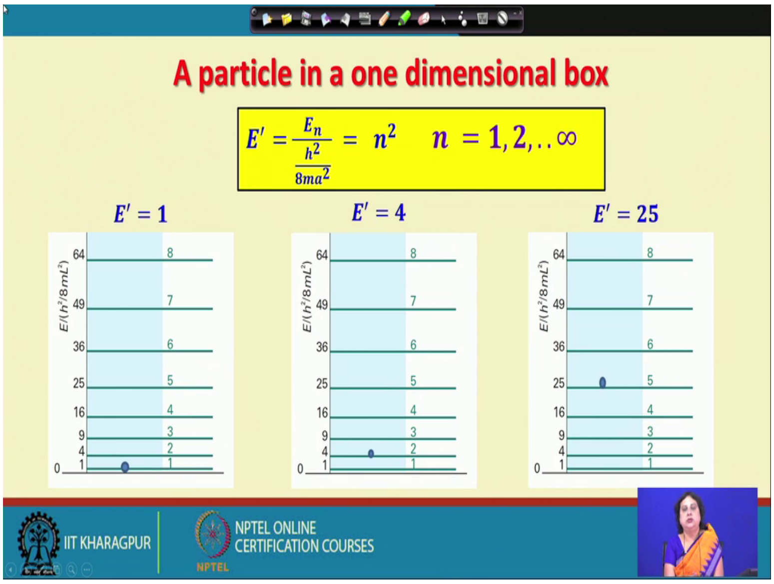


And if I want to visualize some of these states in the for a particle in a one dimensional box. So, can we guess what is going to be the energy E prime that is defined here, which is equal to n square. So, here I find that my system is present in the state where n is equal to 1. As a result I would say that the energy of the system is going to be e prime is equal to1. Similarly here the system is present corresponding to n equal to 2 and therefore, e prime that energy of the system in units of h square by 8 m a square is equal to 4 similarly this is a pictorial representation of the system corresponding to n equal to 5 and E prime value e prime equal to 25.

So, we have come to the conclusion of this very simple lecture where we have used the quantum numbers to define the microscopic states of the system. Every microscopic state has a specific value for it the quantum number of their Eigen states that we are interested in. We have looked at the system, where we have only a single particle for which the Schrodinger equation is solved under constant volume and constant number of particle condition and the solutions give us the different discrete energy Eigen states. What we will see next is how the increase in dimension and the increase in the number of particles complicate the situation and increase the number of microscopic states possible.

Thank you.