Introduction to Molecular Thermodynamics
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Lecture - 23
Ideal Gases (Contd.)

Welcome back, today we are going to talk about the Statistical Thermodynamics of a Diatomic Ideal Gas system.

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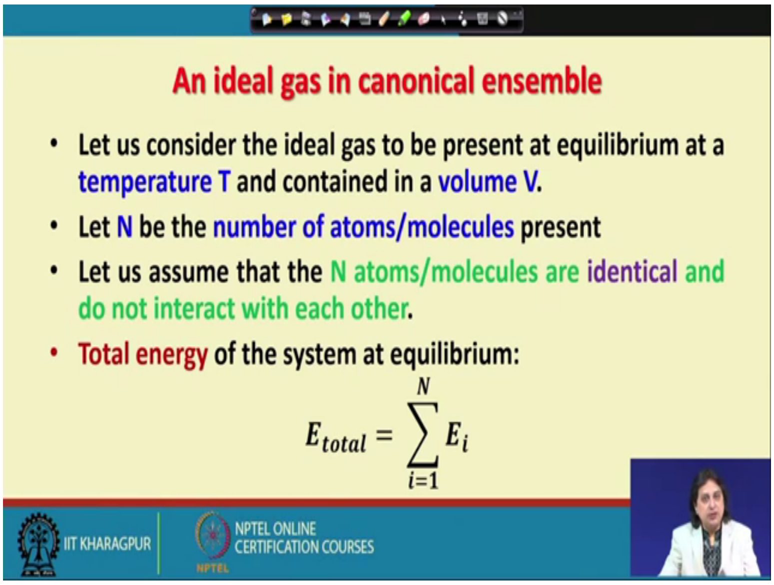

An ideal gas in canonical ensemble

- Let us consider the ideal gas to be present at equilibrium at a temperature T and contained in a volume V.
- Let N be the number of atoms/molecules present
- Let us assume that the N atoms/molecules are identical and do not interact with each other.
- Total energy of the system at equilibrium:

$$E_{total} = \sum_{i=1}^{N} E_i$$

So, in this system as before for the monatomic case we have an ideal gas is present at equilibrium at a temperature T and it is contained in a volume V.

We assume that there are capital N number of particles or atoms present in the system. So, if I am talking about a diatomic ideal gas I will have capital N number of molecules present in the system. Now let us assume that these molecules are identical and they do not interact with each other. And then we would say that the total energy of the system at equilibrium is comprised of all the individual energies of the molecules present in the system. And this is possible to write so, simply because there is no interaction between the different molecules.

The molecules are formed by the interaction between the constituent atoms, but different molecules they do not interact in the ideal gas system.

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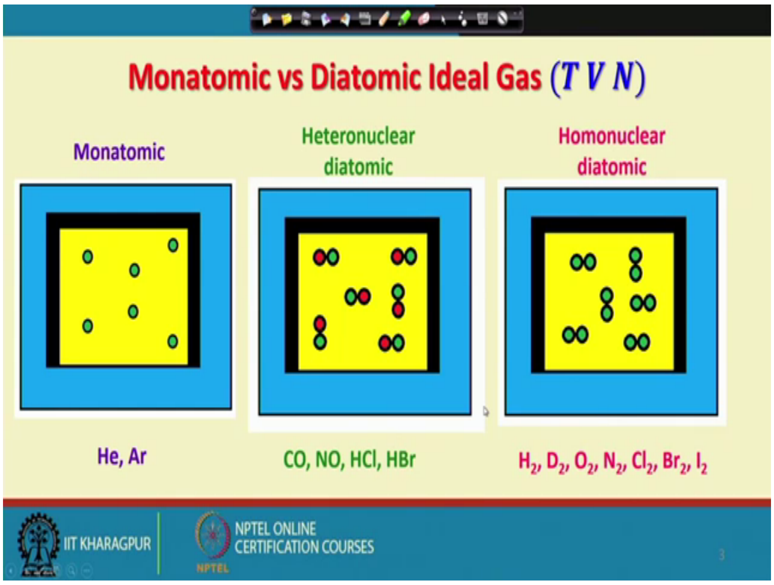

Monatomic vs Diatomic Ideal Gas ($T\ V\ N$)

Monatomic

Heteronuclear diatomic

Homonuclear diatomic

He, Ar

CO, NO, HCl, HBr

H_2, D_2, O_2, N_2, Cl_2, Br_2, I_2

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Now from here let us try and visualize the difference that we are going to appreciate as we go from a monatomic ideal gas to the treatment of a diatomic ideal gas. So, this was a picture that we used for the monatomic ideal gas. So, thermodynamically we would know if it is a monatomic or an ideal diatomic ideal gas in terms of the macroscopic states that you see that are T, V or N. But if I look at the microscopic picture of the system, this is how typically the monatomic system would look like. So, examples of such type of system would be helium gas or argon gas.

Now, for the diatomic system I can have a heteronuclear diatomic; gas molecule. So, what happens here is two different types of atoms combined with each other, they form a bond between each other and they form this heteronuclear molecule. And examples are carbon monoxide, nitric oxide, hydrogen chloride and hydrogen bromide gas. Obviously, you can also have two atoms of the same type forming the diatomic molecule. And therefore, they are called homonuclear diatomic and examples are hydrogen, deuterium, oxygen, nitrogen etcetera etcetera.

So, basically then we would like to demonstrate here that part of the treatment of statistical thermodynamics for ideal gases is the same for all these three systems; apart from the fact that the underlying structure, microscopic structure is going to be different for these three systems. So, let us try and have a look at what I mean by this.

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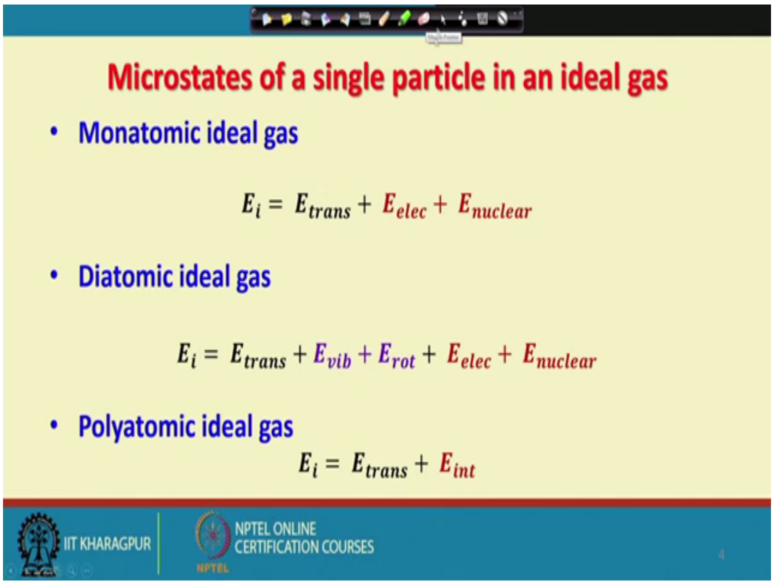

Microstates of a single particle in an ideal gas

- Monatomic ideal gas

$$E_i = E_{trans} + E_{elec} + E_{nuclear}$$

- Diatomic ideal gas

$$E_i = E_{trans} + E_{vib} + E_{rot} + E_{elec} + E_{nuclear}$$

- Polyatomic ideal gas

$$E_i = E_{trans} + E_{int}$$

So, if I remind you of the microstates of a single particle in an ideal gas; when we talk about the monatomic ideal gases, what we find is the total energy of every single atom that can be separated into a term which corresponds to the translation of the atom in the three dimensional box in which it is confined.

And there is another contribution as a sum of two terms, which come from the underlying microscopic structure of the atom. So, now if I look back and see what happens to the diatomic ideal gas; what I find is yes; I still have this translational part sorry I am going back [FL]

[FL]

So, let us talk about the microstates of a single [FL]

[FL]

In order to appreciate the importance of difference in structure between a monatomic ideal gas and a diatomic ideal gas. Let us first look very closely at what happens to the microstates of a single particle in these systems.

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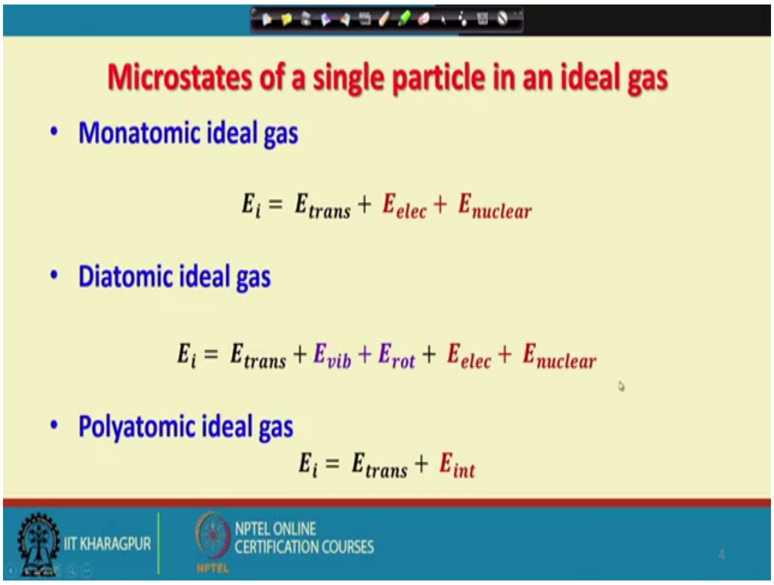

Microstates of a single particle in an ideal gas

- **Monatomic ideal gas**

$$E_i = E_{trans} + E_{elec} + E_{nuclear}$$

- **Diatomic ideal gas**

$$E_i = E_{trans} + E_{vib} + E_{rot} + E_{elec} + E_{nuclear}$$

- **Polyatomic ideal gas**

$$E_i = E_{trans} + E_{int}$$

So, this is what we are trying to highlight over here; if you would remember then for monatomic ideal gases, for every atom present in the system the allowed values of energy for this single atom could be separated into the contribution of the translational motion of the atom as a whole within the volume in which where it is confined. And a sum of electronic and nuclear energies which are associated with the underlying microscopic structure of the atom itself.

And therefore, we saw that it was possible to separate out this problem into two distinct parts. One is the overall movement of the atom in the 3 dimensional space; the other one is the underlying structure; the underlying microscopic structure of the atom as obtained from experiments or by solving the Schrodinger equation in quantum mechanics. Now let us try and understand what will happen to this kind of relationship when we talk about an diatomic molecule.

So, that is exactly what we are going to see next and in the case of a diatomic ideal gas; for each molecule constituting the system this is what we are going to have. So, as before I have two parts in the energy; this part is corresponding to the overall motion of the molecule in the three dimensional space in which this molecule is confined. There is another term which is a summation of different contributions that comes because of the underlying structure of the molecule.

So, the corresponding term here was E electronic plus E nuclear and now you see that we have two extra terms coming here because of the fact that as a diatomic molecule; this system will have additional features in the structure, in terms of vibration of the chemical bond connecting the two atoms; as well as rotation of this molecule about a principal axis of rotation.

So, now as we understand that the difference between a monatomic and diatomic molecule therefore, would come in terms of the seperabilty of its internal structure; that is underlying microscopic structure into these different parts. One is the vibrational energy, another one is a rotational energy and as before I will have electronic energy and nuclear energy; where each of the atoms present in the system is going to contribute to the observed and allowed values of these energies.

Actually this is a part of a very general description and this description is valid for any polyatomic molecule. If I have an ideal gas comprised of any polyatomic molecule like carbon dioxide or water vapor H 2 O vapor; in that case I have more than two atoms forming the molecules of the gas. In that case also, it is possible to separate out the problem into two parts so, the energy of each molecule will have one part which is the translational part, another part will have the internal structure part.

Therefore, the treatment of any ideal gas which is comprised of a diatomic or higher number of atoms forming a polyatomic molecule in the gas; the treatment of statistical thermodynamics of the gas requires us to understand if I can separate out the translational motion of the molecule as a whole from the contribution of the internal structure.

And then especially in this lecture for the diatomic case, we will try to understand how this internal structure can be separated into contributions coming from vibrational motion of the single chemical bond that is present; rotational motion of the molecule itself and also the contributions of electronic and the nuclear energy levels.

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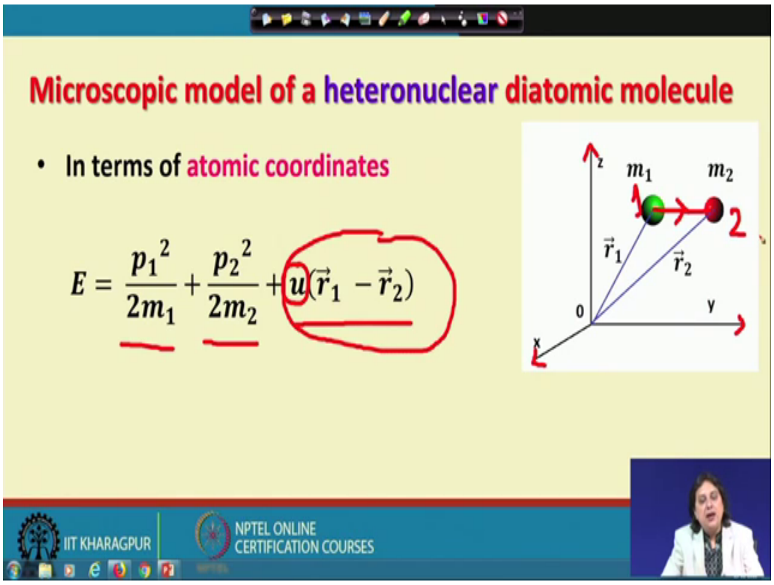

Microscopic model of a heteronuclear diatomic molecule

- In terms of atomic coordinates

$$E = \underline{\frac{p_1^{\,2}}{2m_1}} + \underline{\frac{p_2^{\,2}}{2m_2}} + \boxed{\boxed{u}(\vec{r}_1 - \underline{\vec{r}_2)}}$$

So, let us start the microscopic model of the diatomic molecule from a very simple picture. Now as you see here; what I have drawn is in the laboratory fixed frame; that means, I am using the cartesian axis. So, this is the direction of the x axis, this is the direction of the y axis and this is the direction of the z axis. Here my diatomic molecule is comprised of one atom which is here and another atom which is placed here and there is a chemical bond let us say between them.

Now, let me denote by r 1; the position vector of this atom 1 with respect to this laboratory fixed cartesian coordinate space. And r 2 is the position vector of this particle 2; in the 3 dimensional space. And for the sake of simplicity, I am going to use a classical mechanics kind of description just to show you that the separation of different types of coordinates is possible.

But please try to understand that although I am using the position and the velocities our momentum together; this kind of description is perfectly general and also applicable when you are solving the problem of this diatomic molecule in Schrodinger equation.

So, let us go back and try and say that well if this particle one is having a mass m 1 and if this particle 2 is having a mass m 2, then the total energy of the system will have one term corresponding to the kinetic energy of particle 1, another term which is corresponding to the kinetic energy of the particle 2; plus one potential energy term which is given by u and that usually depends on the difference in the position vectors r 1 and r 2 so; that means, this must be this position vector.

So, if I can write down the heteronuclear diatomic molecule energy in terms of atomic coordinates; as you see here the coordinates r 1 and r 2 and these are dependent on x 1, y 1, z 1 and x 2, y 2, z 2. And in this problem, I have the motion of these two atoms coupled to each other through this potential energy term. Therefore, in the present form; it is impossible to separate out any kind of motion of one atom to the other; that is simply because they are bonded to each other and their interaction is represented in terms of that u term that I have shown you in the total energy.

So, let us go back and try some mathematical treatment to see if we can have a better separation of variables with in this kind of formalism. So, this is what we are going to look for.

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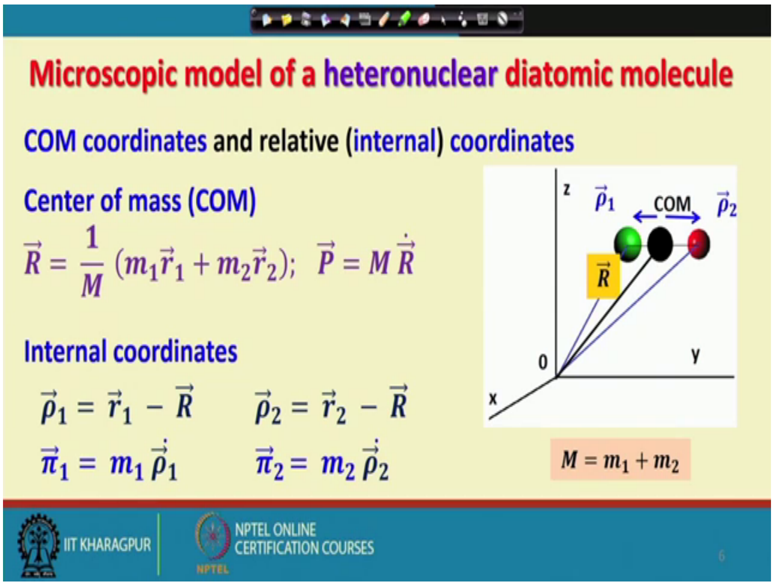

Microscopic model of a heteronuclear diatomic molecule

COM coordinates and relative (internal) coordinates

Center of mass (COM)

$$\vec{R} = \frac{1}{M}(m_1\vec{r}_1 + m_2\vec{r}_2); \quad \vec{P} = M\dot{\vec{R}}$$

Internal coordinates

$$\vec{\rho}_1 = \vec{r}_1 - \vec{R} \qquad \vec{\rho}_2 = \vec{r}_2 - \vec{R}$$

$$\vec{\pi}_1 = m_1\dot{\vec{\rho}}_1 \qquad \vec{\pi}_2 = m_2\dot{\vec{\rho}}_2$$

$$M = m_1 + m_2$$

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We are going to look for the center of mass of the this particular system and some relative or internal coordinates. So, let us first start by defining the center of mass; so, let me define capital M as m 1 plus m 2; that is the total mass of the molecule, which is comprised of the atom 1 having mass m 1 and atom 2 having mass m 2.

Now, I understand that I can always define the center of mass which is tentatively put here as a black ball. And the position vector of this the center of mass can be assigned this notation capital R, where capital R by definition depends on small r 1 and small r 2 that is where these individual atoms are present and what are their masses m 1 and m 2.

And therefore, when this molecule moves, the overall translational motion can be seen in terms of the center of mass motion also. And then the center of mass will move with a momentum P which is capital M into time derivative of this position vector capital R; which has been presented here as R dot. Now then what do I mean by the internal coordinates? I find that with respect to the center of mass atom 1 is now located at this position, which is given by this particular vector rho 1.

Similarly, I can assign another vector to denote the position of the atom 2 with respect to the center of mass. And these are now termed as the internal coordinates are defined as rho 1 and rho 2. Therefore, in this system we will see that atom 1 is now moving with a momentum which is given by m 1 into rho 1 dot. And atom 2 is moving with another momentum that is m 2 into rho 2 dot. Now once I have introduced this center of mass coordinates and the relative coordinates, let us see if they give us any kind of advantage in terms of separating out different types of motions present in the system.

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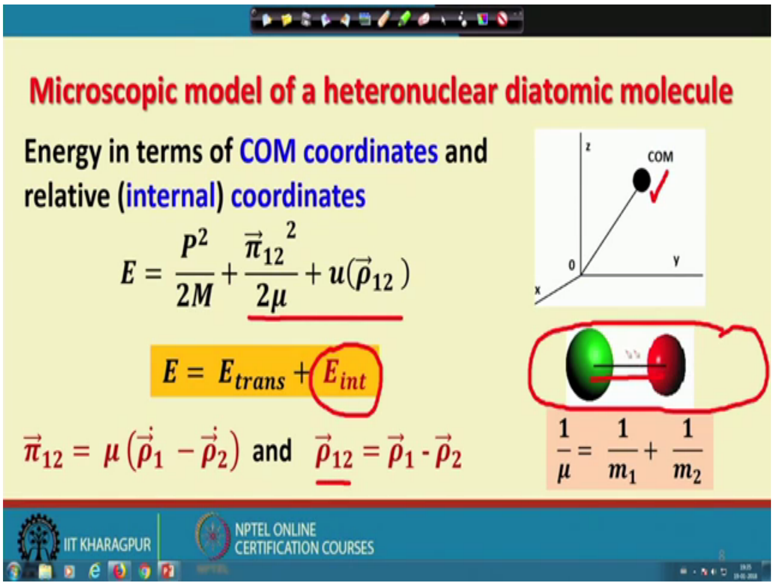

Microscopic model of a heteronuclear diatomic molecule

Energy in terms of COM coordinates and relative (internal) coordinates

$$E = \frac{P^2}{2M} + \underline{\frac{\vec{\pi}_{12}^{\;2}}{2\mu} + u(\vec{\rho}_{12})}$$

$$E = E_{trans} + E_{int}$$

$\vec{\pi}_{12} = \mu\left(\dot{\vec{\rho}}_1 - \dot{\vec{\rho}}_2\right)$ and $\underline{\vec{\rho}_{12}} = \vec{\rho}_1 - \vec{\rho}_2$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

So, that is exactly what we will see here; we will introduce a few more changes in the total energy.

So, what we have done is we have introduced one more change in variable whereby; we say that row 1 2 is equal to rho 1 minus rho 2. So, rho 1 2 is the relative separation vector between the atom 1 and atom 2 and it does not depend on where the origin of your coordinates access are. And then I would say that the associated momentum is pi 1 2; if I take these two expressions and plug them back into the original expression for energy that I derived; what I will find is I will find an expression like this through this change of variable.

So, what does it mean? It means that what I have gained here is as follows; first of all I have one part over here, which says that look at what I have in the energy. This part tells you that this is the kinetic energy of the center of mass which is having a mass capital M and whose momentum is capital P.

Now, what is this term? This term corresponds to the kinetic energy of a body, whose mass is mu and which is moving with a momentum of pi 1 2. And this one is an interaction term potential energy term between the atom 1 and 2, which depends only on the vector separating the two atoms. And therefore, I would say that in this case what we have introduced is as follows. The first term is corresponding to the translational motion of the center of mass and there is no interaction term involving involving the coordinate of the center of mass; that is capital R.

Now, in the second part what we have got is we have said that this is the relative separation vector of the 2 atoms, which I call rho 1 2. And then I said that if I fix this atom and observe the movement of the second atom with respect to the green one, then it would be as if a particle of reduced mass mu that is defined like this is moving about this fixed point.

So, that is what I mean by the internal coordinate and the associated momentum is pi 1 2. So, what we have achieved through this is; we have achieved a separation of the entire energy into one part, that is a translational motion of the molecule as a whole; that is being represented in terms of the motion of the center of mass without paying any attention to what exactly is the structure of the molecule.

I have another part, which depends on the internal structure of the molecule which is now called the internal energy; in terms of the internal core quad net rho 1 2; which is a relative separation between the 2 atoms. And I find that, this internal structure or the motion of the internal motion is now being modeled as this atom being fixed. And whatever motion the entire molecule executes is being modeled is being approximated as the movement of a reduced mass m u about this fixed atom.

So, now that we have seen that the energy of a given molecule can be separated out into these two terms. Let us now see the separate ability of the energy term that is designated here as the internal structure. So, that is going to be the topic of our next of the discussion.

So, we will start by reminding you about the energy levels of a diatomic molecule.

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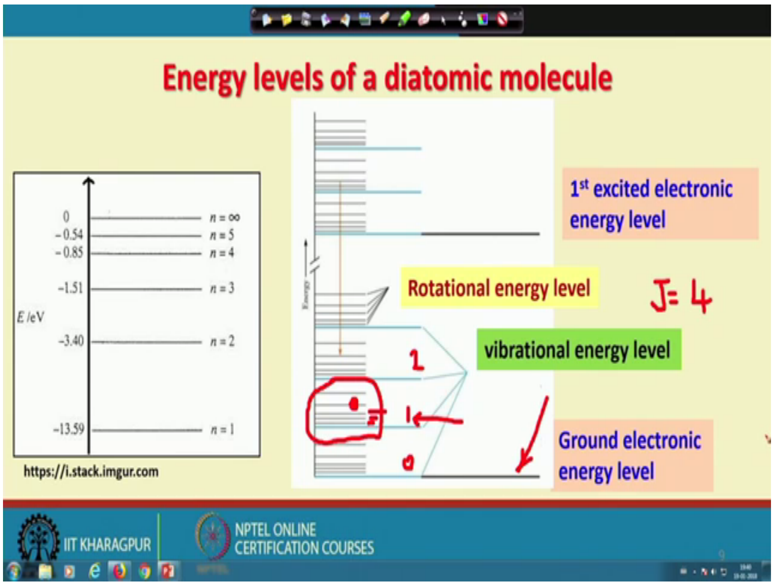

Energy levels of a diatomic molecule

And if you look back this one what we saw as the energy level diagram for an atom, which is constituting the monatomic ideal gas. In contrast, if I look at the energy level diagram for a diatomic molecule as you see that this is a lot more complicated. So, let me highlight over here some of the more important features of the energy level diagram for the diatomic molecule. So, as you see that this is the ground electronic energy level and you must remember that this corresponds exactly to the ground electronic energy level that we have seen in the monatomic case.

Now, here I also have the first excited electronic level and this is this energy level. So, as you see that this is this energy level and what was the corresponding first excited electronic energy level in the single atom case? This was the first excited background electronic energy level in the monatomic case. Now here corresponding to each of the electronic energy levels, I see that there are many many sub levels associated and this structure is associated with the ground electronic energy level.

And this structure that is a presence of several other sub energy levels, these are associated with the first excited energy electronic energy level. And let us next try and understand what this final energy levels are? And so, let us first have a look at what these energy levels are? So, these are the vibrational energy levels associated with the ground electronic energy level.

Now, if I look at what happens with each vibrational energy level; as you see over here very clearly corresponding to each vibrational energy level, there are other energy levels associated which have a much lower difference in energy and these are nothing, but the rotational energy levels. Now if I ask you can you point out the energy level of a molecule which is occupying the ground electronic state and which has a vibrational quantum number equal to 1 and rotational quantum number equal to 2.

So, what I will have to do here is I have to first look back at where I am as far as the ground electronic level is concerned? I am here I said V equal to 1, I know that the vibrational quantum number is equal to 0 for this, it is 1 for this and 2 for this. So, I must be looking at this vibrational energy level, when I am talking about V equal to 1 for the ground electronic level energy level. Then I said well do I know what are these different energy states? Yes these are these other rotational energy levels associated with V equal to 1 and here I have the quantum number J, which can vary from 0 to infinity.

So, this is j equal to 0, this is j equal to 1, this is j equal to 2. So, if you are looking for J equal to say 4; then your molecule must be associated with this energy level. So, that is how you interpret the energy levels of a diatomic molecule. And as you understand then the summation while calculating the single particle partition function, a summation over all energy levels would require you to sum over all these different energy levels and this is; obviously, a much more complicated task than the simple case, where I had only the atom electronic energy states.

So, let us next go and try and see if we can understand some of the interesting results from the solution of Schrodinger equation in quantum mechanics for a diatomic molecule as well as from spectroscopy.

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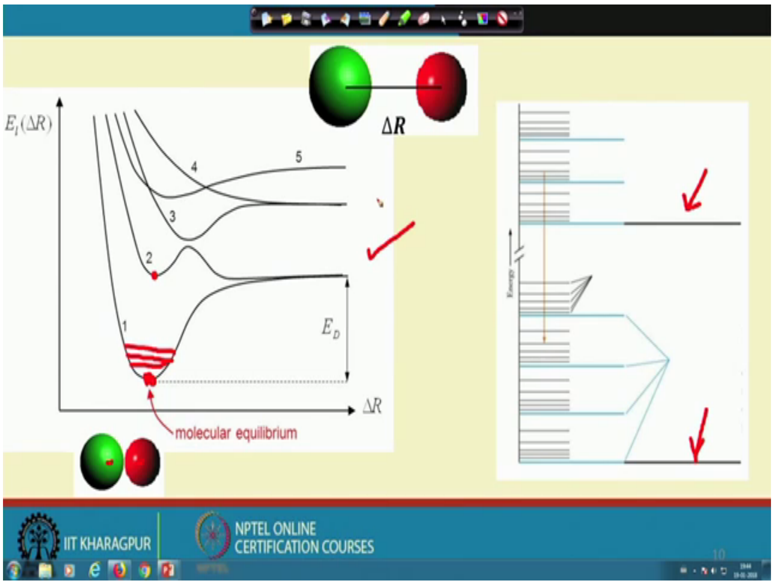

So, this is what I will start with; so, this is once again the same diatomic molecule that I am talking about it is a heteronuclear diatomic molecule. And let us say the inter nuclear separation between these two atoms is delta R in the molecule. So, for different molecular geometries in the simple case will can be generated for different values of this delta R.

So, what we can do is; one can for different values of delta R we can fix the nucleo of the two atoms at these different distances and solve the Schrodinger equation and that will give me; at this particular value of delta R, this is the value of the energy electronic energy Eigenstate; corresponding to the ground electronic energy state. This is the first excited electronic energy state, this is the energy value for the second excited electronic state and so on and so, forth.

So, when I fix geometry; these are the energy values that I get. Now if I change geometry for example, if I come here then if I draw a vertical line then what are the possible values that we will get by solving the schrodinger equation by fixing the two atoms here? This would be the lowest energy Eigenvalue, this would be the next highest Eigen value, this would be the next highest Eigen value.

So, this way by varying the delta R value; we can actually explore all the possible energy Eigen states and then construct this big picture, where you have the potential energy surface over which the two nuclei move; as a function of their inter nuclear separation.

If that happens then how do I connect it to the picture that I have already shown to you? Let us say that in this case I have a chemical bond that is formed between the two atoms and that is the most stable configuration in the ground electronic state corresponding to this minimum.

Now, if I look back at the structure; the very complicated energy level diagram that I had then what I have here is this is my ground electronic energy state. And this corresponds to this point here, corresponding to the formation of the stable chemical bond between this atom and this atom; so, that this distance is the bond distance.

Now what does this energy level correspond to? That must be the point here this is the first excited electronic state and now where will these fine structures come into the picture? If I draw corresponding to the ground electronic state, it has these vibrational structures and corresponding to each of these vibrational levels; you will have the rotational fine structures.

So, that is the idea that is associated here and this is the connection between the kind of energy level diagram and the molecule potential energy surface that one encounters while handling these systems.

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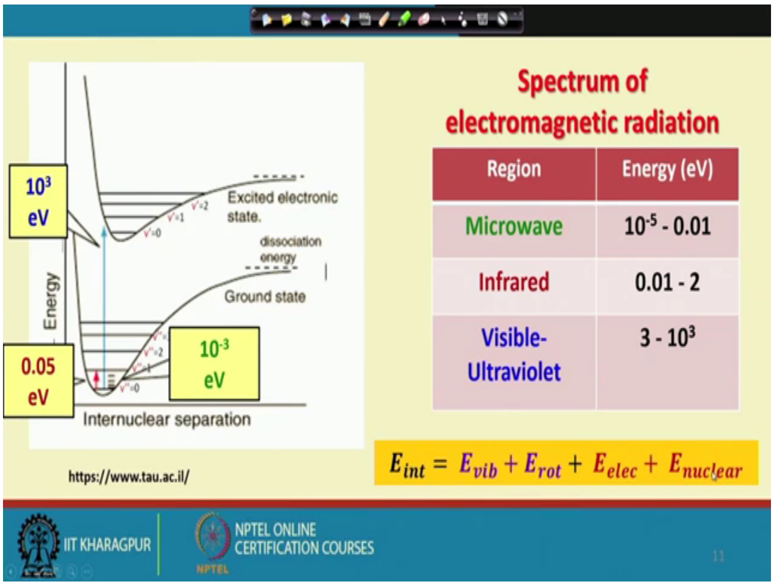

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Spectrum of electromagnetic radiation

Region	Energy (eV)
Microwave	10^{-5} - 0.01
Infrared	0.01 - 2
Visible-Ultraviolet	3 - 10^3

$$E_{int} = E_{vib} + E_{rot} + E_{elec} + E_{nuclear}$$

And once we understand this; so, let us next go and try and understand what are the typical difference in energy values as I go from the ground electronic state to the excited electronic state?

You will find that there are three types of energy skills involved; the first one if you go from ground electronic state to the excited electronic state, you would require typically an absorption of energy about say 100 to 1000 electron volt. And this is actually in the we all talk about the kind of range; how one can excite the population from here to here? But this is a very large number.

Now, if I look at how much energy you require if you are in the electronic ground state, but you want to go from say the ground vibrational level to the first excited vibrational level; associated with the ground electronic state, that is about 0.05 electron volt; much much smaller than what you require for the electronic transition. And then I still have finer structures associated with each vibrational level.

So, what is the amount of energy if I want to go from one rotational sub state of a given vibrational state to the another? This is about 10 to the power minus 3 electron volt; so, how do I know these energy values? Actually, it is known from the spectrum of electromagnetic radiation that if you look at the different regions, this is the energy scale that is associated with the visible ultraviolet region. Therefore, if you shine the diatomic molecule with visible ultraviolet light, it will induce a transition from here to here so, that there is a electronic transition.

So, that the system goes from the ground electronic state to the first excited electronic state. And the next part is this energy range for the vibrational excitation falls in the infrared region. And these are much smaller energy values and if you look at the energy scale for the transition between rotational energy levels, you find that they are even smaller and they require microwave radiation to promote these transitions.

So, what is very very clear from all these presentations is that; we indeed have a clear separation in the internal energy part of the molecule into a vibrational part, a rotational part in addition to having the electronic part and the nuclear part. We have already discussed about the nuclear part being about 1000 times of the electronic energies. Therefore, we can say that the different contributions to the internal energy of the diatomic molecule, these are separable into independent contributions.

If I am talking about rotational transitions, I can effectively fix my system into a given electronic state, a given nuclear energy state and a given vibrational energy state and then think about what is happening as a system goes from one rotational state to the other.

In the next lecture, we are going to see how the seperabilty can be used to calculate the single particle partition function for a diatomic molecule and from there how to get the thermodynamics of the diatomic ideal gas.

Thank you.