Fundamentals of Statistical Thermodynamics

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Lecture: 28

The Thermodynamic Functions (The Molecular Partition Function)

Welcome back. Now time has come that we start discussing different contributions to molecular partition function. Having connected canonical partition function with almost all thermodynamic quantities, now we will start appreciating how these canonical partition functions take up the shape once different contributions from the different degrees of freedom of the molecule start coming in. So, therefore, in this lecture, we will now talk about the molecular partition function and the different contributions which affect the value of molecular partition function. Different modes of motion make contributions to the energy of a molecule. What is the meaning of this statement? So far we have been talking about monatomic systems and we have been discussing that monatomic gas, for example, a gas consisting of single atoms.

The constituent atoms will have translational degrees of freedom and will have electronic degrees of freedom. And, we have several times discussed that the electronic contribution under normal conditions these are very less usually equal to the degeneracy of the ground state. And the major contribution comes from the translational part. If it is a diatomic molecule, now the molecule can rotate, the molecule can vibrate.

Therefore the rotational contribution can also come in, vibrational contribution can also come in. Therefore, the comment says different modes of motion make contributions to the energy of a molecule as follows. For any j^{th} state, the energy of a molecule is equal to the energy of the molecule in the same state due to translational contribution, the energy in the jth state due to rotational contribution, energy due to vibrational contribution, energy due to electronic contribution and if there is any type other type of contribution that can also be accounted for. And we also know that the molecular partition function is defined as summation j exponential minus βE_j. Let us substitute now that means now Q is equal to summation j exponential minus β and I will have E_j translational plus E_j rotational plus E_j vibrational plus E_j electronic right.

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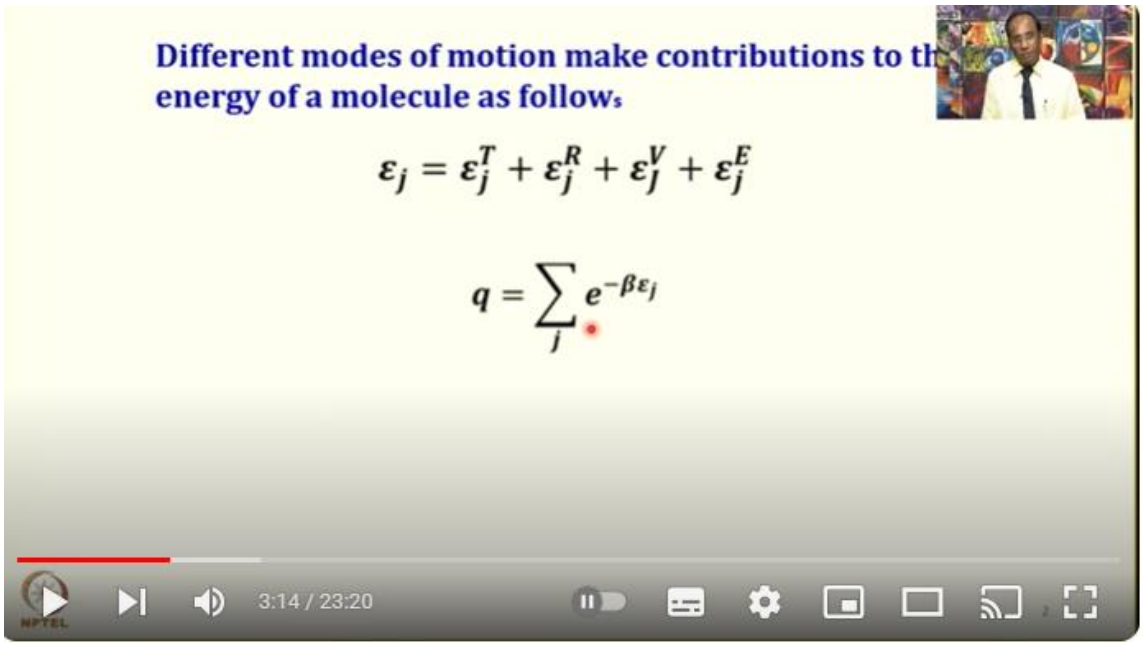

So translational rotational vibrational electronic summation for all over these states. I can separate this summation for individual contributions. Mathematically this is permitted. So that means I have J, I can sum over all translational state summation j exponential minus βE_j rotational. Then I have summation J exponential minus βE_j vibrational.

Let us include the last contribution also. Here summation j exponential minus βE_j electronic and now recognize each one. First one is q^T, the second one is q^R, third one is q^V and fourth one is q^E. The overall molecular partition function is equal to translational contribution to molecular partition function multiplied by rotational contribution to molecular partition function multiplied by the vibrational contribution to the molecular partition function multiplied by the electronic contribution to the molecular partition function. I want you to pay attention to energy expression and the molecular partition function expression.

Energy is additive due to all contributions. The molecular partition function is multiplicative, a very important point to be noted. When you write energies, this is addition of translational, rotational, vibrational electronic, but when you write the molecular partition function, it is multiplicative, translational contribution into rotational contribution into vibrational contribution into electronic contribution.

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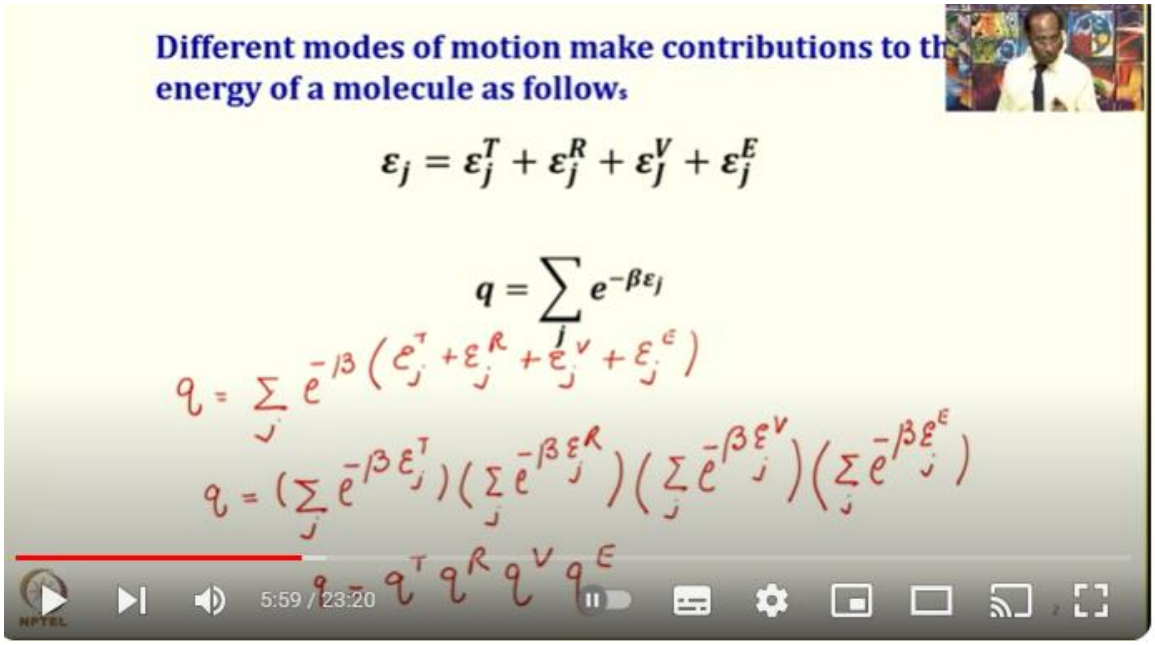

What we have is that q is equal to q^T multiplied by q^R multiplied by q^V multiplied by q^E. So therefore, when we talk about any thermodynamic quantities, for example, U minus U 0 is equal to minus del log q del β at constant volume.

We have derived this equation. Now for distinguishable or indistinguishable molecules, q is equal to q raise to the power n or q is equal to q raise to the power n by n factorial. You will use one of these equations, right, and we have already shown that in both cases whether you use this the q raise to the power n or q raise to the power n by n factorial, it comes out to be minus n by q del q del β at constant volume. Now so far we have been considering q is equal to q^T because most of the problems that we dealt with included monatomic systems, and if it is diatomic, triatomic, or polytomic, then we need to consider rotational, vibrational, and electronic contribution. In that case, q will have to be the multiplication of the molecular partition function which are translational, rotational, vibrational, or electron.

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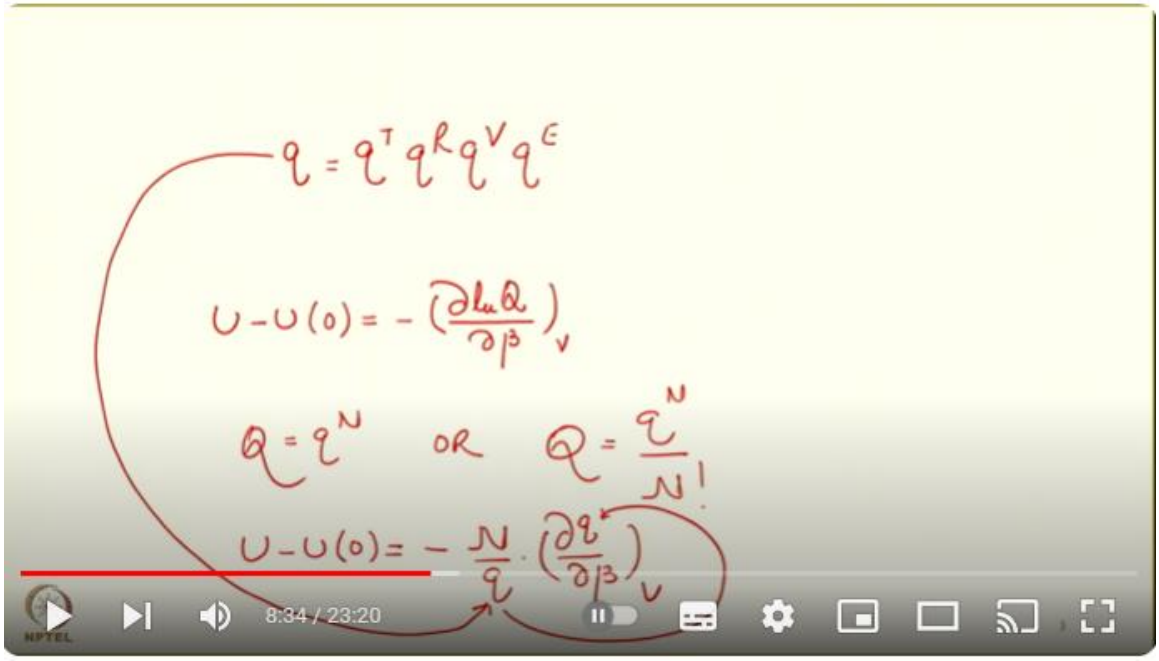

Similarly, when you talk about entropy or you talk about Gibbs function or Helmholtz function or enthalpy, you will have to first analyze whether the system involves translational contribution only or the system involves other contributions also. Now monatomic, for example, I will just take helium gas, and argon gas. Monatomic I will take iodine, hydrogen, bromine, O_3, H_2O, and then multiatomic. There can be many examples. Let us say CH_3CH_3.

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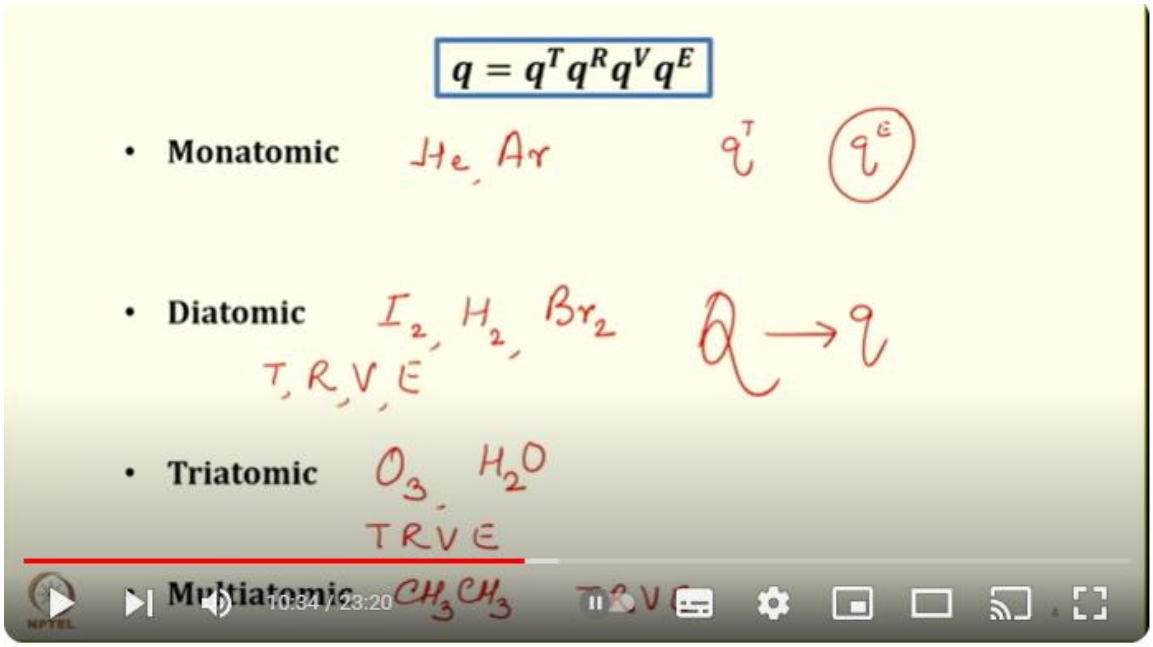

So when you are dealing with such systems, you need to make a careful choice when you connect q with q. Here if you are dealing with a monatomic that is helium, argon, then only the translational contributions will come in. That means here you will mostly worry about translational and of course electronic. We already discussed that electronic contribution is very small. When it is diatomic, now you will have translational, you have rotational, you have vibrational, you have electronic.

Triatomic, translational, rotational, vibrational, electronic. Multiatomic, translational, rotational, vibrational, and electronic. And you also need to make a choice of whether the connection of q to q involves a 1 by n factorial factor or not. Translational contribution to partition function, we have derived the expression earlier. When we talked about the movement of a particle, the movement of a molecule or atom in one dimension.

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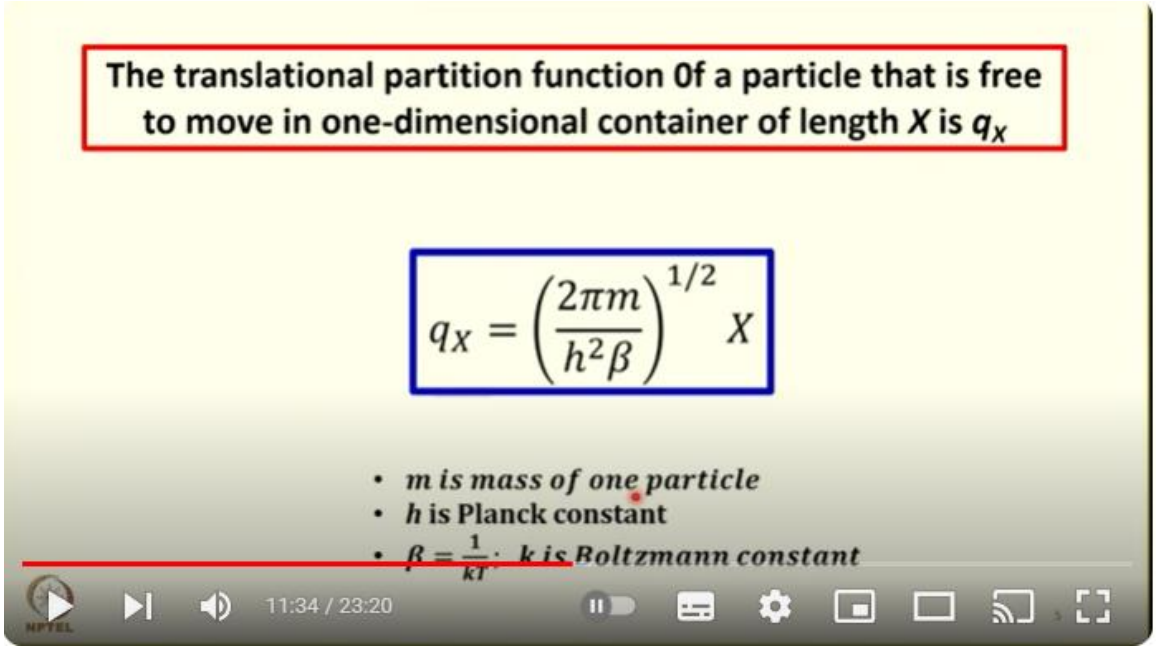

And remember that at that time, we derived this expression q_x is equal to 2 pi m over β h square square root into x, where x is the length of the container, length of one dimensional container. In this expression, m is the mass of one particle, one particle. As discussed earlier, if it is hydrogen, let us say h^2, then it is going to be 2 divided by Avogadro constant and you convert into kilogram. h is Planck's constant, β is expressed in terms of temperature, which is equal to 1 by kT. When we derived this, q_x is equal to 2 pi m over β h square square root.

You can write into x, you can write this is equal to x by λ, where λ which is equal to thermal wavelength because its units are in terms of length. Thermal wavelength which has the form β over 2 pi m square root into h or β h square root 2 pi m or h over square root 2 pi m kT, any of the form. And we already talked that λ has dimensions of the length. So, q_x was written as x divided by λ. We had this expression by using which the molecular partition function for a particle, for an atom, for a molecule can be obtained which is free to move in one-dimensional container of a specified length.

We then also discussed the translational partition function of a particle which is free to move in two dimensions. Two dimension means the container will have two lengths x and y, where x and y can be different or x and y can be equal. If x is equal to y, then it becomes a square. So, in that case, the partition function q_{xy} will be equal to 2 pi m over β h square square root where x into x and y which is equal to xy over λ square, right. And this term will actually come twice xy over λ square where λ, what is the meaning of λ? We have already discussed.

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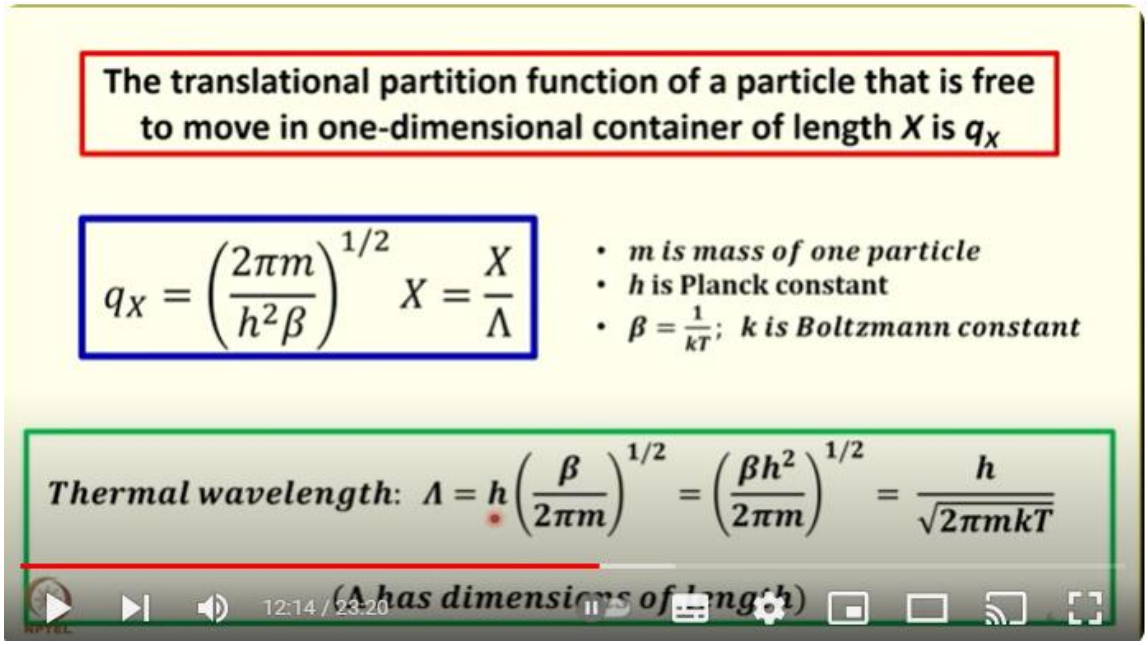

And the meaning of this m, h and β are usual. So, if you are now considering that a particle is free to move only on a surface, only on the surface, two-dimensional surface and the surface can have different values of the lengths that is edges x and y or it can be having same value. If x is equal to y, it becomes area. So, in that case, if x is equal to y, then this has to be square and xy. If x is equal to y, then you can use area, area of the surface.

That means if you were to deal with a particle, a molecule which is free to move only on the surface, then q_x is equal to area divided by λ square. And now if you then move into three dimension, then in that case, then this has to come three times and you have xyz. That means XYZ divided by Λ cube, XYZ is equal to volume divided by Λ cube where Λ is thermal wavelength. And the value of thermal wavelength can be calculated from the knowledge of mass of the particle and from the knowledge of temperature. This is translational contribution.

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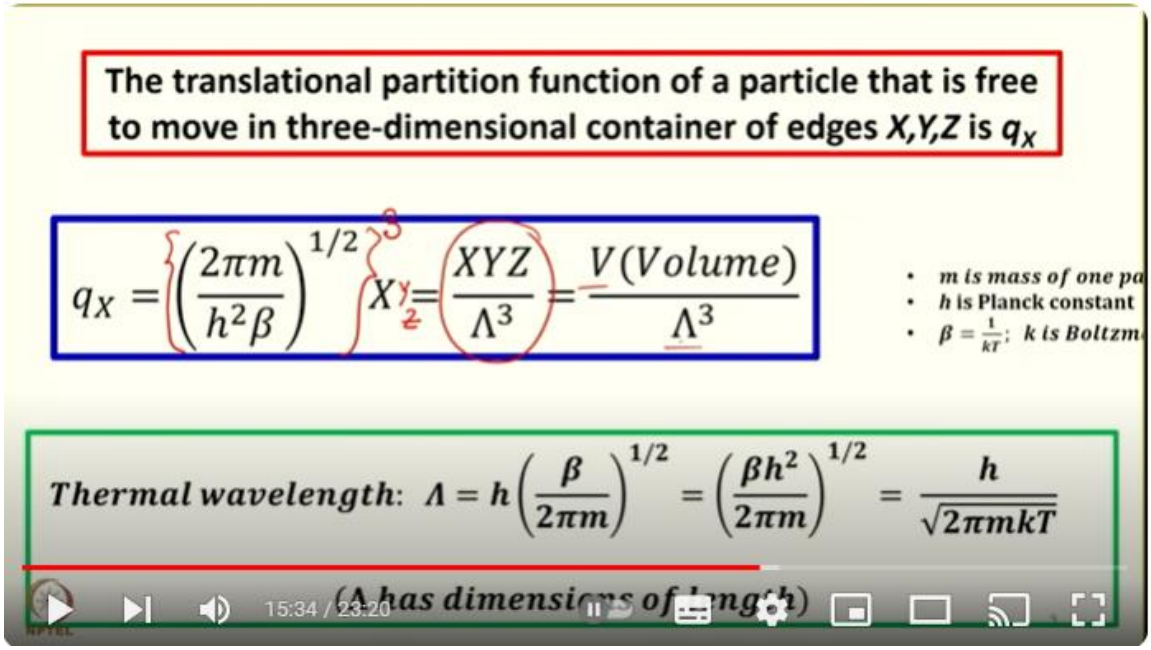

Translational contribution which we write as q^T is equal to V upon Λ cube depends upon the volume, depends upon Λ. That means if the volume of the container is large, then the value of translational contribution to partition function is also going to be large. Obviously, you know, when you go back and try to connect the energy levels of a particle which is free to move in one dimension, two dimension, three dimension, those energy levels are inversely proportional to the length of the container. E_n is equal to n square h square over 8 mL square. So if the lengths or edges or the volume is large, that means energy levels are crucial to each other. Therefore, there will be more population of energy levels at a given temperature. At a given temperature, there will be more thermally accessible states. And that is why when you are talking about a particle which is free to move in one dimension, which is free to move in two dimension or which is free to move in three dimension, and if the dimensions are large, then the value of the partition function is also large because the energy levels are closer to each other. Similarly, you can also comment upon the effect of mass of a particle on the value of translational contribution to partition function. Obviously, if the mass is higher, then the thermal wavelength is going to be small. If the thermal wavelength is going to be small, then the value of molecular partition function is going to be large. So therefore, when you need to comment upon what is the effect of temperature or what is the effect of size of the container on the value of translational contribution to partition function, you should be able to discuss in terms of energy levels which depend upon the length of the container and also in terms of the mass of the particle atom or molecule which is under consideration. Therefore, when I talk about the overall molecular partition function which is the product of translational, rotational, vibrational and electronic contribution, we need to think about obtain translational contribution and multiply it with the other contributions, the rotational

contribution, vibrational contribution or electronic contribution to the molecular partition function. By now we have discussed the translational contribution to the partition function. Now in the lectures ahead, we need to discuss the rotational contributions and vibrational contributions.

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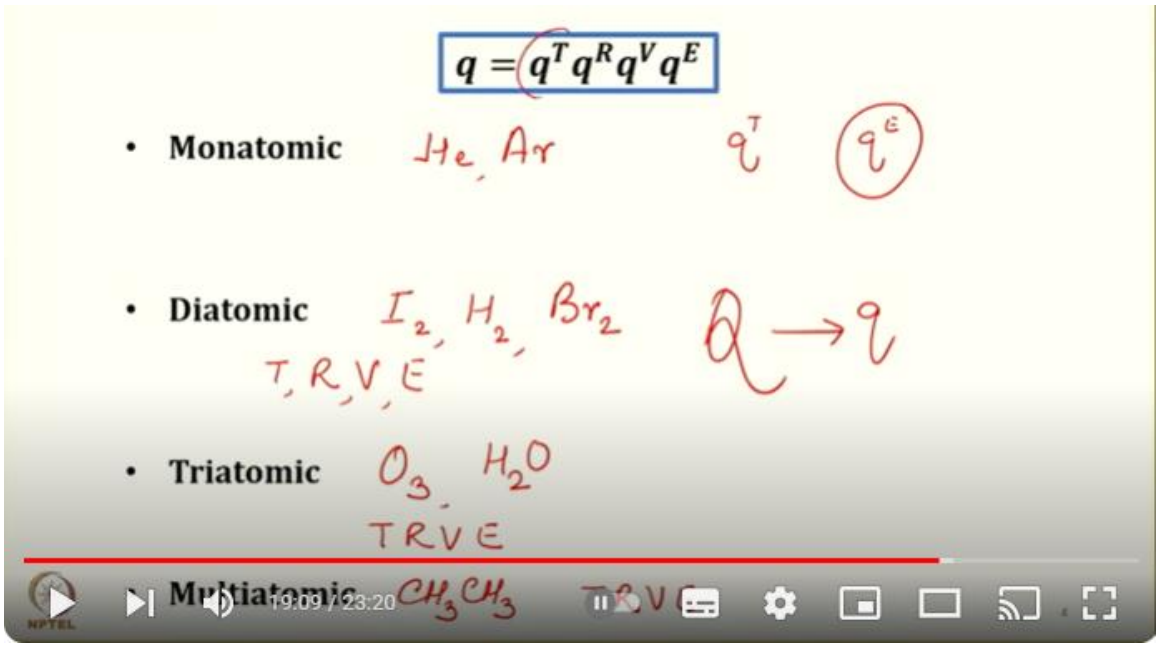

We also will need to discuss the electronic contributions, but this we have been commenting upon from time to time that the electronic contribution to the molecular partition function can be obtained from direct summation method that is q is equal to summation jg_j exponential minus βE_j. When we started our discussion on deriving translational contribution to partition function, we remember that we started with this expression and then we talked in terms of the energy levels of a particle or a molecule which is free to move in one dimension, two dimension or three dimension and eventually we came up with an expression that q^T is equal to V over Λq.

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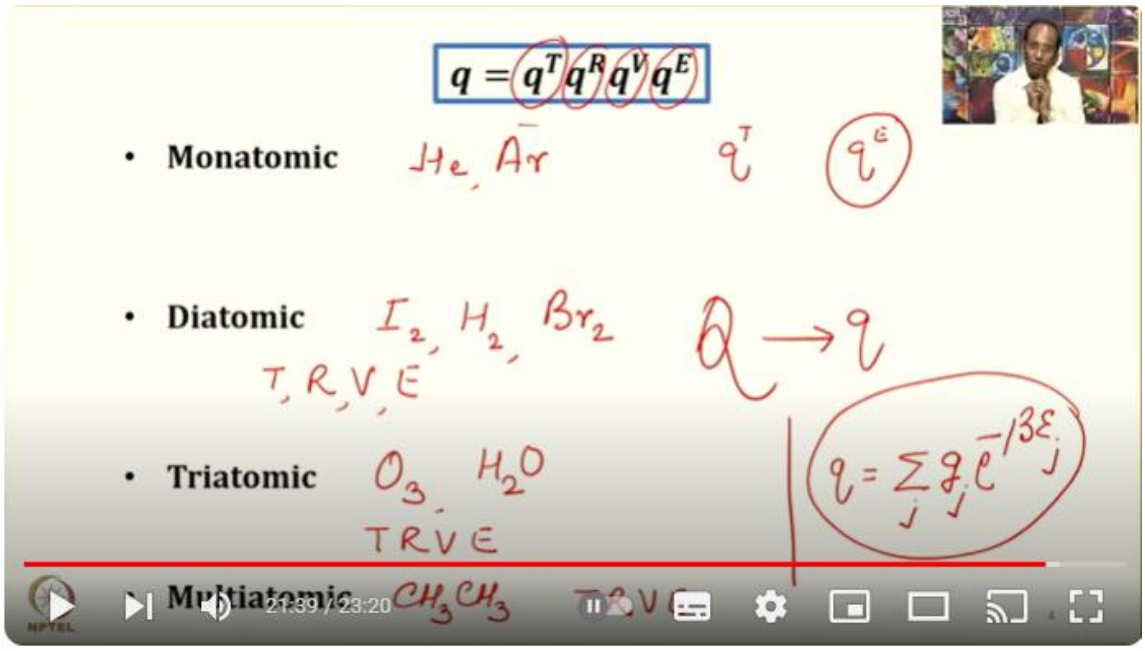

For electronic contribution to partition function, since the order of energy levels is like translational then rotational then vibrational and then electronic, electronic energy levels are far separated. Therefore, at room temperatures not many electronic energy levels will be occupied and that contribution can be obtained from the direct summation method. So therefore, in addition to translational contribution, we should now focus on what are the rotational energy levels, what are the vibrational energy levels of a system and here again we will go back to the concepts that we learnt from spectroscopy that is the energy levels of a rotor and when we talk about a rotor, the rotor can be a linear rotor or the rotor can be a non-linear rotor.

When we talk about the vibration, there can be linear molecules, there can be non-linear molecules and therefore, the vibrational degrees of freedom or the number of normal modes of vibration will also depend upon the type of system that we are dealing with. All these details we are going to discuss in the lectures which are coming up ahead and therefore, it is very important to have a continuity in this discussion that is after having discussed translational contribution, now we will discuss the rotational contribution starting from the discussion on their energy levels, but that we will discuss in the next lecture. Thank you very much. Thank you.