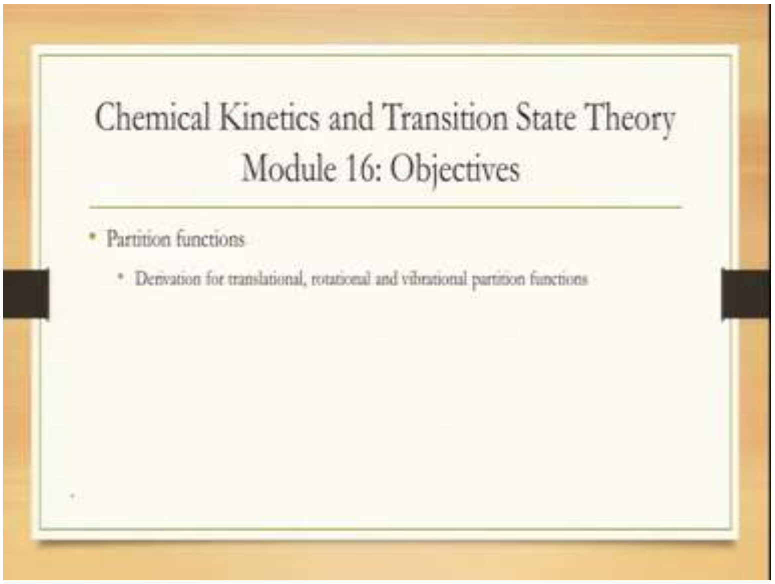
Chemical Kinetics and Transition State Theory
Professor Amber Jain
Department of Chemistry
Indian Institute of Technology, Bombay
Lecture no. 16
Partitioning the partition function

(Refer Slide Time: 0:16)

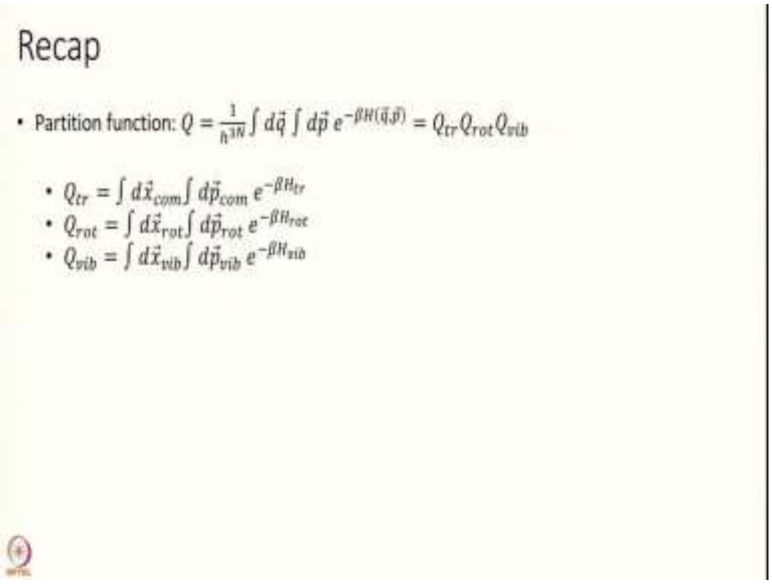


Chemical Kinetics and Transition State Theory
Module 16: Objectives

- Partition functions
  - Derivation for translational, rotational and vibrational partition functions

Hello and welcome to Module 16 of Chemical Kinetics and Transition State Theory. In the last module, we developed over the very basic idea of transition state theory. And for understanding that we need a little bit of knowledge of partition functions and we developed the basics of partition functions in the last module. Today, we are going to make things much more concrete and go on from where we left in the last module.

(Refer Slide Time: 0:55)

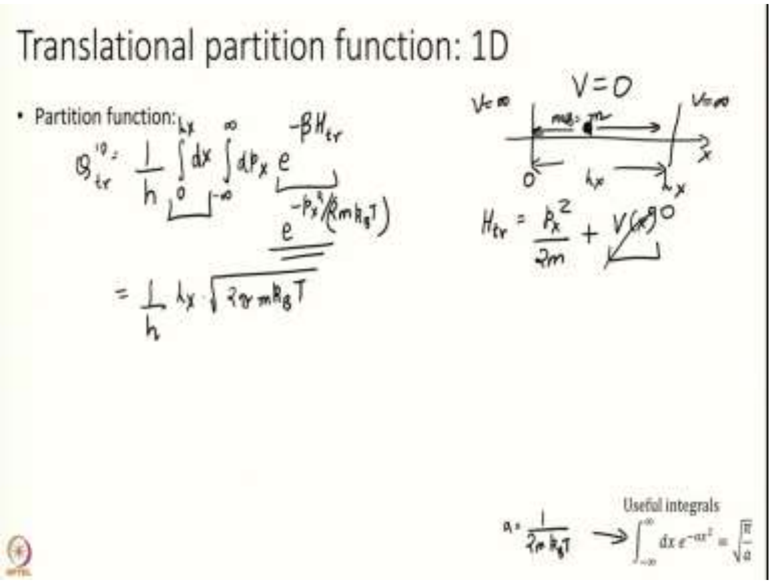


Recap

- Partition function: $Q = \frac{1}{h^{3N}}\int d\vec{q}\int d\vec{p}\, e^{-\beta H(\vec{q},\vec{p})} = Q_{tr}Q_{rot}Q_{vib}$
  - $Q_{tr} = \int d\vec{x}_{com}\int d\vec{p}_{com}\, e^{-\beta H_{tr}}$
  - $Q_{rot} = \int d\vec{x}_{rot}\int d\vec{p}_{rot}\, e^{-\beta H_{rot}}$
  - $Q_{vib} = \int d\vec{x}_{vib}\int d\vec{p}_{vib}\, e^{-\beta H_{vib}}$

So, in the last module, we partitioned the total number of variables into translational, vibrational and rotational. And we also saw that the partition function gets separated into these 3. So, you get Q is equal to Q translation Q rotation into Q vibration, where the translational 1 is an integral over 3 degrees of freedom, 3 x and 3 p, 6 dimension integral over translational Hamiltonian, rotation 1 is over rotational Hamiltonian and vibration 1 is the vibrational Hamiltonian. And so, today we are going to calculate these exactly, so we are in a position to actually do these integrals.

(Refer Slide Time: 1:35)



Translational partition function: 1D

- Partition function:

$$Q_{tr}^{1D} = \frac{1}{h}\underbrace{\int_0^{L_x} dx}\int_{-\infty}^{\infty} dp_x\, \underbrace{e^{-\beta H_{tr}}}_{e^{-p_x^2/(2mk_BT)}}$$

$$= \frac{1}{h} L_x \sqrt{2\pi m k_B T}$$

$$H_{tr} = \frac{p_x^2}{2m} + \cancel{V(x)}^{0}$$

Useful integrals

$$a = \frac{1}{2mk_BT} \rightarrow \int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

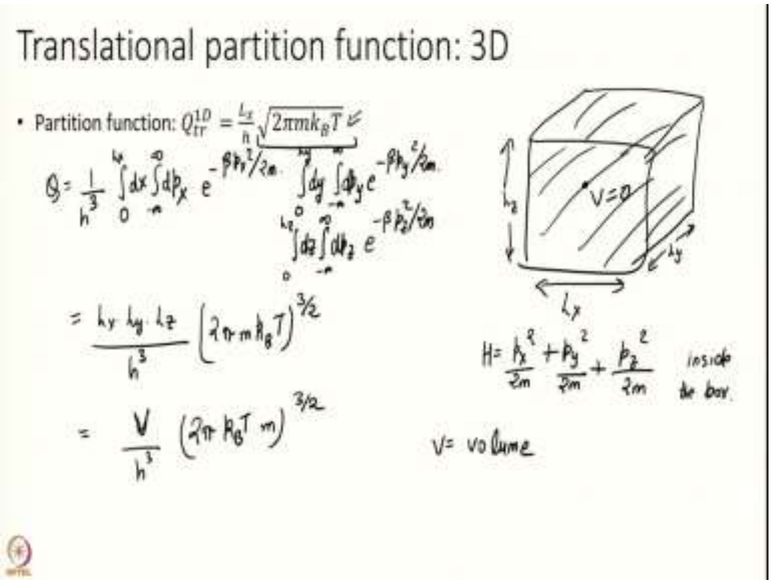
So, let us start with translational. Let us first do it in 1 dimension, I know our world is in 3D, but doing the integral in 1D is easier and then we will generalize in 3D. So, imagine I have a particle in a box from x equal to 0 to x equal to LX, so my potential is 0 inside and potential is infinite outside, effectively my particle is stuck inside here, so the particle can only move within this box of length LX.

So, if you look at the definition of your partition function in 1D, this will be 1 over h, it is only 1D integral over dx from 0 to LX particle cannot be found outside at all. So, I do not have to worry about positions outside, momentum and momentum can be anything into e to the power of minus beta H translation.

But my Hamiltonian is p square over 2 m let us say the mass of the particle is m plus the potential but my potential is 0 inside. So this part is 0. So, this part becomes e to the power of minus p x square over 2 m, potential is 0 inside and potential is infinite outside that is why I integrate it from position only from 0 to Lx, because I know that outside my potential is infinite, so it does not matter anywhere.

So, this I can quickly integrate, remember, note that this, there is no dependence on x at all. So, this integral is LX and this is a Gaussian integral I have provided the integral here, again you do not have to memorize these kind of integrals, anytime it is needed we will provide and if you compare I have forgotten my kbT a is 1 over 2 m kbT. So, it is a into x square, here is p square over 2 m kt, so a is 1 over 2 m kt. So I can straightforwardly put it here and I get 2 pi m kbT. So, straightforward integral nothing hard here.

(Refer Slide Time: 4:27)



Translational partition function: 3D

- Partition function: $Q_{tr}^{1D} = \frac{L_x}{h}\underbrace{\sqrt{2\pi m k_B T}}_{} \checkmark$

$$Q = \frac{1}{h^3}\int_0^{L_x} dx \int_{-\infty}^{\infty} dp_x\, e^{-\beta p_x^2/2m} \int_0^{L_y} dy \int_{-\infty}^{\infty} dp_y\, e^{-\beta p_y^2/2m} \int_0^{L_z} dz \int_{-\infty}^{\infty} dp_z\, e^{-\beta p_z^2/2m}$$

$$= \frac{L_x L_y L_z}{h^3}\left(2\pi m k_B T\right)^{3/2}$$

$$= \frac{V}{h^3}\left(2\pi k_B T m\right)^{3/2}$$

$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$ inside the box.

V= volume

So, I get this translational partition function in 1D. But again, our problem is in 3D. But note that whenever the Hamiltonian is additive,, so now I am thinking of a 3D box of let us say dimensions Lx, Ly and Lz and a particle is stuck inside the this cube, not this cube, cuboid and the potential is 0 inside and the potential is infinite outside.

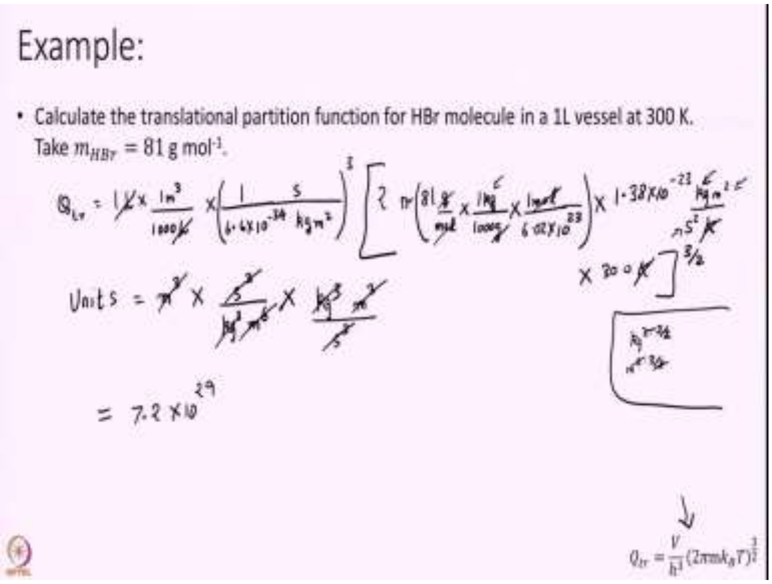
Then I have to do a bigger integral h to the power of 3, I have 3 coordinates and 3 momenta. Well, what do you notice that we have actually kind of done this now, my Hamiltonian is actually additive, m again is the mass inside the box. So, the potential is 0 inside, so I have only kinetic energy.

So, I will be left with like this dy dpy dz dpz, I just have to be a little bit careful of limits, this 1 y will be 0 to Ly, Z will be 0 to Lz, but note that I have done this integral already. So, I will take it from my previous slide and this will become Lx into Ly into Lz divided by h cube into 2 pi m kBT to the power of 3 half.

So, you can look into the previous slide in 1D that I have already written here, so it will become Lx over h into Ly over h into Lz over h, that gives me this Lx into Ly into Lz over h cube. And this factor will come 3 times for all x, y and z. So I get 2 pi m kBT over to the power of 3 half.

Now, what we notice Lx into Ly into Lz is volume divided by h cube, v is volume, so that is essentially your translational partition function. So, we will do a quick example on how to calculate the translational partition function.

(Refer Slide Time: 7:20)



Example:

- Calculate the translational partition function for HBr molecule in a 1L vessel at 300 K. Take $m_{HBr} = 81\ \mathrm{g\ mol^{-1}}$.

$$Q_{tr} = 1\cancel{L} \times \frac{1\,m^3}{1000\cancel{L}} \times \left(\frac{1}{6.6\times10^{-34}}\frac{s}{kg\,m^2}\right)^3 \left[2\pi\left(81\frac{\cancel{g}}{\cancel{mol}} \times \frac{1\,kg}{1000\cancel{g}} \times \frac{1\cancel{mol}}{6.02\times10^{23}}\right) \times 1.38\times10^{-23}\frac{kg\,m^2}{s^2\cancel{K}} \times 300\cancel{K}\right]^{3/2}$$

$$\text{Units} = \cancel{m^3} \times \frac{\cancel{s^3}}{\cancel{kg^3}\cancel{m^6}} \times \frac{\cancel{kg^3}\cancel{m^3}}{\cancel{s^3}}$$

$$= 7.2\times10^{29}$$

$$Q_{tr} = \frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$$

So, let us look at a concrete example of let us say HBr molecules in a 1 liter vessel at room temperature 300 Kelvin. So, how can we calculate the partition function for it? So, the formula we have just calculated, and it is all about putting the numbers carefully, and why I am doing this example is because of units, that you have to be very careful about.

So, Q translation is the first term is volume, volume is 1 liter, but we will convert everything in SI units, so that everything remains consistent. Now, 1 liter is 1 meter cube divided by 1000 liter, that is a conversion between liter and meter cube into 1 over h cube. So, h cube is 6.6 into 10 to the power of minus 34. What are the units? Kilogram meters square second cube, so that is a unit of h kilogram meter square per second or joules into second into 2 pi mass, mass is 8one gram per mole.

But again, we want SI units and without mole, we are looking at this translational partition function in molecular units. So, this will become 1 kilogram divided by 1000 gram into 1 mole divided by Avogadro number, so that is my mass in kilograms. So, gram will cancel with gram, mole will cancel with mole. So, I get in kilogram into kBT, kB is 1.38 into 10 to the power of minus 23 kilogram meter square per second square Kelvin into temperature 300 Kelvin, the whole thing to the power of 3 half. So, note that Kelvin also cancels.

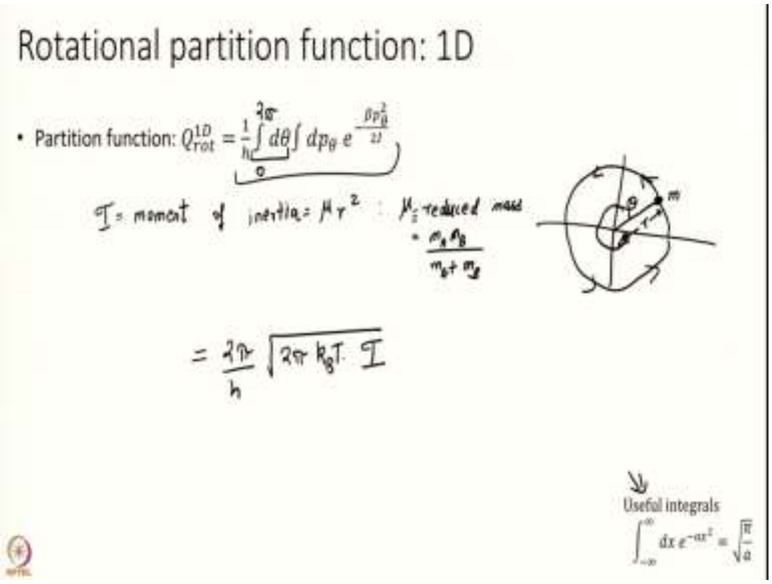
So, let us just make sure that the units has worked out, liter cancels with liter, the unit says meter cube here into second cube divided by kilogram cube meter to the power of 6 into, so let us just carefully look, I am left with a kilogram here, a kilogram here, so I have kilogram square in the bracket and kilogram square to the power into power of 3 half, so 2 cancels, I am left with kilogram cube.

Similarly, I have you see meter square here. So, that will become meter cube and I have second square here that will become second cube, the same way meter square to the power of 3 half so that becomes a meter cube and similarly for second square. So, you will see that all terms are going to now cancel.

So, as I have already told, partition function is dimensionless. And so all units should have canceled, so that gives a little bit of confidence that what we are doing is good. After that it is just a matter of punching the numbers correctly on a calculator or a computer and you can do this calculation and I have done it myself and I get this is equal to 7.2 into 10 to the power of 29.

So, as a I mean, just a rule of thumb remember that translational partition function is usually very large, they do go into 10 to the power of 20 to 30. So, what we are getting is actually something reasonable. So, let us move on to rotational component.

(Refer Slide Time: 11:20)



Rotational partition function: 1D

- Partition function: $Q_{rot}^{1D} = \underbrace{\frac{1}{h}\underbrace{\int_{0}^{2\pi} d\theta}_{} \int dp_\theta \, e^{-\frac{\beta p_\theta^2}{2I}}}_{}$

I = moment of inertia $= \mu r^2$: μ = reduced mass $= \frac{m_A m_B}{m_A + m_B}$

$$= \frac{2\pi}{h}\sqrt{2\pi k_B T \cdot I}$$

Useful integrals

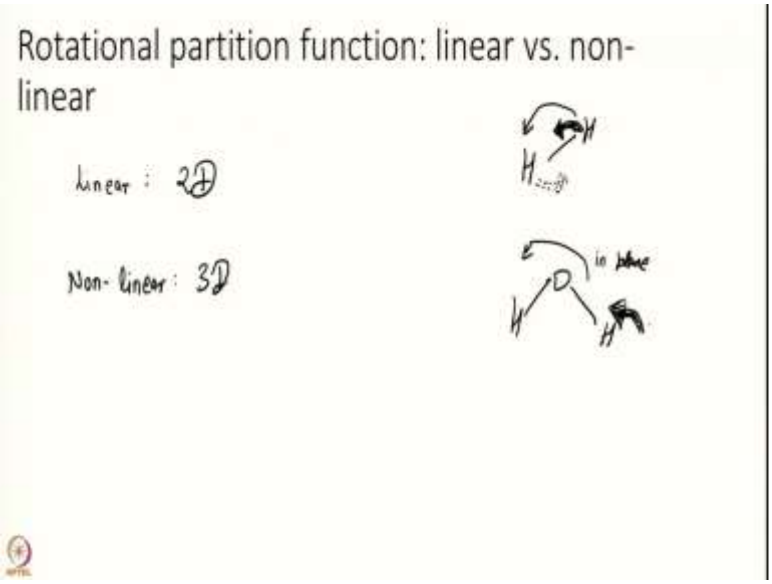
$$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

So, again, let us just think in 1 dimension first and then we will provide you the answer in multiple dimensions. So, in 1 dimension, what we are really thinking is that there is a particle, a rigid rotor of some mass m, rotating like this with 1 angle theta. And I am trying to find the partition function for this 1D motion only on this ring.

So, again, I have to calculate something like this, the potential is 0 and the kinetic energy simply looks like some kind of t square over 2 y where I is called the moment of inertia and P here is really angular momentum and mu is called the reduced mass and r is this r. Well, you note that this integral is actually exactly the same as for translation; same format just variable name has changed.

So, I will write away the answer right away. 1 difference is this integral over d theta goes from 0 to 2 pi. So, theta can go from 0 to 2 pi. So, this becomes equal to 2 pi over h and I will use this integral and write the answer right away, so, instead of mass I have moment of inertia, that is the difference.

(Refer Slide Time: 13:04)



Rotational partition function: linear vs. non-linear

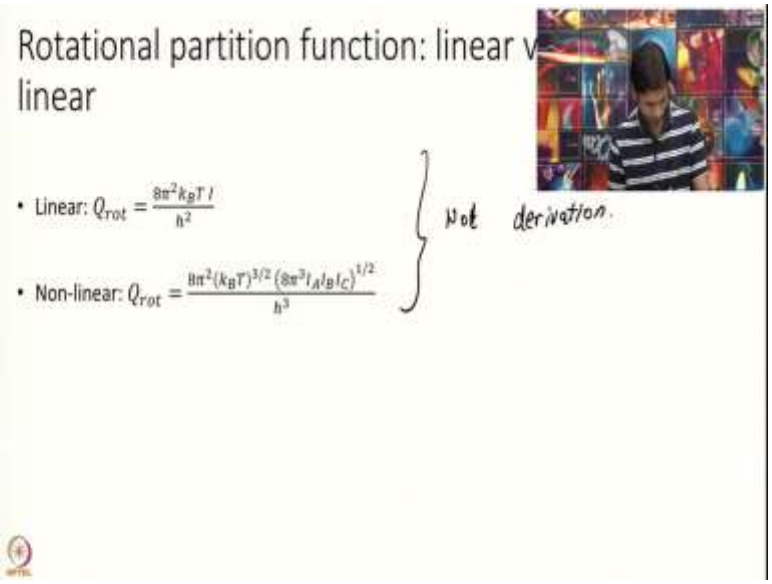
Linear : 2D

Non-linear : 3D

Now, we have to think about this linear and nonlinear molecules very carefully, we discussed that a little bit in the last module. The point is for linear I have only that is in 2D. So, for a molecule like H2, this can rotate in plane or out of the plane. So, H2 I can rotate in the plane like this or I can rotate it out of the plane like this, there are only 2 kind of rotations that are possible.

For nonlinear it can rotate in 3 dimensions. So, the example we were looking at in the last module was water, it can rotate in plane and you can rotate it in 2 different ways out of the plane, for 1 out of plane rotation is this you can take the whole thing and rotate like this, and the other 1 is like this, so I cannot rotate my hand that much, but you can imagine it is like this motion. So, you have in nonlinear 3D rotations, in linear only 2D rotations.

(Refer Slide Time: 14:39)



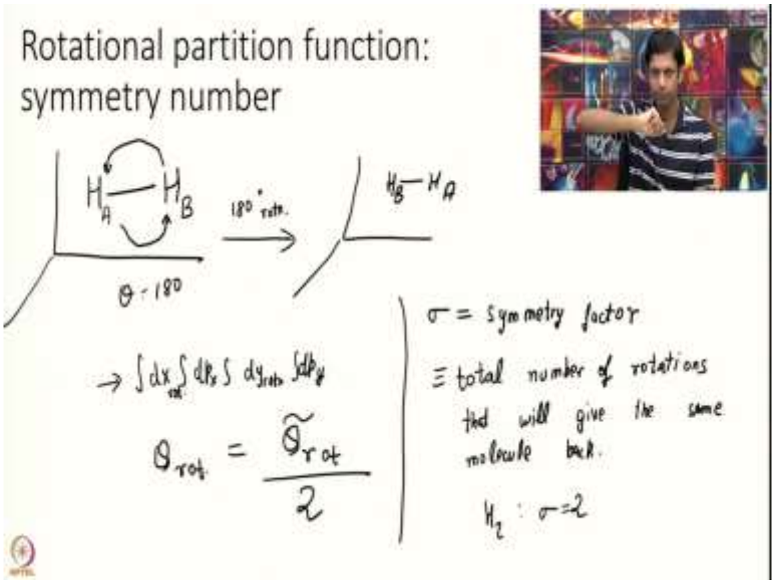
Rotational partition function: linear v
linear

- Linear: $Q_{rot} = \frac{8\pi^2 k_B T I}{h^2}$
- Non-linear: $Q_{rot} = \frac{8\pi^2 (k_B T)^{3/2} (8\pi^3 I_A I_B I_C)^{1/2}}{h^3}$

Not derivation.

And so, the formula for rotational partition function is different for linear molecule versus nonlinear molecule. We are not going into the derivation of this here, no derivation. A derivation gets slightly complex because you have to think about how the more Hamiltonian looks like in 2D and 3D and it is slightly more complex. That is why I am not getting into it. It is not important for this course. For this course we will assume this formula.

(Refer Slide Time: 15:12)



Rotational partition function:
symmetry number

$\rightarrow \int dx_{rot} \int dp_x \int dy_{rot} \int dp_y$

$$Q_{rot} = \frac{\tilde{Q}_{rot}}{2}$$

σ = symmetry factor
≡ total number of rotations that will give the same molecule back.

$H_2 : \sigma = 2$

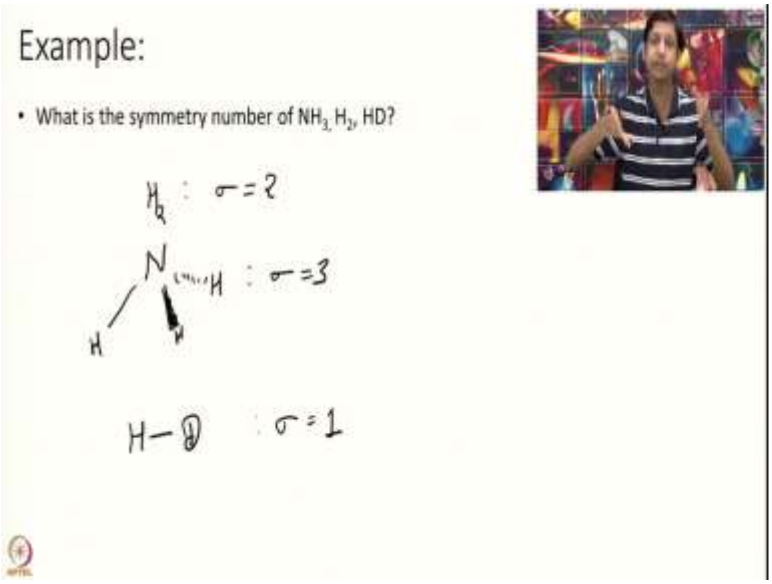
Another very important factor that comes for rotational partition function is the symmetry. So, let us just think about this for 1 moment, let us look at the molecule for example H 2. Now, the point is, let me call this H A, and let me call this H B. If I rotate this by 180 degrees, this will transform to H B and H A. 180 degree rotation but that is exactly the same molecule this A and B is only for bookkeeping for me, the both the hydrogens are exactly the same.

So, if I rotate by 180 degree, you get exactly the same molecule. So, when you are doing your integrations, remember you are doing some integration that looks like this; you are actually doing the integration twice because the same molecule will appear twice if you do the full integration over all space.

So, this integration is essentially integrating over all possible orientations of H A and H b, but half of the orientations sorry, the same orientation will appear twice. So, the correct rotational partition function will be q rotation that we have derived divided by 2. Because when we do the integration, the same orientation appears twice. So, that is why should divide it by 2.

So, in general, we define sigma which is called the symmetry factor. This symmetry factor is essentially the total number of rotations that will give the same molecule back. So, for 4 H 2 sigma is 2. Yeah, because I can rotate it by 180 degree and I will get the same molecule back.

(Refer Slide Time: 18:06)



Example:

- What is the symmetry number of NH_3, H_2, HD?

H_2 : $\sigma = 2$

: $\sigma = 3$

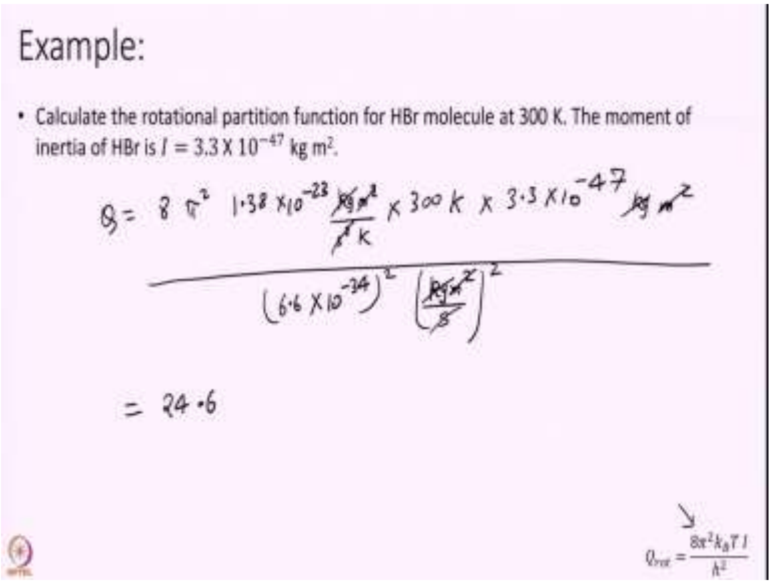
H—D : $\sigma = 1$

So, let us think of a few examples. Let us think of symmetry number of ammonia H 2 and HD. For H 2 we have already shown sigma is 2, let us think of ammonia. So, ammonia looks like this, you have nitrogen, hydrogen coming out. So, now take a moment, pause the video and calculate what do you think the sigma for ammonia will be? So, please pause the video and calculate it on your own.

So, hopefully you have a number. So ammonia, basically, just imagine I have a nitrogen here and 3 hydrogens are coming out here. I can rotate it in 3 different fashions, I can rotate it essentially by 120 degree and the same molecule will come back. Yeah. So, sigma will be 3, you understand that, I have 3 hydrogens coming out and I can rotate it by 120 degree I get the same molecule, another 120 degrees same molecule, another 120 degrees same molecule. So, sigma is 3 here.

Finally, let us look at H D. Again, take a pause, think on what you will think the sigma for H D is, hopefully you have made your own estimate, sigma 4 H D is simply 1, because H and D are different atoms. So, whatever rotation I do, I will not get the same molecule back, if I rotate by 180 degree now, I will get D H instead which is different from H D. So, it should come out to be exactly the same molecule.

(Refer Slide Time: 19:53)



Example:

- Calculate the rotational partition function for HBr molecule at 300 K. The moment of inertia of HBr is $I = 3.3 \times 10^{-47}$ kg m^2.

$$Q = \frac{8\pi^2 \; 1.38\times10^{-23} \frac{\cancel{kg}\,\cancel{m^2}}{\cancel{s^2}\,K} \times 300\,K \times 3.3\times10^{-47}\,\cancel{kg}\,\cancel{m^2}}{(6.6\times10^{-34})^2 \left(\frac{\cancel{kg\,m^2}}{\cancel{s}}\right)^2}$$

$$= 24.6$$

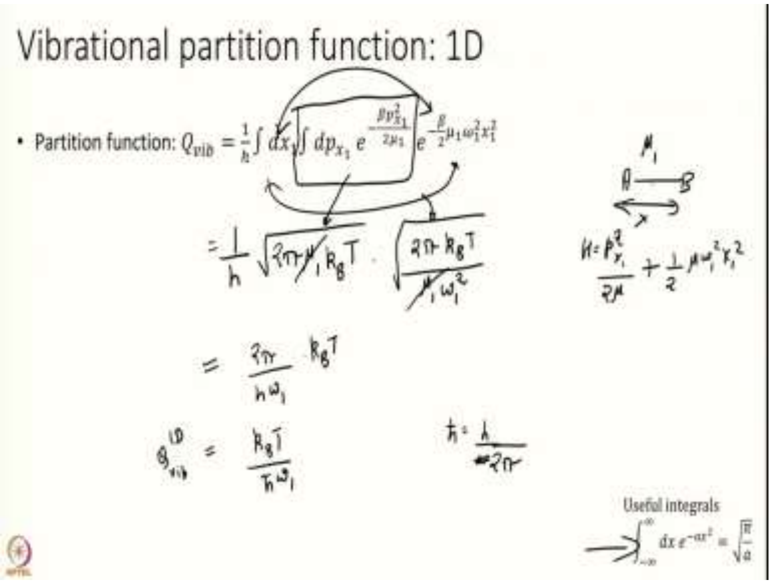
$$Q_{rot} = \frac{8\pi^2 k_B T I}{h^2}$$

So, now let us also calculate the rotational partition function. Earlier we looked at the example of HBr’s translational. Now, let us look at HBr’s rotational. So, the formula again is provided here. So, once again we have to be careful with units. So, Q is 8 pi square, KB is 1.38 into 10 to the power of minus 23 kilogram meter square per second square Kelvin into 300 Kelvin into I, which is 3.3 into 10 to the power of minus 47 kilogram meter square divided by h square, h is 6.6 into 10 to the power of minus 34 square and the unit is kilogram meter square per second square.

So, let us make sure that the units cancel; once more partition functions are dimensionless. So, I have a kilogram here and a kilogram square. So, kilogram into kilogram is kilogram square that cancels with this kilogram square, I have meter to the power of 4 in the denominator; I have meter to the power of 4 in the numerator and second is second square with second. So, all units happily cancel as they should. So, again a little bit of confidence in our calculations.

And again I have punch this on a calculator and I found this is equal to 24.6. So, if you go back a few slides for translational we calculated it something like 10 to the power of 29, rotational partition functions are much smaller, they are in the order of 10 or 20. So, again a rule of thumb to remember when you do a calculation and you find a rotational partition function comes out to be a million, you have done something wrong. Ordinarily, it will not come out like that.

(Refer Slide Time: 22:00)



Vibrational partition function: 1D

- Partition function: $Q_{vib} = \frac{1}{h}\int dx_1 \boxed{\int dp_{x_1}\, e^{-\frac{\beta p_{x_1}^2}{2\mu_1}}} e^{-\frac{\beta}{2}\mu_1\omega_1^2 x_1^2}$

$$= \frac{1}{h}\sqrt{2\pi\cancel{\mu_1} k_B T} \cdot \sqrt{\frac{2\pi k_B T}{\cancel{\mu_1}\omega_1^2}}$$

$$= \frac{2\pi}{h\omega_1} k_B T$$

$$q_{vib}^{1D} = \frac{k_B T}{\hbar\omega_1}$$

$$\hbar = \frac{h}{2\pi}$$

μ_1

$A - B$

$$H = \frac{p_{x_1}^2}{2\mu} + \frac{1}{2}\mu\omega_1^2 x_1^2$$

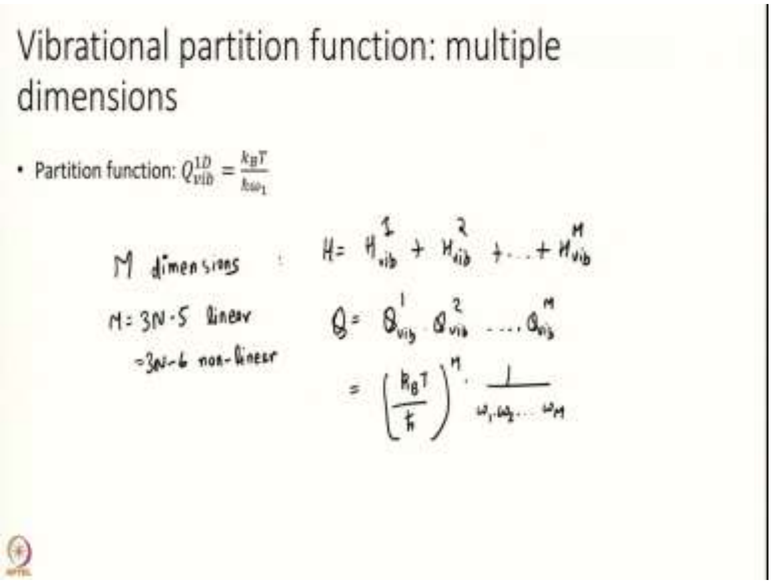
Useful integrals

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

Finally, let us quickly look at vibrational partition function. So, again, let us look at 1 D first I have some molecule with some coordinate x 1 and reduce mass mu 1. So, my Hamiltonian of this is basically p x 1 square over 2 mu plus half mu omega 1 square x 1 square, where omega is the vibrational frequency. So, we are assuming the harmonic motion. It is an assumption.

So, we have to just integrate this. And what you notice that I can integrate the x and p separately and both of them are Gaussians. So, let me do that 1 over h for the momentum part, I will get root 2 pi mu 1 kT. Again, I am using this formula into root I am integrating the x 1 here, which is going to be 2 pi kT over mu 1 omega 1 square. So, just using this integral very carefully, that is all, mu 1 cancels with mu 1. And I get 2 pi over h omega 1 into kBT. What you notice h over 2 pi is h bar, so you get in 1D equal to this.

(Refer Slide Time: 23:47)



Vibrational partition function: multiple dimensions

- Partition function: $Q_{vib}^{1D} = \frac{k_B T}{\hbar\omega_1}$

M dimensions : $H = H_{vib}^{1} + H_{vib}^{2} + \ldots + H_{vib}^{M}$

$M = 3N-5$ linear

$= 3N-6$ non-linear

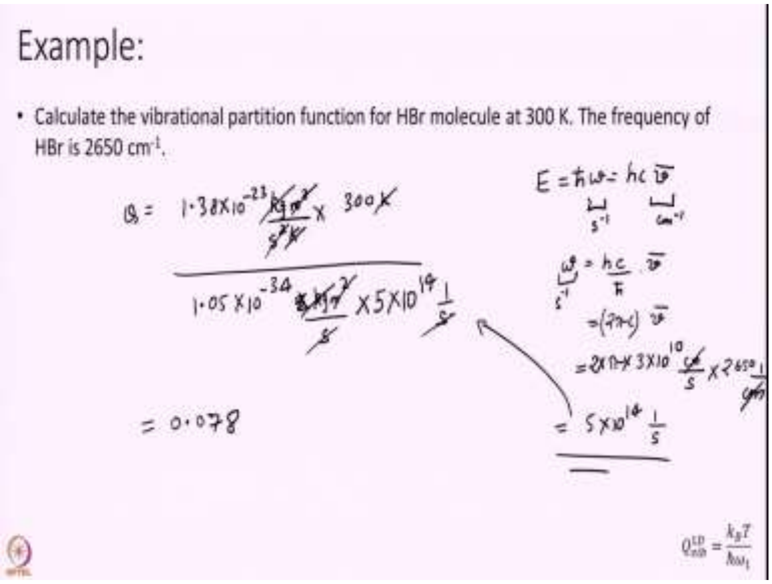
$Q = Q_{vib}^{1} \cdot Q_{vib}^{2} \ldots Q_{vib}^{M}$

$= \left(\frac{k_B T}{\hbar}\right)^{M} \cdot \frac{1}{\omega_1 \cdot \omega_2 \ldots \omega_M}$

Well, in multiple dimensions. It is not much harder. I have some M dimensions, where M is 3 N minus 5 for a linear and 3 N minus 6 for nonlinear. Well, we assume our Hamiltonian is separable of dimension 1 of dimension 2 of dimension N so all vibrations have their own Hamiltonian with all of their own reduced mass their own frequency.

So, the partition function becomes multiplicative. Whenever Hamiltonian is separable, my partition function is multiplicative Q vibration 1, Q vibration 2 and so on. So, we just multiply these together. So, as simple as that.

(Refer Slide Time: 25:11)



Example:

- Calculate the vibrational partition function for HBr molecule at 300 K. The frequency of HBr is 2650 cm^{-1}.

$$Q = \frac{1.38\times10^{-23}\,\frac{\cancel{kg\,m^2}}{\cancel{s^2 K}} \times 300\,\cancel{K}}{1.05\times10^{-34}\,\frac{\cancel{kg\,m^2}}{\cancel{s}} \times 5\times10^{14}\,\frac{1}{\cancel{s}}}$$

$$= 0.078$$

$$E = \underbrace{\hbar\omega}_{s^{-1}} = hc\underbrace{\bar{\nu}}_{cm^{-1}}$$

$$\underbrace{\omega}_{s^{-1}} = \frac{hc}{\hbar}\,\bar{\nu}$$

$$= (2\pi c)\,\bar{\nu}$$

$$= 2\times\pi\times3\times10^{10}\,\frac{\cancel{cm}}{s}\times2650\,\frac{1}{\cancel{cm}}$$

$$= 5\times10^{14}\,\frac{1}{s}$$

$$Q_{vib}^{HT} = \frac{k_B T}{\hbar\omega_1}$$

So, finally, let us calculate the vibrational partition function of HBr as well. So, in the few examples in the last slides, I have discussed rotational and translational partition function. So, let us complete with vibrational partition function of HBr as well. So, once more the trick is in the units we have to be careful.

So, Q is KB which is 1.38 into 10 to the power of minus 23 kilo gram meter square per second square Kelvin temperature is 300 Kelvin divided by H bar, H bar is 1.05 into 10 to the power of minus 34 into, my bad, the units is kilogram meter square per second into omega. So, let, we have to be very careful, should I write 2650 here for omega? No, we have to be careful; omega unit is 1 over time second inverse.

So, first thing is we have to convert, and this is something you have to know, because generally the number for frequency is given in way numbers, that is how experimentalists calculate it, but in the actual calculation, it has to be in second inverse. So, how do we do that? I have always remember this formula, energy is h bar omega equal to hc in nu bar where this thing is in wave numbers and this thing is in second inverse.

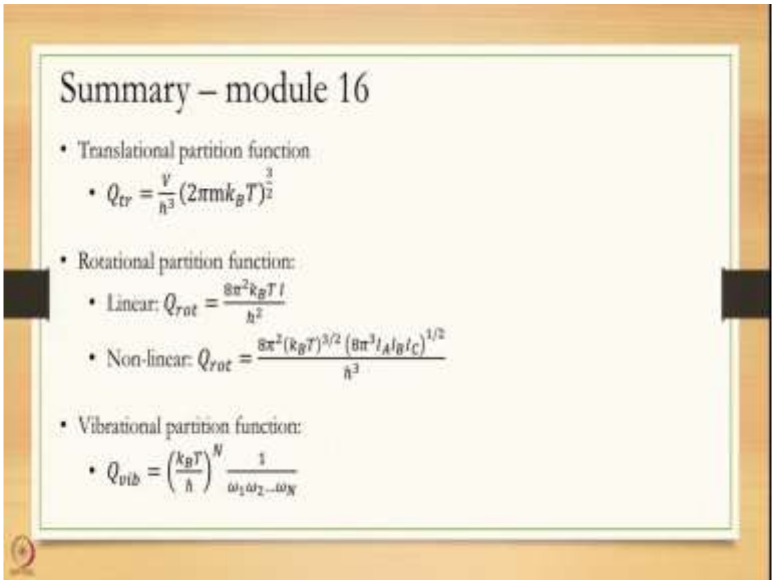
So, if you remember this formula, then your life will be easier. So, omega will be equal to omega in second inverse will be equal to hc over h bar into this nu bar in wave numbers, but h bar is h over 2 pi. So, this becomes 2 pi c nu bar. So, this is then equal to 2 into pi into speed of light, which is about 3 into 10 to the power of 10 centimeter per second.

So, the reason I am using centimeter instead of meter is because the frequency is provided in centimeter inverse, so the units cancel. So, I am anticipating that in advance and frequency is given to me 2650 centimeter inverse, centimeters cancel and you see, you get it in 1 over second which is what we wanted and I have used a calculator to calculate this, I get 5 into 10 to the power of 14 1 over second. So, this is what has to go here.

So, let us make sure that the partition function is dimensionless, Kelvin cancels with Kelvin, kilogram cancels with kilogram meter square, second square cancels with second into second. So, all of the units cancel nicely and if I calculate this I get 0.078. So, vibrational partition function is even lesser than rotational, once more translational is of the order of 10 to the power of 30 roughly, 10 to the power of 20 to 30, very large.

Rotational is 10 to 20 very small, big jump, and typically vibrational will be 1 or less. So, that is your order of magnitude of partition functions.

(Refer Slide Time: 28:36)



Summary – module 16

- Translational partition function
  - $Q_{tr} = \frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$
- Rotational partition function:
  - Linear: $Q_{rot} = \frac{8\pi^2 k_B T I}{h^2}$
  - Non-linear: $Q_{rot} = \frac{8\pi^2 (k_B T)^{3/2} (8\pi^3 I_A I_B I_C)^{1/2}}{h^3}$
- Vibrational partition function:
  - $Q_{vib} = \left(\frac{k_B T}{\hbar}\right)^N \frac{1}{\omega_1 \omega_2 ... \omega_N}$

So, in summary, today, we have looked at the 3 components of the partition function, the translational, vibrational and rotational and we have derived specific formulas for that. The translational partition function, we drive to be equal to this, again please do not memorize, we provide you appropriate equations when needed. For rotational, the answer is different depending on linear versus nonlinear and the formulas are here. And for vibration we derive for in general for m dimensions to be equal to this, for 1D it is kT over h bar omega. Thank you very much.