Chemical Kinetics and Transition State Theory
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Lecture 17
Translating, rotating and vibrating quantum mechanically

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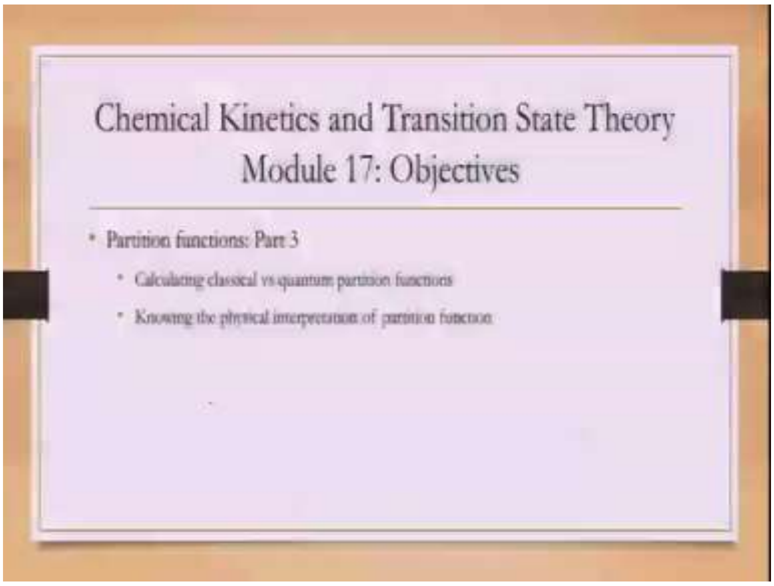

Chemical Kinetics and Transition State Theory
Module 17: Objectives

- Partition functions: Part 3
  - Calculating classical vs quantum partition functions
  - Knowing the physical interpretation of partition function

Hello and welcome to module 17 of Chemical Kinetics and Transition State Theory. In the last module we were discussing partition functions. We looked at Translational, Rotational and Vibrational partition function. Today, I just want to connect with another very related concept, which is the Quantum Partition Function.

What we have done so far is an integral over x and p and x and p are classical concepts, Newtonian concepts and that is what we have been doing so far everything has been Newtonian. But as it turns out, in some occasions, a little bit of quantum mechanical effects are important, we cannot ignore them. So, we will discuss quantum partition functions today and we will end up with a little bit of physical understanding of what partition function means really.

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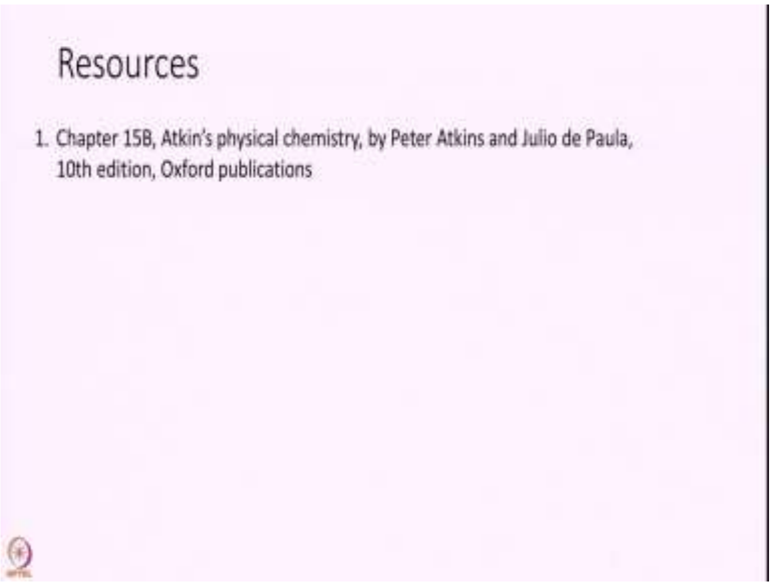

Resources

1. Chapter 15B, Atkin's physical chemistry, by Peter Atkins and Julio de Paula, 10th edition, Oxford publications

What I am describing is from Atkins chapter number 15B of volume number 10 of the 10th edition. But again, if your addition is different, do not worry the same information you can find in a different chapter number.

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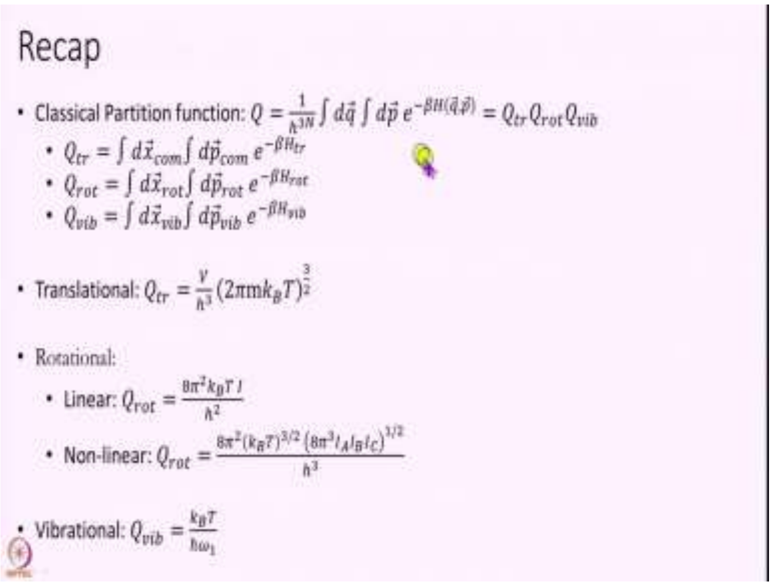

Recap

- Classical Partition function: $Q = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p}\, e^{-\beta H(\vec{q},\vec{p})} = Q_{tr} Q_{rot} Q_{vib}$
  - $Q_{tr} = \int d\vec{x}_{com} \int d\vec{p}_{com}\, e^{-\beta H_{tr}}$
  - $Q_{rot} = \int d\vec{x}_{rot} \int d\vec{p}_{rot}\, e^{-\beta H_{rot}}$
  - $Q_{vib} = \int d\vec{x}_{vib} \int d\vec{p}_{vib}\, e^{-\beta H_{vib}}$
- Translational: $Q_{tr} = \frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$
- Rotational:
  - 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: $Q_{vib} = \frac{k_B T}{\hbar\omega_1}$

So, just a quick recap, what we have covered, we have defined the partition function as this integral over phase space divided by h to the power of 3 N of e to the power of minus beta H. Then we looked at separating the variables and Hamiltonian into translation rotation and vibration and so we get our partition functions also separated into translation rotation and vibrations. So, we get 3 different Qtr, Q rotation and vibration.

And in the last module, we calculated these and showed that Q translation is equal to this. For rotational we did not provide it the full proof, but just an intuition on what how these come about, but you get importantly two different rotational partition functions for linear versus nonlinear molecules and for vibrational we showed that the partition function is equal to this for one vibration, if you have multiple vibrations with different frequencies omega 1, omega 2, omega 3, so on, you just multiply the respective partition functions for vibrations.

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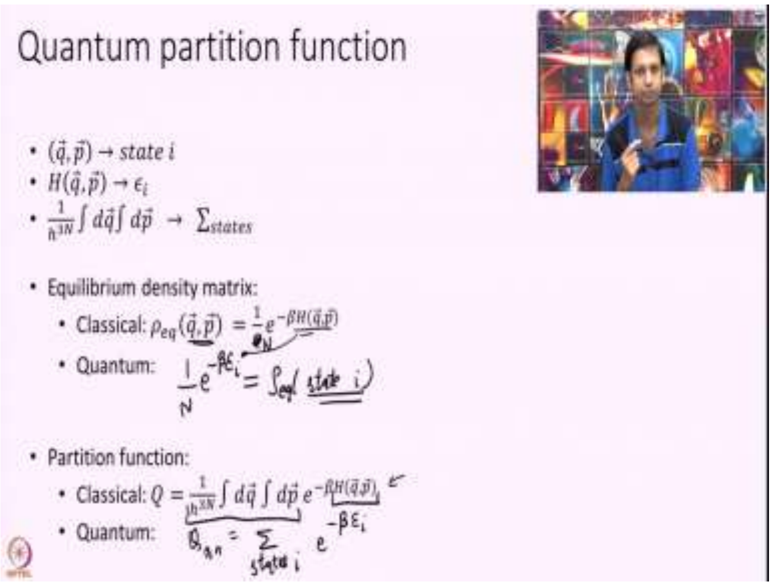

Quantum partition function

- $(\vec{q},\vec{p}) \rightarrow state\ i$
- $H(\vec{q},\vec{p}) \rightarrow \epsilon_i$
- $\frac{1}{h^{3N}}\int d\vec{q}\int d\vec{p} \rightarrow \sum_{states}$
- Equilibrium density matrix:
  - Classical: $\underline{\rho_{eq}(\vec{q},\vec{p})} = \frac{1}{Q_N}e^{-\beta H(\vec{q},\vec{p})}$
  - Quantum: $\frac{1}{N}e^{-\beta\epsilon_i} = \rho_{eq}(\underline{state\ i})$
- Partition function:
  - Classical: $Q = \underbrace{\frac{1}{h^{3N}}\int d\vec{q}\int d\vec{p}}\, e^{\underbrace{-\beta H(\vec{q},\vec{p})}}$
  - Quantum: $Q_{qn} = \sum_{state\ i} e^{-\beta\epsilon_i}$

So, now we will move on to how to define quantum partition function. So, I will not get too much deep into what is quantum mechanics as much that is not really a part of this course. The main thing to know is in quantum mechanics, there is no such thing as phase space. So, the notion of q, p that we have been using so far, it disappears.

What we instead have in place of q, p is called wave functions and I will not get into what wave functions really are, but we denote a wave function by some state i we just give a label. So, main point here is that is q, p is completely continuous, I have, q can take any number from minus infinity to plus infinity and so can p, but the states are discretized, they are quantized that is the origin of the word quantum.

So, q, p gets replaced with state I, Hamiltonian of q, p gets replaced with ei, energies and these ei are the Eigen energies of that system. So, we solve something called the Schrodinger equation and get these eis. Again we are not going to cover the Schrodinger equation really in this course and the final thing is the integral over phase space that we have been doing so far, divided by h to the power of 3 N, gets replaced by our discrete summation over all possible states.

So, we had earlier shown that the equilibrium density matrix for classical mechanics is 1 over Q e to the power of minus beta H, where q was a partition function. I apologise this should be a normalisation constant. In quantum mechanics, that thing will become 1 over N into e to the power of minus beta ei, this will be rho equilibrium of state.

So, wherever you see q, p that gets replaced with state and wherever you see this H that gets replaced with energy and finally we have to define this partition function in quantum mechanics. So, in classical mechanics doing this integral, in quantum mechanics we replace this integral as a sum over all states, e to the power of minus beta and H gets replaced with ei.

So in this slide, I am not really giving you proof on why you can do it, I am simply giving you a recipe. Because the proof of all of this is much beyond the scope of this course, we have to understand quantum mechanics much deeper to derive all of this. So, we will just use this recipe to calculate quantum partition functions now.

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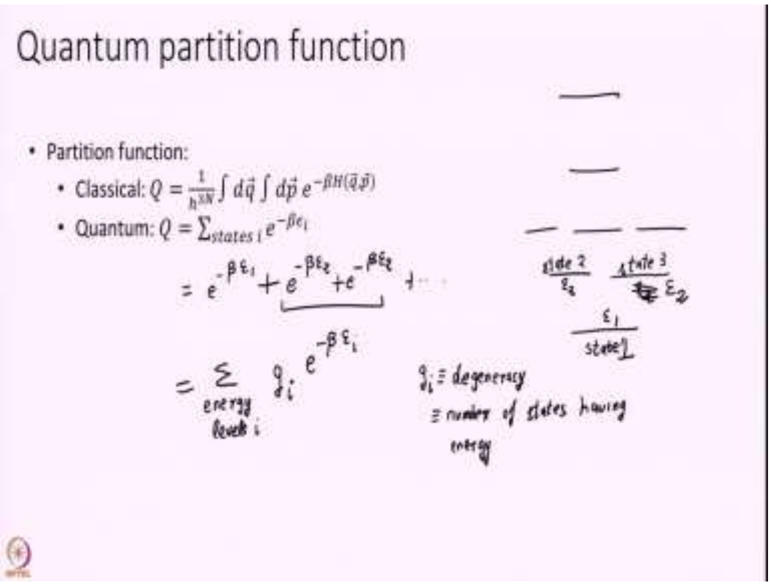

Quantum partition function

- Partition function:
  - Classical: $Q = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p}\, e^{-\beta H(\vec{q},\vec{p})}$
  - Quantum: $Q = \sum_{states\ i} e^{-\beta e_i}$

$$= e^{-\beta \varepsilon_1} + \underbrace{e^{-\beta \varepsilon_2} + e^{-\beta \varepsilon_2}} + \cdots$$

$$= \sum_{\substack{energy \\ levels\ i}} g_i\, e^{-\beta \varepsilon_i}$$

$g_i \equiv$ degeneracy

$\equiv$ number of states having energy

So, we have our quantum partition function defined as this Q equal to sum over states of i e to the power of minus beta i, I will just provide one little comment. So, imagine you have these states. So, what happens in quantum mechanics is, you have different states with different energies. So, let us say I have a bunch of states with different energy, this is let us say state one and its energy is e1, this is state 2 and this is state 3. But interestingly, you can in quantum mechanics have states with equal energy.

So, this is energy e2 and this is energy e3, this is also energy e2. So, state 2 and state 3, let us say have equal energy and so on and so forth, you have different states and all states, some of the states have equal energy. So, if I am summing over states, what I will have is something like e to the power of minus beta e1 plus e to the power of minus beta e2 plus e to the power of minus beta e2 will appear twice, once for state 2 and once for state 3 plus so on.

So, you see that well, whichever states will appear twice will get a factor of 2. Similarly, if a state is occurring three times, it will get a factor of 3 then. So in general, I can write this as sum over energy levels into gi into e to the power of minus beta ei, where gi is the degeneracy. Degeneracy simply means number of states having energy ei. So, I can go from a summation over states to a summation over energy levels.

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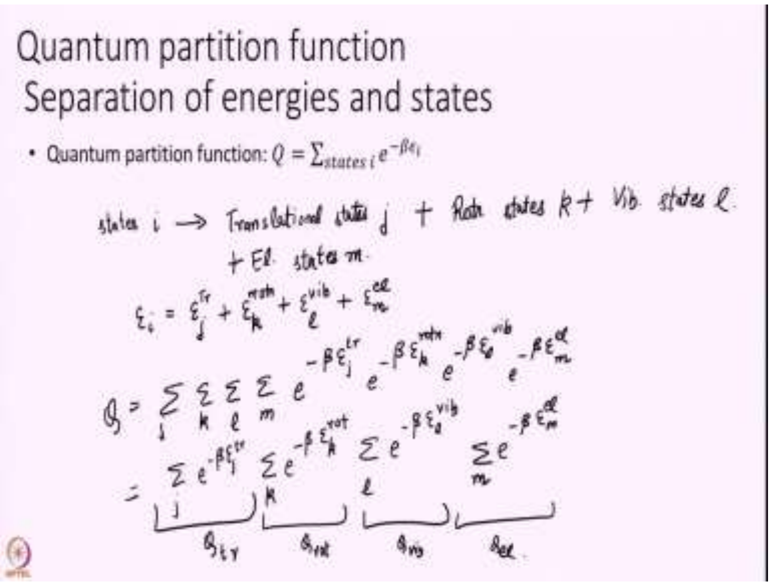

Quantum partition function

Separation of energies and states

- Quantum partition function: $Q = \sum_{states\,i} e^{-\beta \epsilon_i}$

states $i \rightarrow$ Translational states j + Rotn states k + Vib. states l + El. states m

$$\epsilon_i = \epsilon_j^{Tr} + \epsilon_k^{rotn} + \epsilon_l^{vib} + \epsilon_m^{el}$$

$$Q = \sum_j \sum_k \sum_l \sum_m e^{-\beta \epsilon_j^{tr}} e^{-\beta \epsilon_k^{rotn}} e^{-\beta \epsilon_l^{vib}} e^{-\beta \epsilon_m^{el}}$$

$$= \underbrace{\sum_j e^{-\beta \epsilon_j^{tr}}}_{Q_{tr}} \underbrace{\sum_k e^{-\beta \epsilon_k^{rot}}}_{Q_{rot}} \underbrace{\sum_l e^{-\beta \epsilon_l^{vib}}}_{Q_{vib}} \underbrace{\sum_m e^{-\beta \epsilon_m^{el}}}_{Q_{el}}$$

So, now we can whichever version we write over states or energies, we want to do the same trick we did in classical mechanics, we do not want to deal with the full partition function, which is much harder. We want to do divide and rule, we want to separate the states and the energies in terms of translational, rotational and vibrational levels. So, how do we do that? The point is, it is the same trick as before.

So, states i gets divided into a translational states j plus rotational states, k plus vibrational states l, now in quantum mechanics, you actually get another one which is the electronic states as well, which we will discuss later. So in quantum mechanics, we have an extra term other than this translation rotation and vibration, which is the electronic energy.

So, that is the same thing as oneness energy versus twoness energy that energies are different and so we have a different electronic state energy as well and the energy themselves get separated into translation, rotation, vibration, and electronic. So, what we do is we divide this summation into other different parts j, k, l, m and this also, we separate a same thing as before, instead of an integral we have a summation that is all.

So, vibration and electronic, so again we play the same trick and we separate the terms out, this is rotation sum over l, which will be referred to vibration and sum of our electronics which will refer to electronic levels. So, this we then define to be Q translation, this we defined to be Q rotation, Q vibration and Q electronics. So, the same decomposition we can also do in quantum mechanics.

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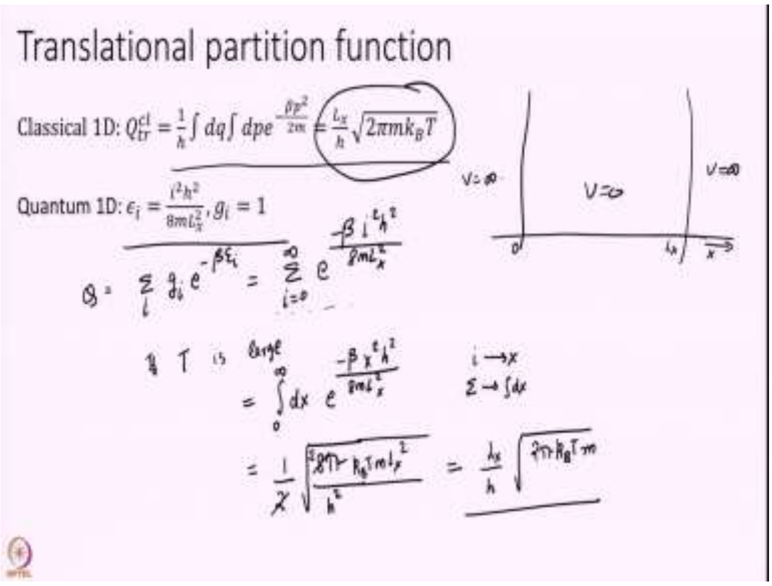

Translational partition function

Classical 1D: $Q_{tr}^{cl} = \frac{1}{h}\int dq \int dp e^{-\frac{\beta p^2}{2m}} = \boxed{\frac{L_x}{h}\sqrt{2\pi m k_B T}}$

Quantum 1D: $\epsilon_i = \frac{i^2 h^2}{8mL_x^2}, g_i = 1$

$$Q = \sum_i g_i e^{-\beta \epsilon_i} = \sum_{i=0}^{\infty} e^{-\frac{\beta i^2 h^2}{8mL_x^2}}$$

if T is large

$$= \int_0^{\infty} dx\, e^{-\frac{\beta x^2 h^2}{8mL_x^2}} \qquad i \to x \quad \Sigma \to \int dx$$

$$= \frac{1}{2}\sqrt{\frac{8\pi k_B T m L_x^2}{h^2}} = \underline{\frac{L_x}{h}\sqrt{2\pi k_B T m}}$$

So, let us calculate the partition function for 1D translation. So the system again is, I have a box, this is particle is located in between 0 to some Lx and the potential is 0 inside and infinite outside. So, we had shown for this potential the classical partition function is here and we will calculate it for the quantum part now.

So, for this part actually the first thing we need to know are what are the energies and degeneracies gis and eis. So, we will see in this course simply provide that this comes from solving Schrodinger equation to be more precise, but we are not following Schrodinger equation and simply providing you the final answer.

So, the Q will be sum over i, gi e to the power of minus beta ei. So, this becomes sum over i gi is 1, e to the power of minus beta i square, h square over 8 mLx square. Now one important note about this part quantum partition functions, we do not include the 0 point energy in here by convention more or less, we can choose the energy whatever we want. So, we set the first ground state energy to be 0. So, my summation will start from 0 to infinity.

Now, this summation is actually a very hard summation to do analytically, but if temperature is large that is I have a lot of these terms, a lot of levels are populated, then I can put this thing as an integral over dx e to the power of minus beta x square h square over 8 mlx square, where I have replaced i with x and the summation with an integral dx.

So, now what you get is Gaussian integral and we know how to solve Gaussian integrals. So, again do not end up memorising these integrals we will always provide you integrals. So, the answer for this is half root of pi over a and a here is a coefficient before x square, which will be h square into 8 pi kBTmLx square, we will just simplify it a little bit, first thing we note, 8 is 4 into 2 and 4 I take out of square root, so I get a 2 that will cancel with this 2, I take h square out and Lx square out and get this.

And you can note that this is exactly the same as this and the reason we get it the same is because we have made the approximation that temperature is large, we went from that summation to integral, the summation will not come out exactly equal to this, it will be slightly different. But in the limit that T is large it will be equal. So that is actually a general result. It is called a classical quantum correspondence. Whenever temperature is large, you will get the classical result back.

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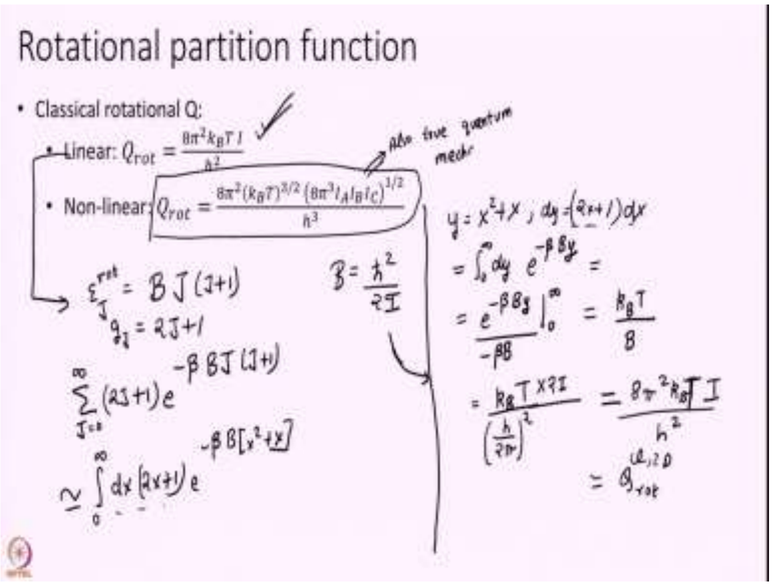

Rotational partition function

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

Also true quantum mech

$\varepsilon_J^{rot} = BJ(J+1)$

$g_J = 2J+1$

$B = \frac{\hbar^2}{2I}$

$\sum_{J=0}^{\infty} (2J+1) e^{-\beta BJ(J+1)}$

$\simeq \int_0^{\infty} dx\,(2x+1)\, e^{-\beta B[x^2+x]}$

$y = x^2+x,\ dy = (2x+1)dx$

$= \int_0^{\infty} dy\, e^{-\beta By} =$

$= \frac{e^{-\beta By}}{-\beta B}\Big|_0^{\infty} = \frac{k_B T}{B}$

$= \frac{k_B T \times 2I}{\left(\frac{h}{2\pi}\right)^2} = \frac{8\pi^2 k_B T I}{h^2}$

$= Q_{rot}^{cl,2D}$

So now let's look at the rotational partition function. For classical we had given you two formulas, one for linear and one for nonlinear. Right now, I will just derive it for linear and nonlinear is slightly harder, it is not fundamentally harder, it is just computationally harder. So, we are not going to do that derivation that we will assume to be true.

So, we will look at the linear part, for the linear part again, the energies, rotational energies are given by a B into J into J plus 1, where B is your h bar square over 2 I and gj is given to be 2j plus 1. This again comes from Schrodinger equation. So, there is some mathematics behind which is solving this rotational Hamiltonian in 2D in linear, for a linear molecule.

What we have to do is sum over j from 0 to infinity gj which is 2j plus 1 into e to the power of minus beta ej. Again, this is a very hard summation to do, so it is a, we are not going to attempt to solve this, we will approximate this is equal to integral from 0 to infinite dx 2 x plus 1 e to the power of minus beta, B x square plus x.

Now, this integral actually might look complex, but it is not really so. We are going to make a substitution y equal to x square plus x, dy is 2x plus 1. So, you know see that this is exactly what appears here, so our life is simple. So, our integral becomes 0 to infinity dy e to the power of minus beta By, which is an easy integral to do, this is equal to e to the power of minus beta By divided by minus beta B from 0 to infinity, once you put in the limits, you can show this is equal to kBT over B.

So, let us just put in the value of B from here, h bar square, h bar is h over 2 pi square divided by 2I. So let us just simplify this, this 2 pi square will go in the numerator. So, I will get 8 pi square kBTI over h square and you will note that this is exactly the same as this. Once more the reason is because we went from a summation to an integral is the reason you get it the same.

So, every time you make this high temperature approximation, you will end up getting the classical answer and often classical answer is easy to calculate because we know simply how to do integrals better than we know how to do summations. So, the nonlinear part I am not going to prove to you, but there as well as in the under high temperature limit this equation will also hold true quantum mechanically as well. Also true quantum mechanically

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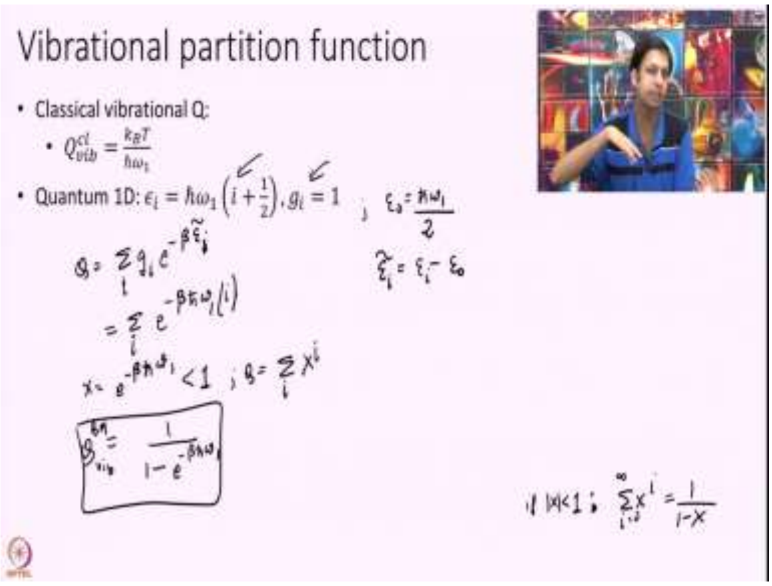

Vibrational partition function

- Classical vibrational Q:
  - $Q^{cl}_{vib} = \frac{k_B T}{\hbar\omega_1}$
- Quantum 1D: $\epsilon_i = \hbar\omega_1\left(i + \frac{1}{2}\right), g_i = 1$; $\epsilon_0 = \frac{\hbar\omega_1}{2}$

$\tilde{\epsilon}_i = \epsilon_i - \epsilon_0$

$Q = \sum_i g_i e^{-\beta\tilde{\epsilon}_i}$

$= \sum_i e^{-\beta\hbar\omega_1(i)}$

$x = e^{-\beta\hbar\omega_1} < 1$; $Q = \sum_i x^i$

$\boxed{Q^{QM}_{vib} = \frac{1}{1 - e^{-\beta\hbar\omega_1}}}$

if $|x| < 1$; $\sum_{i=0}^{\infty} x^i = \frac{1}{1-x}$

So finally, let us look at the vibrational partition function and here we have a little bit of a surprise. So, this is not the same as translation and rotation, we have to be more careful with vibrational. So, our cue again is sum over i gi, e to the power of minus beta ei, where ei here are vibrational energies provided here and gis are the degeneracies which is equal to 1 for vibration. So, let me substitute this, energy is h bar omega 1 i plus half. But what we always do is as I mentioned earlier, we set the 0 point energy to be 0.

So, we ignore the half part away. So, the point is that our e0 is h bar omega 1 over 2. So, that is our base. We consider all energies now as ei minus e naught and what we are doing here is summation over the ei tilde, so that 0 point energy gets removed. It is a matter of convention only, it is nothing more. I am free to choose my base energy, where energy is equal to 0, so that is all I am doing.

I am not really saying that 0 point energy does not, is not there, I am simply calling that 0 point energy is 0 value, that is my choice, it just mathematics. So, I will just provide you a summation sum over i x to the power of i, i equal to 0 to infinity is equal to 1 over 1 minus x, if x is less than 1.

So, I am going to call my x as e to the power of minus beta h bar omega 1. Note that this is less than 1, you are taking exponent of some negative number beta h bar omega 1 is positive, so e to the power of something negative which is less than 1. So, I can do this is equal to 1 over 1 minus x. So, this summation Q has become some over i x to the power of i, vibration quantum mechanical.

So we here, we have to be more careful for vibration, first we can do the summation exactly that is good for us. But more importantly for vibration the high temperature limit does not really hold. For rotation and translation, room temperature is usually higher. So, the approximation that we made in the last few slides of calling the submission as integral and calling the high temperature limit is a good approximation. But here generally it is not and we will show it to you.

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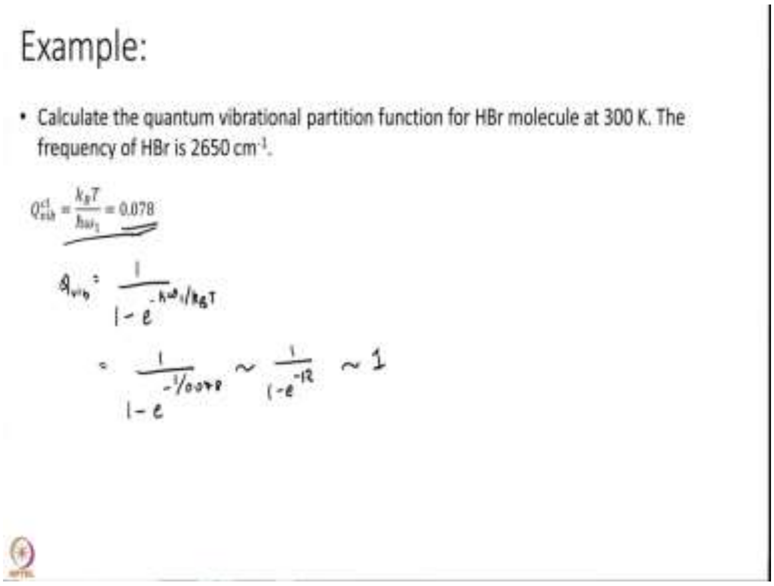

Example:

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

$$Q_{vib}^{cl} = \frac{k_B T}{\hbar\omega_1} = 0.078$$

$$Q_{vib} = \frac{1}{1 - e^{-\hbar\omega_1/k_B T}}$$

$$= \frac{1}{1 - e^{-1/0.078}} \sim \frac{1}{1 - e^{-12}} \sim 1$$

So, we have looked at the quantum vibrational partition function and we have realised it is slightly different from the classical version. So, let us get back to our favourite example of

HBr for which we have found all the rotational classical, classical either rotational translation vibration and if you go back to your last module, we showed the vibrational classical partition function was came out to be 0.078.

So, let us see if the quantum version makes a difference. So, the quantum vibration partition function that we just derived is equal to 1 minus e to the power of minus h bar omega 1 divided by kT. So, this is equal to nothing but 1 minus e to the power of I will just use this number here, 1 divided by 0.078, which is 1 minus roughly 12. What you realise is e to the power of minus 12 is actually a very, very small number. It is 0.0000 something.

It is so, we can almost neglect it. So, this is roughly equal to 1, you can of course, put it on our calculator and calculate this out exactly and what you are going to get is 1.00000 something that is a lot of 0 after 1 and so we do not care about that level of significant figures and so you see that the quantum partition function is very, very different from the classical partition function or more than a factor of 10.

So, that is very important to know that vibrational partition function, quantum mechanical version can be very, very different. So, unless otherwise specified for vibrational partition function, we will always use the quantum version and not the classical version.

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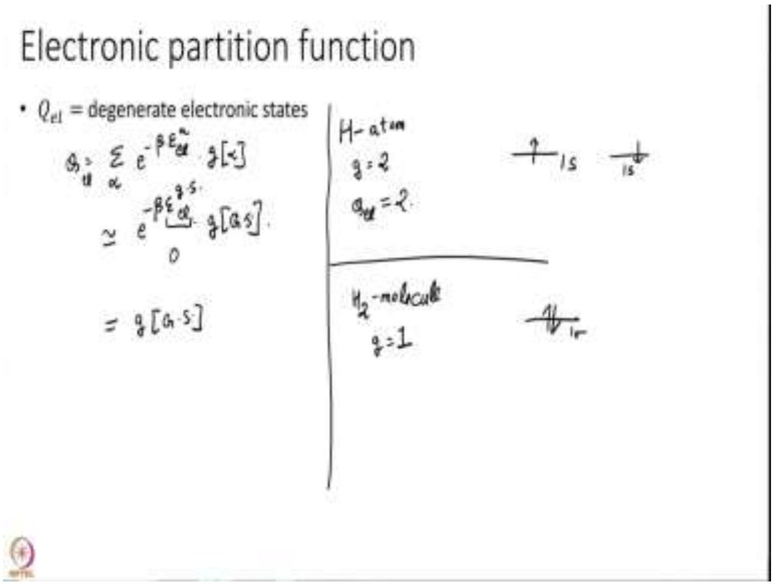

Electronic partition function

- Q_{el} = degenerate electronic states

$$Q_{el} = \sum_{\alpha} e^{-\beta \varepsilon_{el}^{\alpha}} g[\alpha]$$

$$\simeq e^{-\beta \underbrace{\varepsilon_{el}^{g.s.}}_{0}} g[g.s]$$

$$= g[g.s]$$

H-atom

$g = 2$

$Q_{el} = 2$

H_2-molecule

$g = 1$

So finally, let us also look at the final component of the partition function which is the electronic part. So remember, we had divided our energies into this translation rotation vibration and electronic and for each partition function, we write this basically as sum over alpha e to the power of minus beta e electronic alpha. Another point is typically the electronic energies are much much more than temperature. Hundreds of times more than temperature, thousands of times more than temperature.

So, generally we approximate this thing as simply e to the power of minus beta e ground state only. I had forgotten the degeneracy I am sorry, g of alpha into g of ground state. But by our convention, this is chosen to be 0. Remember once more, for a quantum partition function we always chose the e electronic ground state to be 0 or e ground state it has to be 0.

So, we get this is equal to simply g of, where g is the number of states with equal energy for the ground state. So, we will go, let us look at a couple of examples. For example, if I want to think of hydrogen atom. So, for hydrogen atom you have one S orbital and you have 1 electron, but you note that this electron can also be in the down spin state. So, this is a little bit quantum mechanical, each orbital can have up spin or down spin.

So, with that basically your degeneracy is 2. So, every time you have an unpaired electron your degeneracy becomes a more than 1. So, your Q electronic I am sorry electronic is equal to 2. The same thing if I do for let us say h2 molecule. Well, h2 molecule in the ground state has only one configuration. So, both electrons are paired.

When that happens, you degeneracy is simply one there is only 1, there is only one possibility that the ground state can be in, which is this 1 sigma 2. So, this is important how do you calculate the electronic partition function as well in quantum mechanics.

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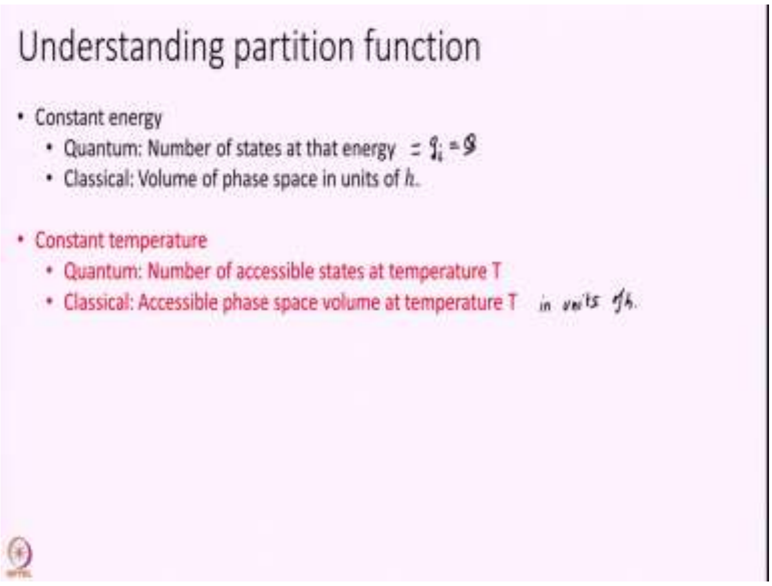

Understanding partition function

- Constant energy
  - Quantum: Number of states at that energy $= g_i = g$
  - Classical: Volume of phase space in units of h.
- Constant temperature
  - Quantum: Number of accessible states at temperature T
  - Classical: Accessible phase space volume at temperature T in units of h.

So, now we have looked at the different partition functions. I want to just spend a few more minutes in explaining how do we understand partition functions, what is the meaning of partition function. So, what we have been looking at is a partition function at a given temperature, we had beta. Actually, you can also define partition function at a given energy and if you do that, that is simply the sum over states of that energy.

So, quantum mechanically partition function at a given energy would simply mean the number of states at that energy, which is actually exactly the same as the degeneracy. So, that is what partition function at constant energy means and classically that would mean the area or the volume that constant energy surface occupies. So, think of a contour plot of that particular energy in a high dimensional space in q, p space and find its volume that is your classical part partition function and that energy.

We can also define the partition function at a given temperature, which is what we have calculated. So, the meaning changes slightly but essence remains the same. Quantum partition function is essentially the number of states that are accessible. So, you are at a given temperature, which means you have a distribution of states. So, the quantum partition function is essentially telling you at this temperature, these are the number of states that have some occupancy.

This is a very broad and rough definition. The exact definition is a summation. So, this is just an intuitive definition of partition function and classically that number of states becomes an volume in units of h. So, the accessible phase space volume at that temperature in units of h. So, that is the fundamental meaning of partition function.

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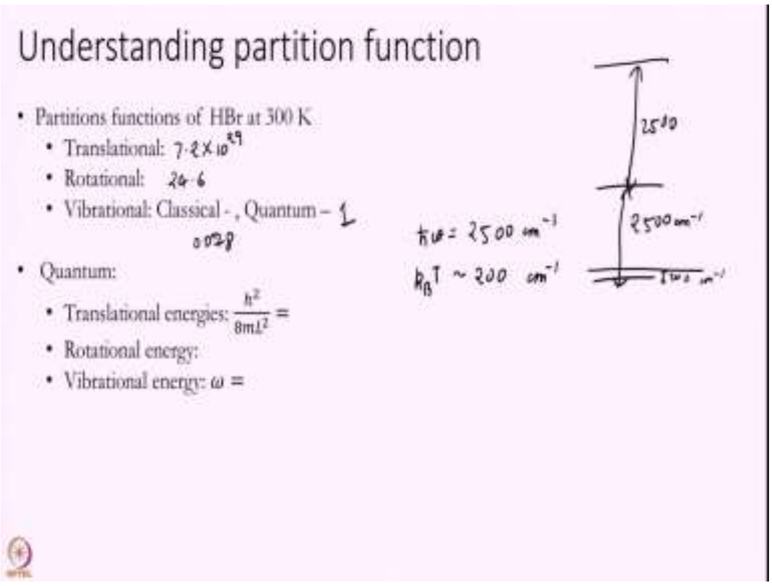

Understanding partition function

- Partitions functions of HBr at 300 K
  - Translational: 7.2×10^{29}
  - Rotational: 24.6
  - Vibrational: Classical - 0.028, Quantum – 1
- Quantum:
  - Translational energies: $\frac{h^2}{8mL^2} =$
  - Rotational energy:
  - Vibrational energy: $\omega =$

$\hbar\omega = 2500\ cm^{-1}$

$k_BT \sim 200\ cm^{-1}$

So, we have found the partition functions for HBr. So, the translational in the last module you can go and we calculated these numbers out. So, the translational partition function came out to be 7.2 into 10 to the power of 29. The rotational came out to be 24.6 and the vibrational the classical number comes out to be 0.078 and today we calculated the quantum number and quantum number is very close to 1.

So, what these numbers really mean is, that the translational states you have roughly 10 to the power of 29 or 10 to the power of 30 states that are accessible at 300 Kelvin. The translational states are very, very closely, the translational energy levels are very closely spaced and so you have a lot of translational states.

Now rotational states are somewhat far apart. For HBr they are roughly like 5 to 10 wave numbers 20 wave numbers actually. So, at 300 Kelvin you have roughly 10 or 20 states that are accessible and in terms of vibrational quantum mechanically you have only 1 state that is accessible. So, what is the reason for that, the reason for that is that the vibrational frequency, so the vibrational frequency is roughly 2500 wave numbers and room temperature is roughly 200 wave numbers.

So, you can do this calculation at 300 Kelvin, what is it in wave numbers, it is 200. So, you see the frequency is much more, so the vibrational levels are very far apart, vibrational levels are separated by 2500 wave numbers. While temperature is here, this is 200 wave numbers. So, you do not have enough energy to access excited states at all and therefore quantum mechanically you get a quantum partition function of 1. So, that is how we understand partition functions.

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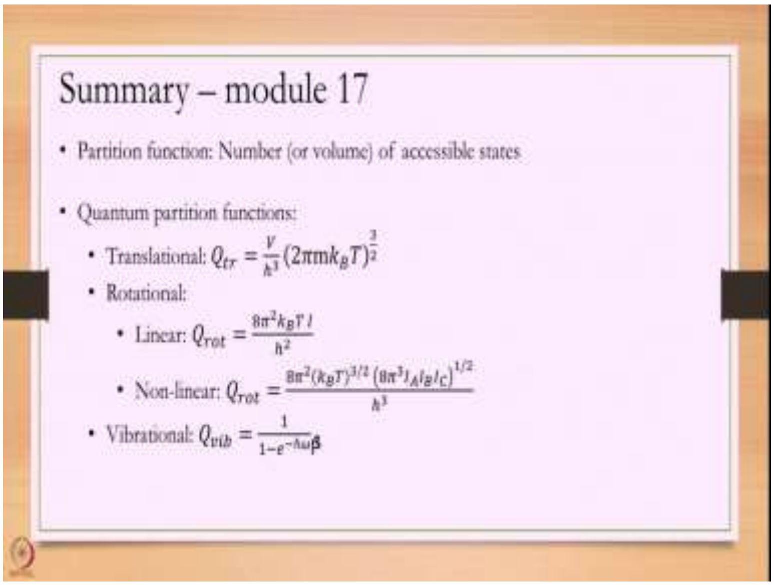

Summary – module 17

- Partition function: Number (or volume) of accessible states
- Quantum partition functions:
  - Translational: $Q_{tr} = \frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$
  - Rotational:
    - 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: $Q_{vib} = \frac{1}{1-e^{-\hbar\omega}\beta}$

So, in summary, today we have looked at partition function and looked at what its physical meaning is it is essentially the number or the volume of accessible states at a given temperature. We have looked at the quantum partition functions today and we are going to use the same classical formula for translation and rotation. But for vibration, we will use a different formula when it comes to quantum mechanics, which is one minus e to the power of, I apologise there is a little mistake. This is beta h by omega. Thank you very much.