Chemical Kinetics and Transition State Theory
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Lecture 42
Sum and density of states

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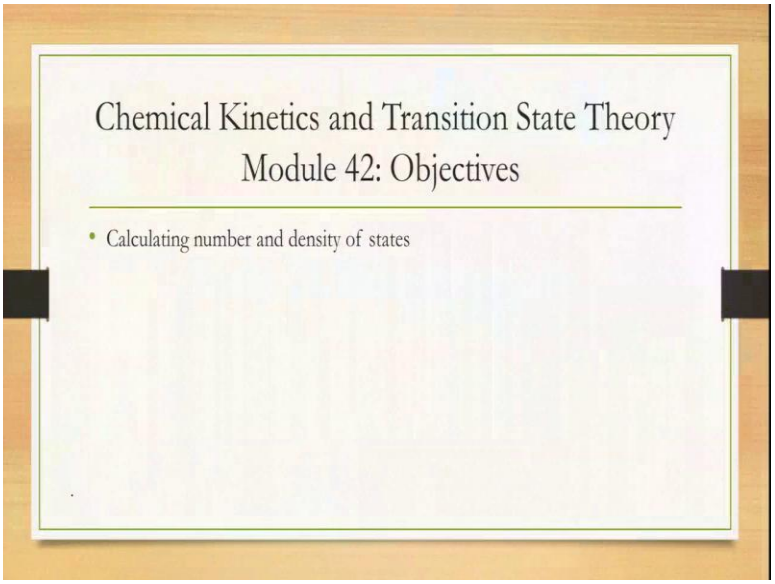

Chemical Kinetics and Transition State Theory
Module 42: Objectives

- Calculating number and density of states

Hello, and welcome to module 42 of Chemical Kinetics and Transition State Theory. In the last module, we discussed transition state theory in microcanonical ensemble. And what we find in that theory is we need to calculate density and sum of states. Now, in this module, we will discuss a little bit more details on how this density of states and total number of states is calculated.

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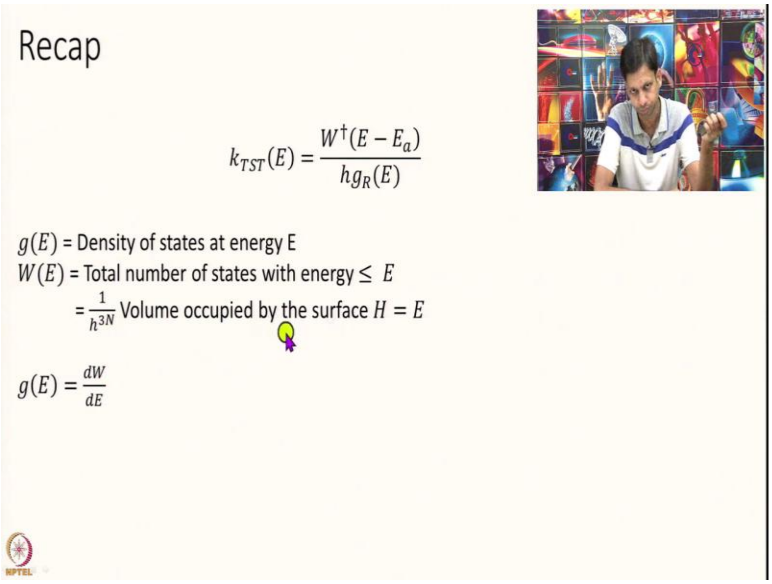

Recap

$$k_{TST}(E) = \frac{W^{\dagger}(E - E_a)}{hg_R(E)}$$

$g(E)$ = Density of states at energy E

$W(E)$ = Total number of states with energy $\leq E$

$= \frac{1}{h^{3N}}$ Volume occupied by the surface $H = E$

$$g(E) = \frac{dW}{dE}$$

So, a quick recap. The transition state theory estimate comes out to be this formula, where W is the total number of states. So W dagger is a total number of states calculated at transition state excluding the reaction coordinate, Ea is the activation energy and g is the density of states at energy E computed in the reactant region only. So this formula we derived in the last module. So today we are going to discuss how to calculate this g and W. g is the density of states at energy E. And W is the total number of states with energy less than equal to E.

Within classical mechanics we also argued, I think two modules ago, that this W can be calculated as the volume occupied by the surface of H equal to E, where H is the Hamiltonian divided by h to the power of 3N, this little h. So this is really the way we typically will calculate W, at least if classical mechanics holds true. And to calculate g, we just differentiate W with respect to E. So this is going to be our main strategy. So, let us see how this works.

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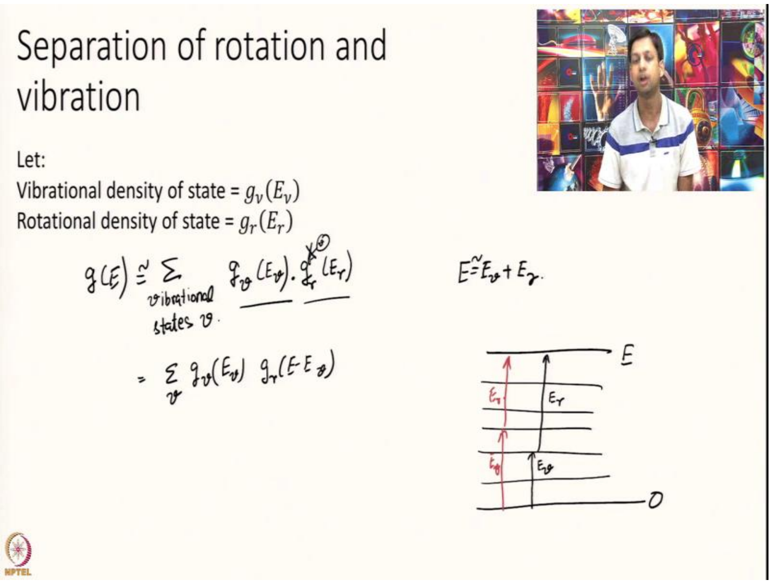

Separation of rotation and vibration

Let:
Vibrational density of state = $g_v(E_v)$
Rotational density of state = $g_r(E_r)$

$$g(E) \simeq \sum_{\substack{\text{vibrational} \\ \text{states } \vartheta}} \underline{g_\vartheta(E_\vartheta)} \cdot \underline{g_r(E_r)}$$

$$= \sum_{\vartheta} g_\vartheta(E_\vartheta)\, g_r(E-E_\vartheta)$$

$E \simeq E_\vartheta + E_r$.

First thing before we calculate these g and W, we will play our regular tricks and separate rotations from vibrations. Because as it turns out, we can analyze both of them individually very well, but combined, it becomes somewhat harder. So the common trick that we again do is, let us say I am trying to calculate the total number of states, so if I want to calculate g of E, total energy, and let us say the total energy is the sum of vibrational energies plus rotational energies, translation can always be separated out exactly. So I am not considering that right now. Translation is there. But that is exactly separable anyway.

So, the g of E is nothing but the total number of states at that energy E or the density of states at that energy E. So what I can do is, I can sum over vibrational estates nu, find the number of states at that energy E nu. So I am thinking I have a total energy E and then I can partition this into E nu and Er.

So let us say the total energy E is this, and this is, let us say, E nu and this is let us say Er. So I am saying, if my the vibrational energy is E nu, well, the total number of states then will be the density of states at E nu multiplied by the density of states at Er and then a sum over all possible combinations of E nu that I can have.

Instead of this E nu, I might have a different combination, where E nu is equal to this and Er is equal to this. So I sum over all possible possibilities of E nu, of course, E nu is less than E. So this I just modify a little bit and state this is equal to sum over nu, g nu, E nu and gr E minus E nu. So this is of course an approximation. What is the approximation really here? The approximation is that the rotational states and vibrational states are independent of each other.

However, vibrations you have excited 1 quanta of vibrational excitation or 2 quanta of vibrational excitation, the rotations are unaffected by it. That is why I have been able to write it as a product form. Otherwise, more accurately, I should include vibrational state as well into the definition of g here. So this is ignored and that is the approximation really. And that is a regular approximation we have made on many, many times that rotation and vibration can be decoupled. It is usually a good approximation except for a few cases when it does not.

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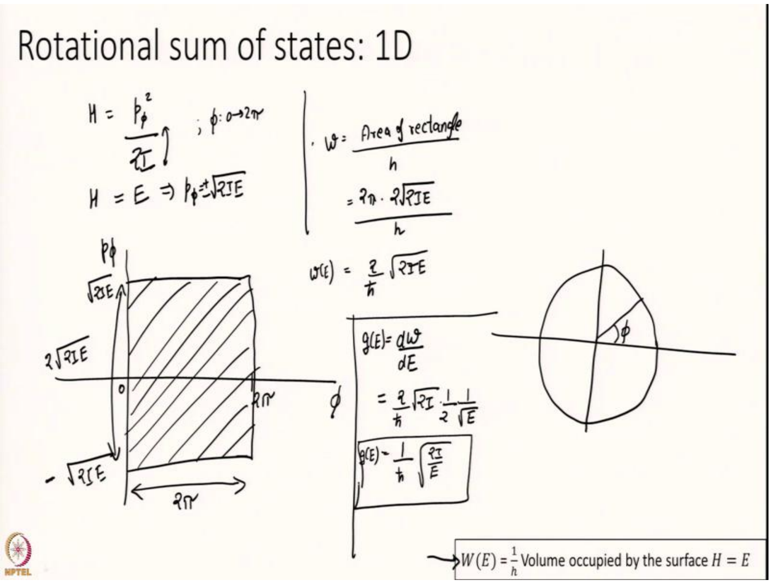

Rotational sum of states: 1D

$H = \frac{p_\phi^2}{2I}$; $\phi : 0 \to 2\pi$

$H = E \Rightarrow p_\phi = \pm\sqrt{2IE}$

$W = \frac{\text{Area of rectangle}}{h} = \frac{2\pi \cdot 2\sqrt{2IE}}{h}$

$W(E) = \frac{2}{\hbar}\sqrt{2IE}$

$g(E) = \frac{dW}{dE} = \frac{2}{\hbar}\sqrt{2I} \cdot \frac{1}{2}\frac{1}{\sqrt{E}}$

$\boxed{g(E) = \frac{1}{\hbar}\sqrt{\frac{2I}{E}}}$

$W(E) = \frac{1}{h}$ Volume occupied by the surface $H = E$

So, our goal becomes in calculating these rotational density and vibrational density separately, which is always good. So I will show you today, let us start out by looking at this rotational density first. So let us look at it in 1D. 3D is the same concept. It is just a math become slightly harder so we will do 1D here. So what we have to do? We have to find, we will do WE, calculate WE first and WE is nothing, but 1 over h into the volume occupied by the surface H equal to E. I am saying 1 over h only because it is 1D only. So it is h to the power of 1.

So, what is H? H for 1D rotor is nothing but p phi square over 2I, where my particle is let us say constrained on a circle and this is phi. So, this is how Hamiltonian for this system is given and phi goes from 0 to 2 pi. So we want to find this is equal to E. I want the contour corresponding to H equal to E and find the volume occupied by this contour.

So, let us make a plot of phi versus p phi. Phi goes from 0 to 2 pi. How much does p phi goes from? Well, minus infinity to plus infinity, but we have a constraint, a constraint is H equal to E. So, H equal to E implies p phi equal to root 2IE plus or minus. So if I equate these two, this is easy to see. So I have a root of 2IE here. I am assuming energy to be positive, E here minus and phi goes from 0 to 2 pi. So, effectively you get a box like this.

So, W is nothing but the area occupied by this rectangle divided by h. So W equal to area of rectangle, the shaded region, divided by h. Well, area is easy to calculate. This length is 2 pi and this side is what 2 into root 2IE. So area of rectangle is 2 pi into 2 root 2IE divided by h. So this is nothing but 2 over h bar root 2IE. So this is W of E.

I can also calculate g of E now as dW over dE. So this is how going to be our strategy for classical mechanics at least. And remember that for rotations, classical mechanics is usually very good. So this is a pretty good approximation on what we are doing. So this will be equal to 2 over h bar root 2I into half of 1 over root E. So this is nothing but 1 over h bar 2I over E. So I am not doing the quantum version here right now, but classical mechanics is usually holds very good anyway.

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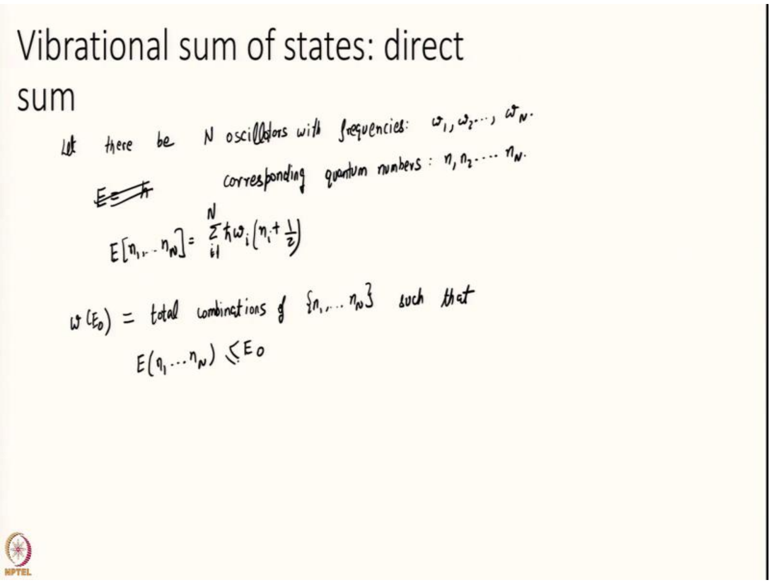

Vibrational sum of states: direct sum

Let there be N oscillators with frequencies: $\omega_1, \omega_2, \ldots, \omega_N$.

~~$E = \hbar$~~ corresponding quantum numbers : $n_1 n_2 \ldots n_N$.

$$E[n_1, \ldots n_N] = \sum_{i=1}^{N} \hbar\omega_i \left(n_i + \frac{1}{2}\right)$$

$\omega(E_0)$ = total combinations of $\{n_1, \ldots n_N\}$ such that

$E(n_1 \ldots n_N) \leq E_0$

So, now, let us look at vibrations. Vibrations, quantum, classical mechanics is not good. One must do a quantum treatment. So in this module I will try to also convince you that is in fact correct. But let us start with the quantum version and then we will do the classical version as well and see how different they are.

So, let us say I have to first get my pen. Let there be n oscillators with frequencies omega 1, omega 2, till omega n. So what is the energy of this? Let us say the corresponding quantum number are n1, n2 till nN. So the energy for this set of quantum numbers will be equal to sum over i h bar omega i ni plus half, i equal to 1 to capital N. So energy of one oscillator is h bar omega into n plus half, so I am simply summing over all possible different modes, different oscillators.

So, the idea is very simple, W of let us say E naught is nothing but total combinations of n1 nN such that E of this n1 to nN is less than E naught. So you really literally count it for all possible n1s to nNs such that the energy, the harmonic oscillator energies comes out to be less than the desired energy.

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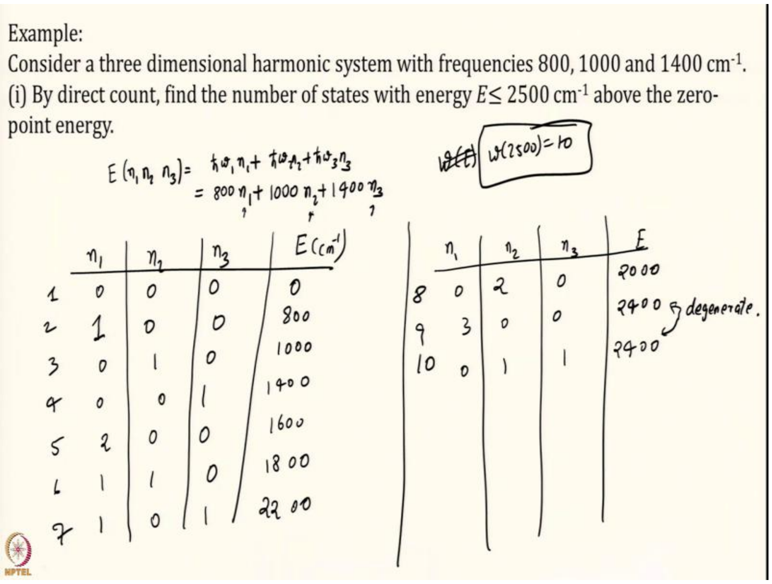

Example:

Consider a three dimensional harmonic system with frequencies 800, 1000 and 1400 cm^{-1}.

(i) By direct count, find the number of states with energy $E \leq 2500$ cm^{-1} above the zero-point energy.

$$E(n_1, n_2, n_3) = \hbar\omega_1 n_1 + \hbar\omega_2 n_2 + \hbar\omega_3 n_3$$
$$= 800 n_1 + 1000 n_2 + 1400 n_3$$

~~W(E)~~ $\boxed{W(2500) = 10}$

	n_1	n_2	n_3	$E(cm^{-1})$
1	0	0	0	0
2	1	0	0	800
3	0	1	0	1000
4	0	0	1	1400
5	2	0	0	1600
6	1	1	0	1800
7	1	0	1	2200
8	0	2	0	2000
9	3	0	0	2400
10	0	1	1	2400

degenerate.

So, we will see one example so that things become clear. So the question statement is that we have let us say only three oscillators with frequencies 800, 1,000 and 1400 wave numbers, calculate the total number of states with energy less than or equal to 2,500 wave numbers above the zero point energy.

So let us exclude a zero point energy. So, 2,500 wave numbers above the zero point energy. So my energy is going to be h bar omega 1 plus h bar omega 2, I am sorry, I have forgotten my n1s, so I have three quantum numbers here n1, n2 and 3, this will be h bar omega 1 n1 plus h bar omega 2 n2 plus h bar omega 3 n3.

I have not written plus half, because that is a zero point energy. So this is the energy above the zero point energy. H bar, so let me just put in the numbers here 800 n1 plus 1,000 n2 plus 1,400 n3. So we have to literally calculate all possible combinations of n1, n2, and n3 such that the energy remains less than or equal to 2,500 wave numbers. So we are going to manually calculate it. There is no formula now, n1, n2, n3, energy, and we will count only those combinations for which E is less than 2,500. So, the lowest one is, of course, 0.

I can put 1 quanta here. So if I put n1 equal to 1, n2 equal to 0 and n3 equal to 0, I will get 800 wave numbers. I can put a 0, 1, 0, that is 1,000 wave numbers, still less than 2,500. 0, 0, 1, 1,400 wave numbers, still less than 2,500 wave numbers. Then let us start putting 2 quanta. Let me put 2 quanta here, then I will get 1,600 wave numbers. What can I do next? I can put 1 and 1 and 0 that will give me 1,800 wave numbers. What do I do next? Let me put 1, 0, 1 that is 2,200 wave numbers. I have actually forgotten 1. So let me make another table here.

So, it is laborious. You have to just do, go ahead and do it. I can also put, could have put this way. I would have gotten 2,000 wave numbers. Finally, I can do 3, 0, 0 that is 2,400 wave numbers or I can do 0, 1, 1, that is also 2,400 wave numbers. These two are degenerate, but they represent different states nonetheless. So we count them equally. So the total number is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, W of E, W of 2,500 is equal to 10. So this is how you calculate W quantum mechanically.

Often, when you have large number of oscillators or large amount of energy, what you can do is to use a program to do this for you, you do not have to do it manually. So you can easily construct a program or you can find a program written by somebody else, which will do this exact job for you, but this is what will always happen, this mathematics.

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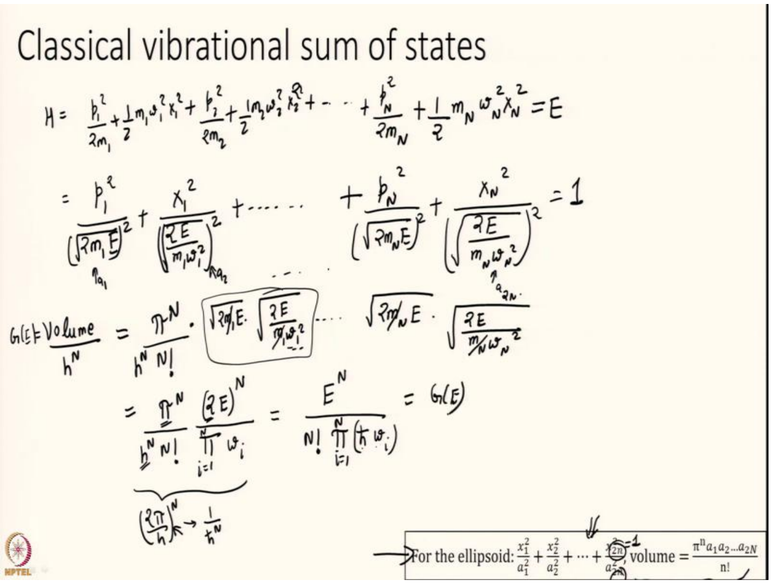

Classical vibrational sum of states

$$H=\frac{p_1^2}{2m_1}+\frac{1}{2}m_1\omega_1^2x_1^2+\frac{p_2^2}{2m_2}+\frac{1}{2}m_2\omega_2^2x_2^2+\cdots+\frac{p_N^2}{2m_N}+\frac{1}{2}m_N\omega_N^2x_N^2=E$$

$$=\frac{p_1^2}{(\underbrace{\sqrt{2m_1E}}_{a_1})^2}+\frac{x_1^2}{(\underbrace{\sqrt{\frac{2E}{m_1\omega_1^2}}}_{a_2})^2}+\cdots\cdots+\frac{p_N^2}{(\sqrt{2m_NE})^2}+\frac{x_N^2}{(\underbrace{\sqrt{\frac{2E}{m_N\omega_N^2}}}_{a_{2N}})^2}=1$$

$$G(E)=\frac{\text{Volume}}{h^N}=\frac{\pi^N}{h^N N!}\cdot\boxed{\sqrt{2\cancel{m_1}E}\cdot\sqrt{\frac{2E}{\cancel{m_1}\omega_1^2}}}\cdots\sqrt{2\cancel{m_N}E}\cdot\sqrt{\frac{2E}{\cancel{m_N}\omega_N^2}}$$

$$=\underbrace{\frac{\pi^N}{h^N N!}}_{\left(\frac{2\pi}{h}\right)^N\to\frac{1}{\hbar^N}}\frac{(2E)^N}{\prod_{i=1}^{N}\omega_i}=\frac{E^N}{N!\prod_{i=1}^{N}(\hbar\omega_i)}=G(E)$$

For the ellipsoid: $\frac{x_1^2}{a_1^2}+\frac{x_2^2}{a_2^2}+\cdots+\frac{x_{2n}^2}{a_{2n}^2}=1$, volume $=\frac{\pi^n a_1a_2\ldots a_{2N}}{n!}$

Now, let me also emphasize upon you what would have happened if I calculated this W classically, maybe I am being a fool, maybe I have, I am doing all this laborious work for no reason, classically I can get an analytical expression and just use that. So let us see what would have happened. So, classically, my H now is what. It is, well, p1 square over 2m plus half, let me write 1, omega 1 square x1 square plus p2 square over 2m2 plus half m2 omega 2 square x2 square plus dot, dot, dot, p sum, I have N oscillators xN square.

So, again I will play the same trick. I will say H is equal to E and this is some n dimensional space, a huge space, but it does not matter, I have this huge space in which I have a contour of H equal to E and I simply have to find the volume occupied by this contour that is still my general recipe, however, large n is, even if I cannot draw the figure even if I cannot imagine the figure.

For this, let me just rewrite this in a different form, the form is p1 square over 2m1E, root 2m1E square plus x1 square divided by, I am of course looking at this formula and trying to get it in that particular format, square root square plus dot, dot, dot plus pN square divided by root 2mNE square plus xN square divided by 2E by mN omega N square, square root, oh my god, I cut it off, this was a brutal be heading, of 2E, is equal to 1. I have forgotten to write, this is equal to 1.

So, for this ellipsoid, the volume is given to be this. It is a mathematical formula that we can assume. So all we have to do is to use this formula, so volume G is volume divided by h to the power of N. So volume will be pi to the power of N into these a1 into a2 into a3 where a1, a2 are here, so this is my a1, this is my a2, dot, dot, dot, this is my aN, this is a2N. I have 2N variables. I have p1 comma x1 comma p2 comma x2 till pN comma xN. So I have 2N. So that is why I have a 2N here.

So, pi to the power of N into root 2m1E into root 2E over m1 omega 1 square dot, dot, dot root 2mNE root 2E divided by mN omega N square divided by N factorial. Masses happily canceled. So I get pi to the power of N, I forgot my h, plant will be angry with me, and here I get 2E to the power of N. I have 2E, this thing is 2E, square root of 2E into square root of 2E N times, so 2E to the power of N divided by product of i of omega i. So I have omega 1 square here. Omega 1 square, square root is omega 1 and I have simply a product divided by h to the power of N, N factorial.

So, I will just write it in a form that is more amenable to us. This I will write as E to the power of N divided by N factorial into product of, see carefully what I am doing, h bar into omega i. So I notice I have here, this is pi into 2 by h to the power of N. You see this constant h 2 pi. I have taken them out, written it in this form, this is nothing but 1 by h bar to the power of N and I put one h bar for each omega i. Omega i is feel lonely. So I have to provide them with h bars. So I get this expression. So this is what g of E finally is for me.

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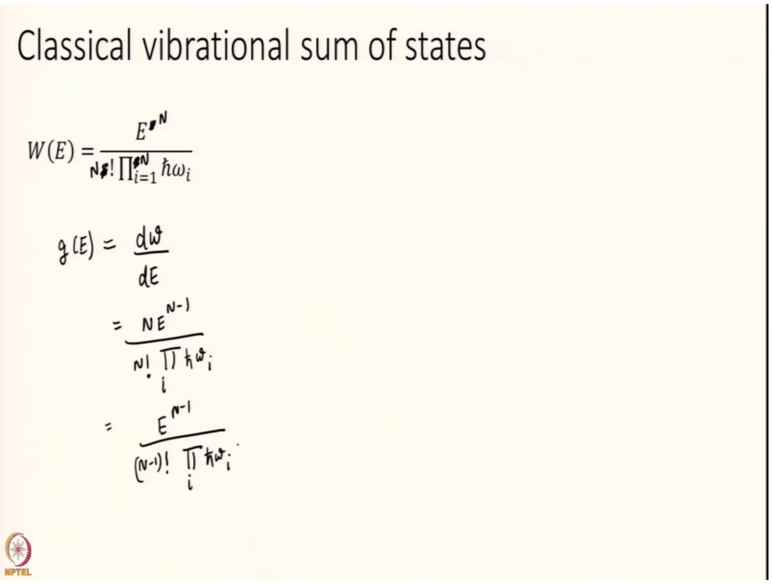

Classical vibrational sum of states

$$W(E) = \frac{E^{N}}{N! \prod_{i=1}^{N} \hbar\omega_i}$$

$$g(E) = \frac{dW}{dE}$$

$$= \frac{N E^{N-1}}{N! \prod_{i} \hbar\omega_i}$$

$$= \frac{E^{N-1}}{(N-1)! \prod_{i} \hbar\omega_i}$$

While I am at it, I forgot I have put s here instead of N. I have been using N for us. So let me just, in my practice, I was using s. While I am at it, let me also just provide you what g of E will be. G of E is nothing but dW over dE. This we will need in the next module. So I am just doing it right now. So this is equal to. So just an extra fact for you that we will use in the next module.

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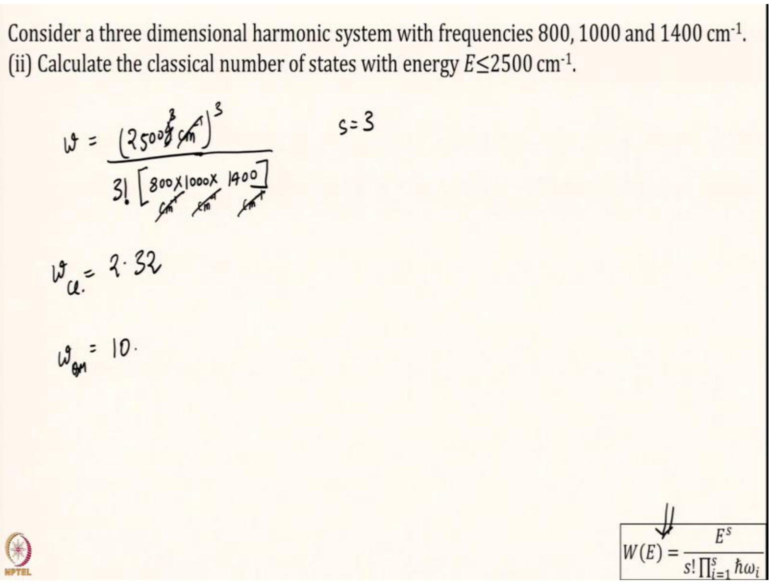

Consider a three dimensional harmonic system with frequencies 800, 1000 and 1400 cm^{-1}.
(ii) Calculate the classical number of states with energy $E \leq 2500$ cm^{-1}.

$$W = \frac{(2500^{3} \cancel{cm^{-1}})^3}{3!\left[800 \cancel{cm^{-1}} \times 1000 \cancel{cm^{-1}} \times 1400 \cancel{cm^{-1}}\right]}$$

$s = 3$

$W_{cl} = 2.32$

$W_{qm} = 10.$

$$W(E) = \frac{E^s}{s!\prod_{i=1}^{s} \hbar\omega_i}$$

So, let us calculate the same problem. We have 3 modes with frequencies 800, 1,000 and 1,400 and I ask you now calculate the classical number of states with energy less than 2,500 wave numbers. So you remember we got 10 for quantum. Let us use this formula now and see what we get now.

So W will be 2,500 cube, here s or N is 3 divided by 3 factorial into product of the frequencies 800 into 1,000 into 1,400. So, note that this is dimensionless. I have 2,500 wave number cube and these are all wave numbers. So this cancels out that is nice. And then I can simply plug it on a calculator. I did earlier and I got 2.32.

So, you see, W quantum was 10, almost 5 times or 4 times more than the classical version. So the classical W is not a good idea. We should do a quantum W. We will discuss a little bit more of this in the coming modules. This is a famous mistake actually made by RRK, so by R and R, by Rice and Ramsperger, Kassel actually corrected it.

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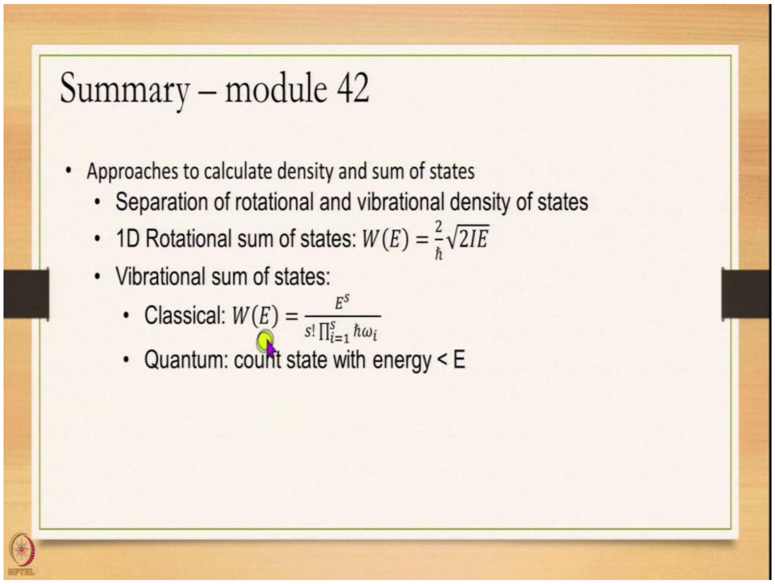

Summary – module 42

- Approaches to calculate density and sum of states
  - Separation of rotational and vibrational density of states
  - 1D Rotational sum of states: $W(E) = \frac{2}{\hbar}\sqrt{2IE}$
  - Vibrational sum of states:
    - Classical: $W(E) = \frac{E^s}{s!\prod_{i=1}^{s}\hbar\omega_i}$
    - Quantum: count state with energy < E

So, in summary, what we have looked today is how to calculate this density and sum of states. We start out by separating out the rotational and vibrational density of states. For 1D rotational, we showed that the classical mechanics is typically good and you can calculate W as 2 over h bar root 2IE. Vibrational quantum version is that you simply count the number of states. It is laborious, but that is the right way of doing it. The classical version nonetheless is E to the power of s divided by s factorial into product of frequencies. Thank you very much.