Chemical Kinetics and Transition State Theory
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Lecture 40
Microcanonical rate constant: magic of Marcus - RRK model

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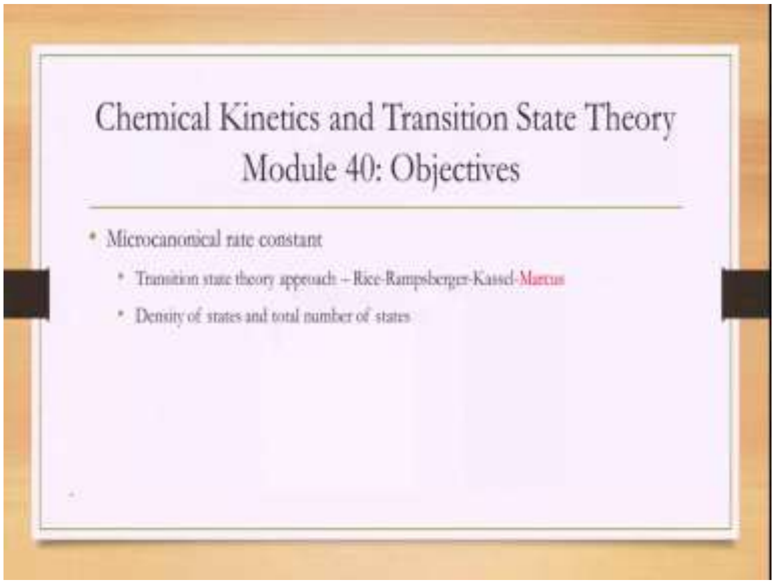

Chemical Kinetics and Transition State Theory
Module 40: Objectives

- Microcanonical rate constant
  - Transition state theory approach – Rice-Rampsberger-Kassel-Marcus
  - Density of states and total number of states

Hello, and welcome to module 40 of Chemical Kinetics and Transition State Theory. In the last two modules, we looked at our theory called RRK theory to look at rate constants calculated at constant energy. Throughout the course, we have been looking at calculating rate constants at constant temperature.

Now, we have been asking the question what if we have a different ensemble, where the energy is constant, not temperature. In the last two modules we looked at a simple model, which we call as the RRK model. Today, we will do, extend that model and fill in the deficiencies of that very simple model. The model that I am discussing today is called RRKM model, which is Rice, Ramsperger, Kassel and Marcus.

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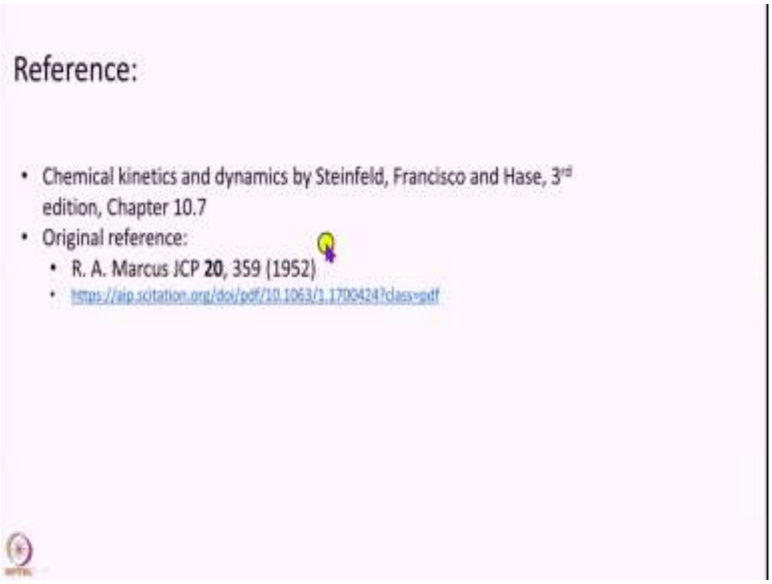

Reference:

- Chemical kinetics and dynamics by Steinfeld, Francisco and Hase, 3rd edition, Chapter 10.7
- Original reference:
  - R. A. Marcus JCP **20**, 359 (1952)
  - https://aip.scitation.org/doi/pdf/10.1063/1.1700424?class=pdf

So what I am teaching today is there in Steinfeld, Francisco and Hase in Chapter 10.7. I have also given you the original reference for those who are extra interested. So the history of this work is as follows. In late 1920s, ‘27 and ‘28, these three authors Rice, Ramsperger and Kassel formulated this theory for unimoleculer decay.

They were trying to understand if a molecule is decaying at a constant energy, how do I calculate the rate constant and match the experimental data? And so we studied their efforts in the last two modules. But that actually does not work well and we discussed that as well. That is a very simple model with a lot of deficiencies.

Enter Marcus. Marcus is really a pioneer in chemical kinetics. This was, he was doing a postdoc with Rice actually of this RRK, the R of RRK. And he was actually before they are doing some experimental work. But Marcus was a genius. And before like when he joined Rice as a postdoc he started looking at papers for the last several decades. He just started reading and reading and reading.

And finally, Rice and one more person, they gave him this problem. This several decades ago in 20s there was this problem of unimolecular decay that never got resolved. We do not know how to deal with it. Marcus, it took him basically only a few months and he solved this problem. And he published a few papers. One I have cited here in ‘52. He published a few more papers in ’53 and that is it.

After that Marcus changed his field and he was looking at electron transfer for practically a good portion of his life. But these few papers he published are authoritative works. They are the final word on this subject on unimolecular decay. And even today, you can open any physical chemistry journal, there will be at least one paper that calculates rate constant using this RRKM theory. So, let us study what Marcus had proposed.

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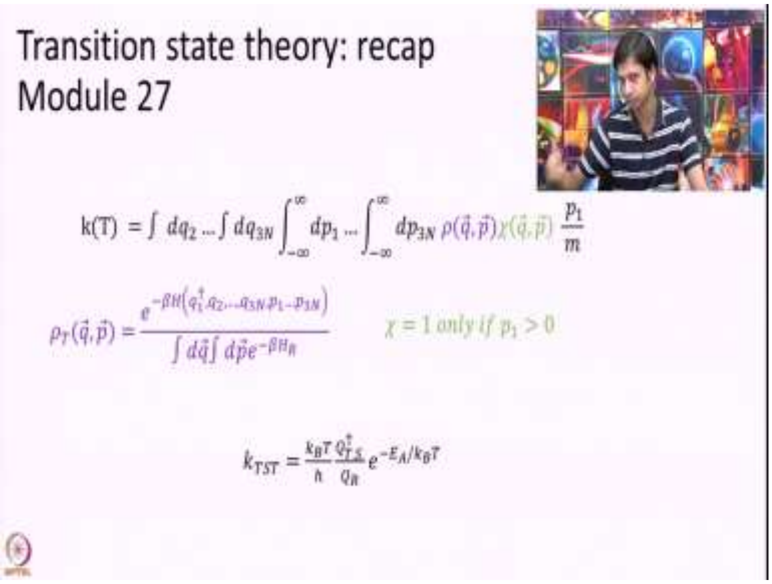

Transition state theory: recap
Module 27

$$k(T) = \int dq_2 \dots \int dq_{3N} \int_{-\infty}^{\infty} dp_1 \dots \int_{-\infty}^{\infty} dp_{3N}\, \rho(\vec{q},\vec{p})\chi(\vec{q},\vec{p})\, \frac{p_1}{m}$$

$$\rho_T(\vec{q},\vec{p}) = \frac{e^{-\beta H\left(q_1^{\ddagger}, q_2, \dots q_{3N}, p_1 \dots p_{3N}\right)}}{\int d\vec{q} \int d\vec{p} e^{-\beta H_R}}$$

$\chi = 1$ only if $p_1 > 0$

$$k_{TST} = \frac{k_B T}{h} \frac{Q_{T.S.}^{\ddagger}}{Q_R} e^{-E_A/k_B T}$$

So we will do a quick recap of what we covered in a long time ago in module 27. We wrote an expression to calculate rate constant at a given temperature earlier. We integrated over dividing surface over momenta. This is the density. This is a transmission factor that we have discussed for some time. And this is the finally the flux. Transition state theory assumes this rho to be the thermal density. This is the Boltzmann density.

And for chi, we put chi equal to 1, if p1 is greater than 0, otherwise chi equal to 0. We put a very simple expression for chi and we assumed that we can derive transition state theory. This is the expression we get out of it. We are going to essentially follow this approach now. So this was really the genius of Marcus. This, since I am presenting in this fashion now I have told you the answer. It might look trivial, but it is not.

When you have a flurry of ideas, what is the right way to think about it? What is the first equation to write? That is the question and that shows the geniusness. And Marcus said all right.

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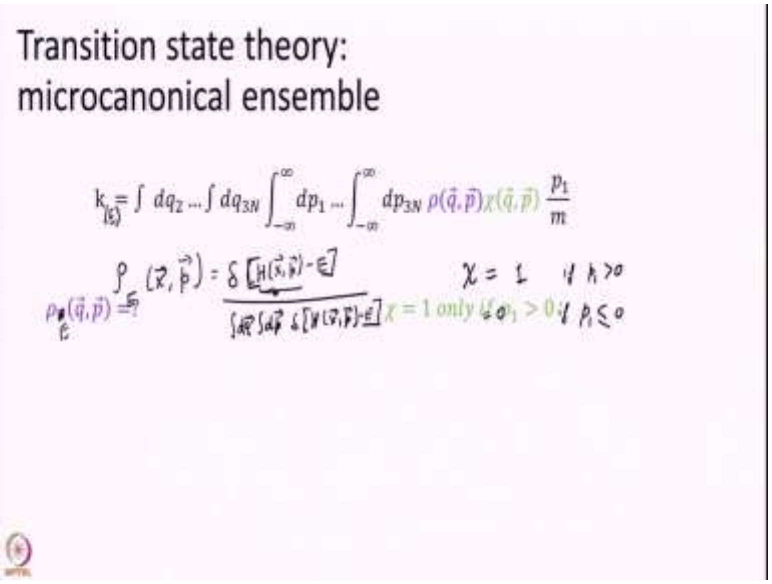


Transition state theory:
microcanonical ensemble

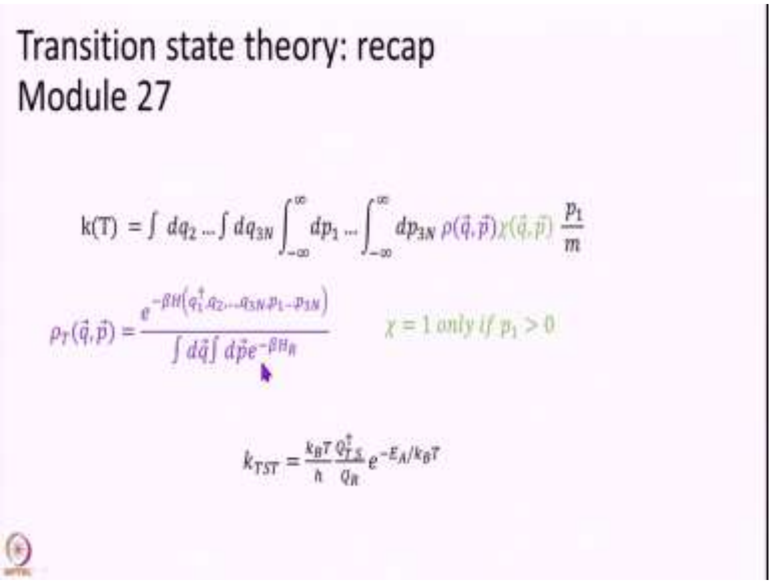
$$k_{(E)} = \int dq_2 \cdots \int dq_{3N} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \rho(\vec{q},\vec{p})\chi(\vec{q},\vec{p})\,\frac{p_1}{m}$$

$$\rho_E(\vec{x},\vec{p}) = \frac{\delta[\underbrace{H(\vec{x},\vec{p})}-E]}{\int d\vec{x}\int d\vec{p}\,\delta[H(\vec{x},\vec{p})-E]}$$

$\rho_E(\vec{q},\vec{p}) = ?$

$\chi = 1$ if $p_1 > 0$

$\chi = 1$ only if $p_1 > 0$; 0 if $p_1 \leq 0$



Transition state theory: recap
Module 27

$$k(T) = \int dq_2 \cdots \int dq_{3N} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \rho(\vec{q},\vec{p})\chi(\vec{q},\vec{p})\,\frac{p_1}{m}$$

$$\rho_T(\vec{q},\vec{p}) = \frac{e^{-\beta H(q_1^{\ddagger}, q_2, \ldots q_{3N}, p_1 \ldots p_{3N})}}{\int d\vec{q}\int d\vec{p}\, e^{-\beta H_R}}$$

$\chi = 1$ only if $p_1 > 0$

$$k_{TST} = \frac{k_B T}{h}\frac{Q_{TS}^{\ddagger}}{Q_R}e^{-E_A/k_B T}$$

So I will write the same expression, perhaps I have to just use different values of this rho and chi. So this rho earlier was for at a given temperature. So, now I must use a rho at a given energy. And what he said is this is then equal to a delta function minus E. H of x comma p is the Hamiltonian, which represents the energy.

So I am saying that rho at that given energy this Hamiltonian must be equal to that energy. And chi we will start with the same as transition state theory. Transition state theory after all is very successful. So chi is equal to 1 if p1 is greater than 0, equal to 0, if p1 less than 0. So that is going to be our starting point. This is the expression we want to simplify.

So we have changed that density from a temperature density to a energy density. I have made a mistake. So let me correct my mistake. This should be normalized. Remember that even in the previous slide, our rho T was normalized. We had this full integral there. So we must write a similar integral as well here.

That integral will now be dq dp delta of H of x comma p minus E. Because delta is essentially constraining those x and p points for which the Hamiltonian takes a value E, so the energy of the system is equal to whatever I want it to be. So just a, sorry, I had put in this nice animation that I had forgotten, but I have written what this rho is supposed to be. This is supposed to be E.

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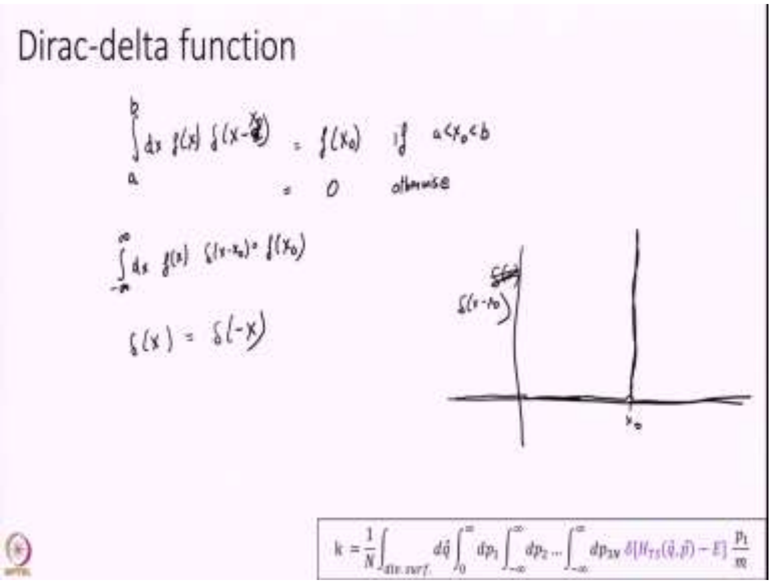

Dirac-delta function

$$\int_a^b dx\, f(x)\,\delta(x-x_0) = f(x_0) \quad \text{if} \quad a<x_0<b$$

$$= 0 \quad \text{otherwise}$$

$$\int_{-\infty}^{\infty} dx\, f(x)\,\delta(x-x_0) = f(x_0)$$

$$\delta(x) = \delta(-x)$$

$$k = \frac{1}{N}\int_{\text{div. surf.}} d\vec{q} \int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \delta[H_{TS}(\vec{q},\vec{p}) - E]\, \frac{p_1}{m}$$

Let me give you a little bit of properties of this Dirac-delta function. This function here is called the Dirac-delta function. So this can get into very deep mathematical details, but I am not going to go into that. We are going to study only a few important properties of Dirac-delta function. First is what if I integrate Dirac-delta function multiplied by some other function.

And let us say, I am sorry, let me write this as x naught and integral from a to b, this is equal to f of x naught if x naught lies between a and b equal to 0, otherwise. So the Dirac-delta function can be thought of as 0 everywhere. And, sorry, let me write delta of x minus x naught. And it takes a very, very large value at x naught. So it is zero everywhere, except at this x naught where it is growing up.

So one other property I can write is if I integrate over all space, then I get f of x naught, because, well, x naught has to lie between minus infinity to plus infinity. And one final property that we will use today is that Dirac-delta function is Eigen, which would be obvious. If I invert it, I still get the same function. So Dirac-delta function is Eigen.

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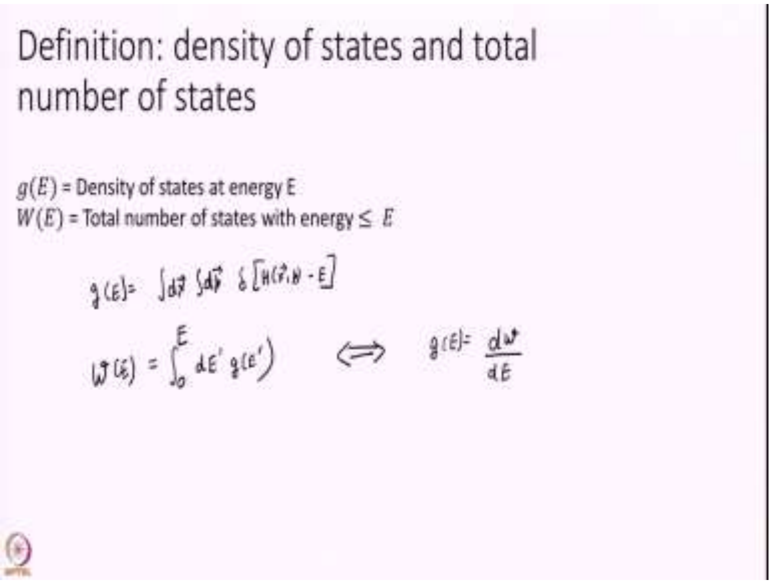


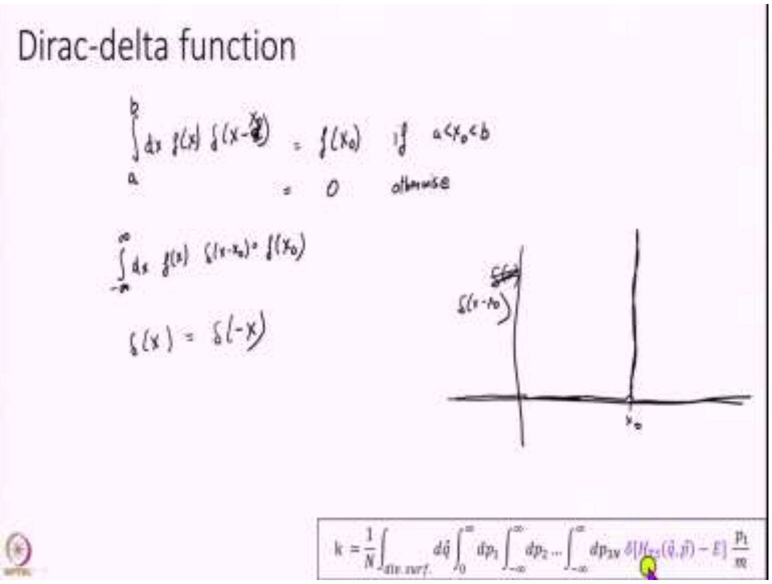
Definition: density of states and total number of states

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

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

$$g(E) = \int d\vec{q} \int d\vec{p}\ \delta[H(\vec{q},\vec{p}) - E]$$

$$W(E) = \int_0^E dE'\, g(E') \iff g(E) = \frac{dW}{dE}$$



Dirac-delta function

$$\int_a^b dx\, f(x)\, \delta(x - x_0) = f(x_0) \quad \text{if } a < x_0 < b$$
$$= 0 \quad \text{otherwise}$$

$$\int_{-\infty}^{\infty} dx\, f(x)\, \delta(x - x_0) = f(x_0)$$

$$\delta(x) = \delta(-x)$$

$$k = \frac{1}{N}\int_{div.surf.} d\vec{q} \int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \delta[H(\vec{q},\vec{p}) - E]\, \frac{p_1}{m}$$

So before we move forward, actually, this expression here is much harder to evaluate than what we had for constant temperature believe it or not, because of this Dirac-delta function. It is not easy to deal with this, because this is H couples all these q and p. So it is not easy for me to simplify the integral over dp1. Earlier, we had e to the power of minus h that I could separate out the p1 term and integrate it out separately.

So it is a slightly more complex. So I will have to introduce a little bit more language, a few more terms added to my language, so that I can simplify this expression a little bit more. So I define two quantities for me now. One is called g of E, which represents the density of states at energy E and W, which represents the total number of states with energy less than E.

So if I am at a given energy E, how many, what is the density of states, how many states per unit energy are present at that energy that is g of E. And W of E is the total number of states that will be there between 0 to that energy E. So what I can do is start writing expressions for these, g of E is then given by an integral over dx, integral over dp, and delta of H of x comma p minus E.

So I integrate over all space, all possible configurations of x and p and I find for what values of x and p is my Hamiltonian equal to the energy so that will give me the density, that will tell me how many states per unit energy are there. That is what delta is doing. So that you can think of as the definition of g.

If this is the density of states and I want to find the total number of states between 0 and E, well, that task is simple. I must integrate g between 0 and E. g is telling me the density at that given energy. So if I want, go from 0 to E and integrate it out, I will get the total number of states, so I write this. And as a consequence, I can also write, g of E equal to dW over dE. So if I differentiate it, dW over dE, you see that I will immediately g of E.

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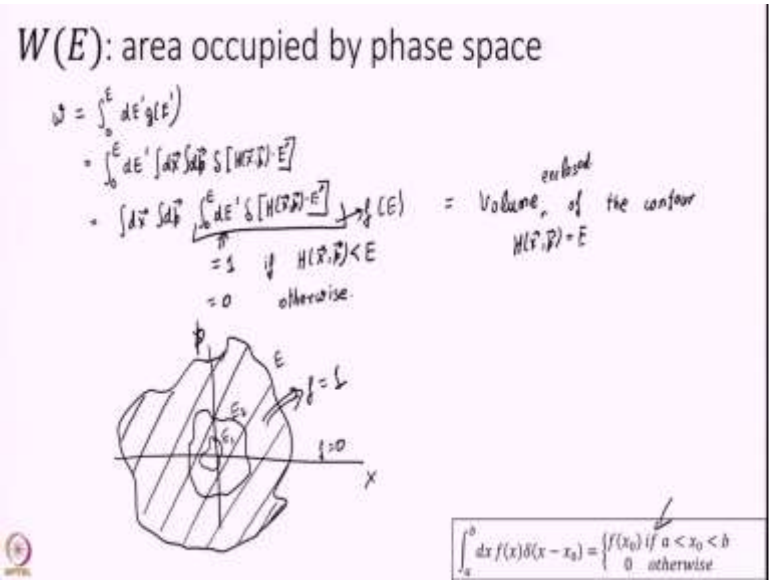

$W(E)$: area occupied by phase space

$$W = \int_0^E dE' g(E')$$

$$= \int_0^E dE' \int d\vec{x} \int d\vec{p}\, \delta[H(\vec{x},\vec{p}) - E']$$

$$= \int d\vec{x} \int d\vec{p}\, \underbrace{\int_0^E dE' \delta[H(\vec{x},\vec{p}) - E']}_{} \rightarrow f(E) \quad = \text{Volume}\overset{\text{enclosed}}{} \text{ of the contour } H(\vec{x},\vec{p}) = E$$

$= 1$ if $H(\vec{x},\vec{p}) < E$

$= 0$ otherwise

$$\int_a^b dx\, f(x)\delta(x - x_0) = \begin{cases} f(x_0) \text{ if } a < x_0 < b \\ 0 \quad \text{otherwise} \end{cases}$$

So let us look at this expression of W little bit, dE prime g of E prime. Well, let us put in the expression of g. It is dx dp delta of H of x comma p minus E. Let me switch around the integrals a little bit. Now, look at this function, what do we get? This is equal to 1 if H of x comma p, sorry, this would be E prime, is less than E equal to 0, otherwise. Agreed, that is what this thing says. So if H is less than E, then I get 1, otherwise I get 0.

Well, what does that mean? Imagine a graph of x comma p. Since I have a 2D screen, I can only make 2D plots. I have imagine some contour lines at given energy. This is let us say energy E1 contour line, E2 energy contour line. E will have its own contour line. I am sorry, it is not E1, it is E. So this function that is there is 1 if I am inside this contour. F is one here, where I am calling this whole thing as f, agreed. Outside I have f frequency 0.

So all I am doing is integrating over all x and p which is completely covered by this contour line. So this is nothing but the volume or the area whatever word you want to use of the contour H equal E. So I look at this contour for H equal to E in a higher dimension you will get this high dimensional surface and a look at the volume enclosed. So let me just say volume enclosed. So that is the physical interpretation of W. W is the area or volume occupied by face space and closed by this contour line.

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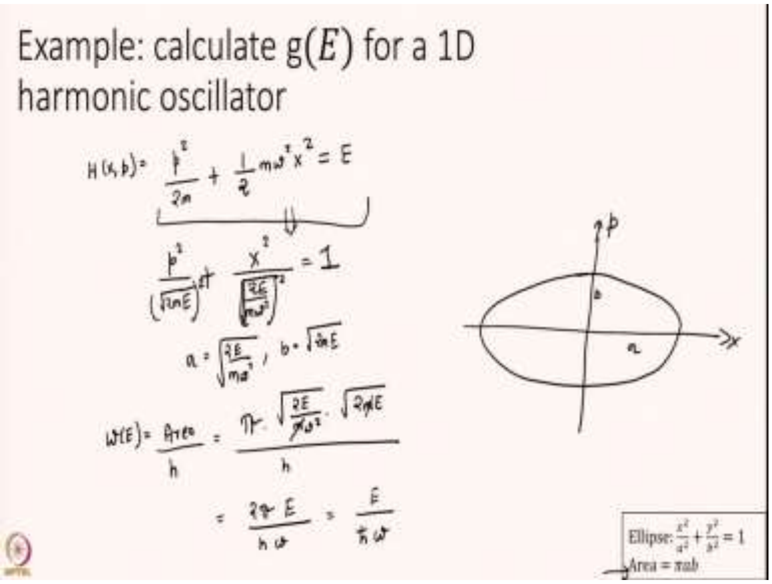


Example: calculate g(E) for a 1D harmonic oscillator

$$H(x,p) = \underbrace{\frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 = E}_{\Downarrow}$$

$$\frac{p^2}{\left(\sqrt{2mE}\right)^2} + \frac{x^2}{\left(\sqrt{\frac{2E}{m\omega^2}}\right)^2} = 1$$

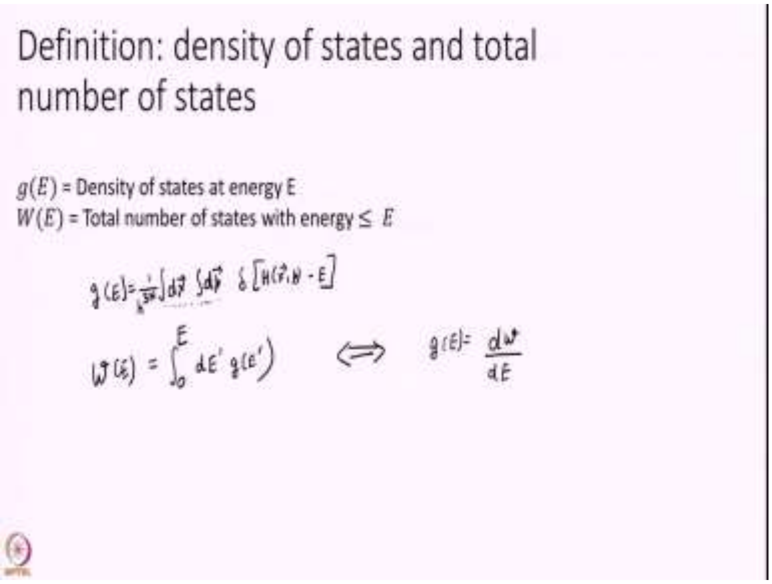
$$a = \sqrt{\frac{2E}{m\omega^2}}, \quad b = \sqrt{2mE}$$

$$W(E) = \frac{\text{Area}}{h} = \frac{\pi \cdot \sqrt{\frac{2E}{\cancel{m}\omega^2}} \cdot \sqrt{2\cancel{m}E}}{h}$$

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

Ellipse: $\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$

Area = πab



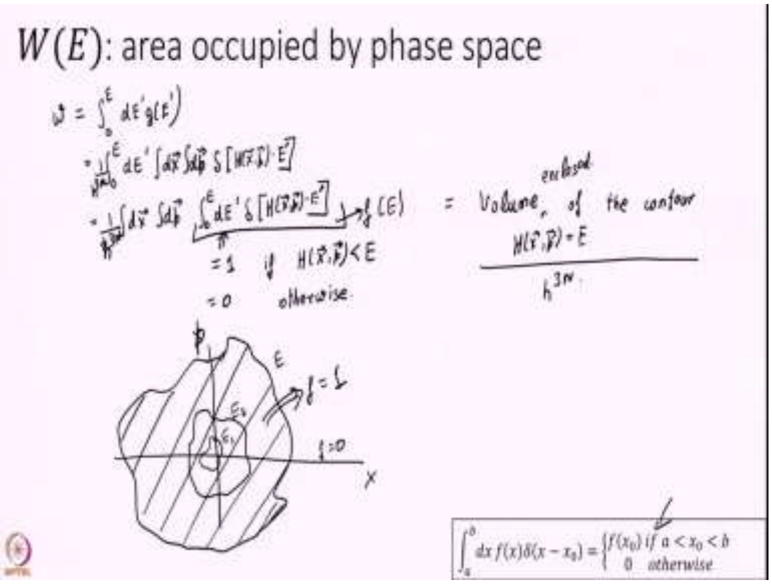
Definition: density of states and total number of states

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

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

$$g(E) = \frac{1}{h^{3N}} \int d\vec{r} \int d\vec{p} \; \delta\left[H(\vec{r},\vec{p}) - E\right]$$

$$W(E) = \int_0^E dE' \, g(E') \quad \Longleftrightarrow \quad g(E) = \frac{dW}{dE}$$



$W(E)$: area occupied by phase space

$$W = \int_0^E dE' g(E')$$

$$= \frac{1}{h^{3N}} \int_0^E dE' \int d\vec{x} \int d\vec{p}\, \delta[H(\vec{x},\vec{p}) - E']$$

$$= \frac{1}{h^{3N}} \int d\vec{x} \int d\vec{p}\, \underbrace{\int_0^E dE' \delta[H(\vec{x},\vec{p}) - E']}_{f(E)} = \frac{\text{Volume}\overset{\text{enclosed}}{} \text{ of the contour } H(\vec{x},\vec{p}) = E}{h^{3N}}$$

$= 1$ if $H(\vec{x},\vec{p}) < E$

$= 0$ otherwise

$$\int_a^b dx\, f(x)\delta(x - x_0) = \begin{cases} f(x_0) & \text{if } a < x_0 < b \\ 0 & \text{otherwise} \end{cases}$$

So we will do one example. We will calculate g and W for a 1D harmonic oscillator. So my Hamiltonian, I have only 1D. Actually, I have made a mistake. Let me correct my mistake. I had forgotten my factors of H. Remember, this is an integral of x and p and an integral of x and p have dimensions. If you remember our discussion on partition functions, I have h to the power 3N. That is what I had forgotten to write.

So let me correct that. So this becomes a true density. I do not have any factors of h floating around. So we divide by h to the power of 3N, just like what we did in partition functions. I apologize, I had forgotten that. Let me correct all of these things here as well. I will have this divided by h to the power of 3N here as well, h to the power of 3N here as well.

So volume enclosed divided by h to the power of 3N, so volume in units of h to the power of 3N. So that minor correction. So the Hamiltonian for a harmonic oscillator is this. So if I have to find W, I have to find the area enclosed by the contour line. So let us say this is equal to E. So, I have to draw the contour line for H is equal to E and find the area enclosed by this contour line.

So you see this expression, this is actually an equation of an ellipse. So I will rewrite this slightly in this fashion. You notice, let me get my energy also in here, so let me correct that. So let me put my energy also in the denominator. So I have done nothing. I have just reorganized it, my equation here and make it look like an equation of an ellipse.

So an ellipse essentially looks like this, where this is a and this is b. So, for me a is equal to 2E, root 2E over m omega square and b is equal to root 2mE. So I know the formula for area of an ellipse. So the area W of E will be nothing but area divided by h, I have only one dimension here, so h to the power of 1 is equal to pi a into b divided by h.

Happily mass cancel. I get root 2E into root 2E which is 2 pi E divided by h omega. Well, I will get E over h bar omega, where h bar of course is h over 2 pi. You start seeing some good expressions, do not you? H bar omega is somehow related to harmonic oscillators quantum mechanically.

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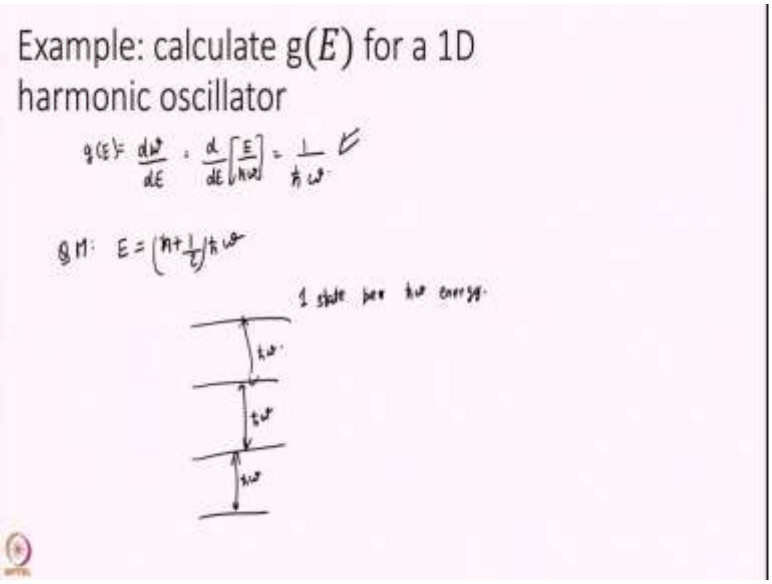

Example: calculate g(E) for a 1D harmonic oscillator

$$g(E) = \frac{dW}{dE} = \frac{d}{dE}\left[\frac{E}{\hbar\omega}\right] = \frac{1}{\hbar\omega}$$

QM: $E = \left(n + \frac{1}{2}\right)\hbar\omega$

1 state per $\hbar\omega$ energy.

So let us move forward. Let us see what we get. Now, g of E is nothing but dw over dE. So this is equal to d over dE of E over h bar omega which is equal to 1 over h bar omega. So the density of states is 1 over h bar omega. Just think of quantum mechanics, quantum mechanically the energy is given as n plus half h bar omega.

We get equal spacing like this quantum mechanically. So what it means is, even quantum mechanically, what is the density of states? I have one state per h bar omega energy. That is what this really means. If I look at 1 quanta of h bar omega, I will have one state in it, which is also what I get classical. So that was a little aside.

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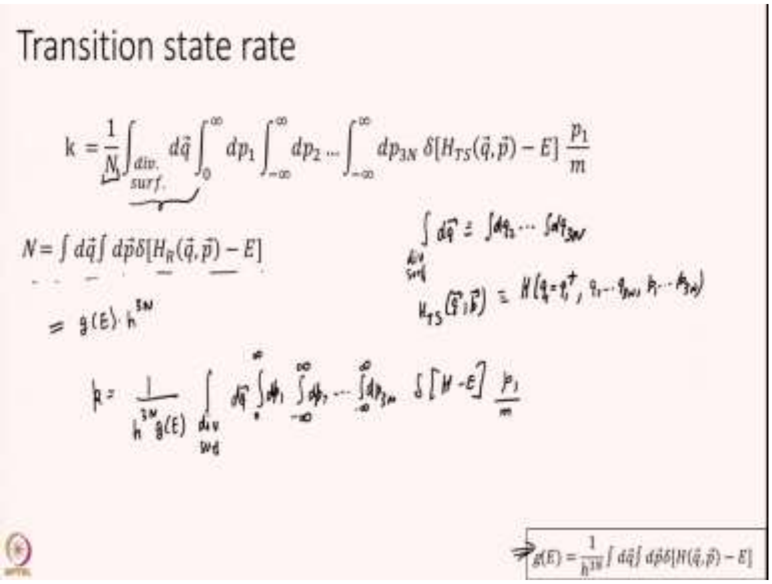

Transition state rate

$$k = \underbrace{\frac{1}{N}\int_{\substack{div.\\surf.}}}\, d\vec{q}\int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \ldots \int_{-\infty}^{\infty} dp_{3N}\, \delta[H_{TS}(\vec{q},\vec{p}) - E]\, \frac{p_1}{m}$$

$$N = \int d\vec{q}\int d\vec{p}\,\delta[H_R(\vec{q},\vec{p}) - E]$$

$$= g(E)\cdot h^{3N}$$

$$\int_{\substack{div\\surf}} d\vec{q} = \int dq_2 \cdots \int dq_{3N}$$

$$H_{TS}(\vec{q},\vec{p}) = H(q_1 = q_1^{\dagger}, q_2 \cdots q_{3N}, p_1 \cdots p_{3N})$$

$$k = \frac{1}{h^{3N} g(E)} \int_{\substack{div\\surf}} d\vec{q} \int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \delta[H - E]\, \frac{p_1}{m}$$

$$\boxed{g(E) = \frac{1}{h^{3N}}\int d\vec{q}\int d\vec{p}\,\delta[H(\vec{q},\vec{p}) - E]}$$

So now let me finish the proof of transition state theory at constant energy. Now that we understand is g of an E and a little bit of Dirac-delta functions. So we start with the expression that we wrote earlier. Let me just clarify a few things from earlier. Integral over dividing surface dq is nothing but it is a shorthand notation for dq2 to dq3N, HTS of q comma p is nothing but h of q1 equal to q1 dagger and all other variables are varying as they wish.

So this is just shorthand notation just to keep my life simple, nothing more. So first let us look at what we had in the denominator. We had this. Now we have defined this g as a density. So we quickly noticed this n is nothing but g of E into h to the power of 3N. So my k becomes 1 over h to the power of 3N g of E into all this integral dq, dp1 dp2 to dp3N and delta of H minus E and p1 over E.

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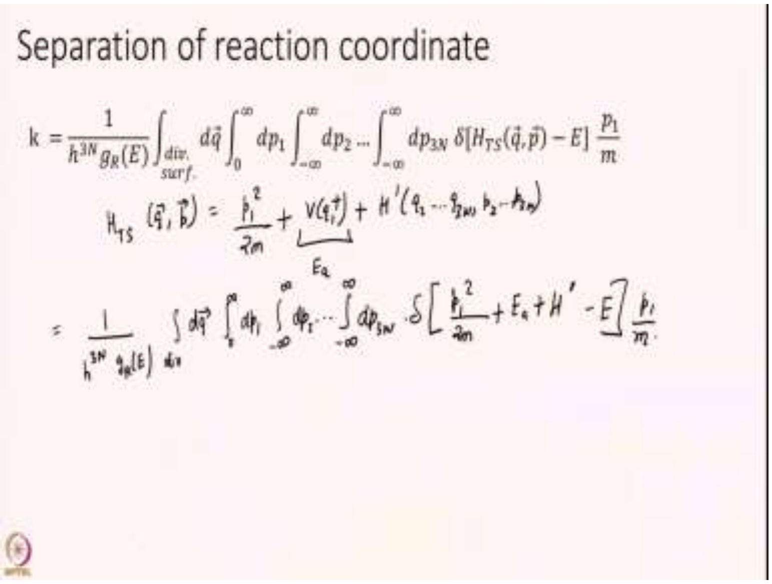
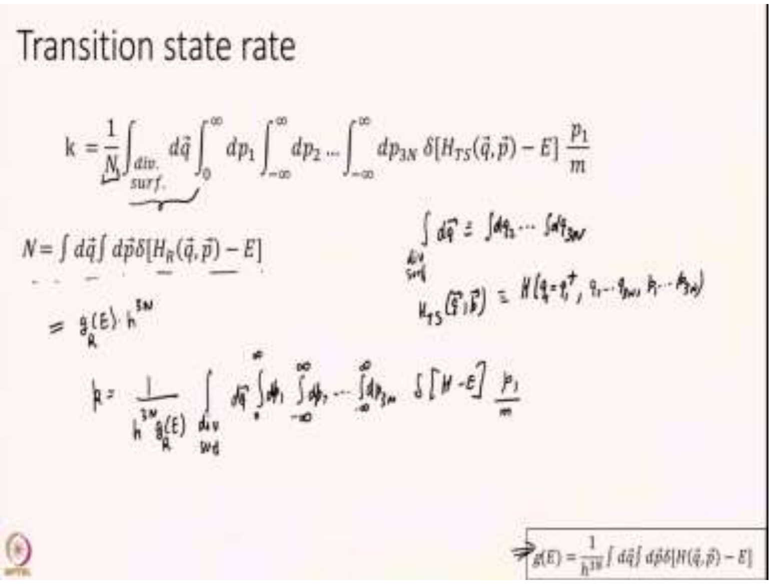


Separation of reaction coordinate

$$k = \frac{1}{h^{3N} g_R(E)} \int_{\substack{div.\\ surf.}} d\vec{q} \int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \delta[H_{TS}(\vec{q},\vec{p}) - E]\, \frac{p_1}{m}$$

$$H_{TS}(\vec{q},\vec{p}) = \frac{p_1^2}{2m} + \underbrace{V(q_1^{\dagger})}_{E_a} + H'(q_2 \cdots q_{3N}, p_2 \cdots p_{3N})$$

$$= \frac{1}{h^{3N} g_R(E)} \int_{div} d\vec{q} \int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \delta\left[\frac{p_1^2}{2m} + E_a + H' - E\right] \frac{p_1}{m}.$$



Transition state rate

$$k = \frac{1}{\underbrace{N}} \underbrace{\int_{\substack{div.\\ surf.}}} d\vec{q} \int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \delta[H_{TS}(\vec{q},\vec{p}) - E]\, \frac{p_1}{m}$$

$$N = \int d\vec{q} \int d\vec{p}\, \delta[H_R(\vec{q},\vec{p}) - E]$$

$$= g_R(E) \cdot h^{3N}$$

$$\int_{\substack{div\\ surf}} d\vec{q} = \int dq_2 \cdots \int dq_{3N}$$

$$H_{TS}(\vec{q},\vec{p}) = H(q_1 = q_1^{\dagger}, q_2 \cdots q_{3N}, p_1 \cdots p_{3N})$$

$$k = \frac{1}{h^{3N} g_R(E)} \int_{\substack{div\\ surf}} d\vec{q} \int_0^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \cdots \int_{-\infty}^{\infty} dp_{3N}\, \delta[H - E]\, \frac{p_1}{m}$$

$$\rightarrow g(E) = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p}\, \delta[H(\vec{q},\vec{p}) - E]$$

What do we do next? We are actually going to use the same set of approximations as we have used for deriving the transition state theory at constant temperature. So the next assumption I am going to make, sorry, if HTS is separable, so this is equal to I will say is equal to p1 square over 2m plus V of q1 dagger plus H prime of everything else. So, again, that is also what we assumed when we were doing transition state theory that is the same thing we do now.

This is nothing but Ea. So what we get, I get these constants out gR of E. One thing I had forgotten to mention, this n that I am calculating is only over the reactant Hamiltonian, just like we did in transition state theory. So I write for that only gR. Just to signify that I am integrating only over the reactant side and not on the product side. I have still this giant integral that takes me 100 minutes to write, dp2 integral of dp3N delta, now H, I will expand, H prime as a function of all this minus E. Have we, are we really achieving anything? Let us see.

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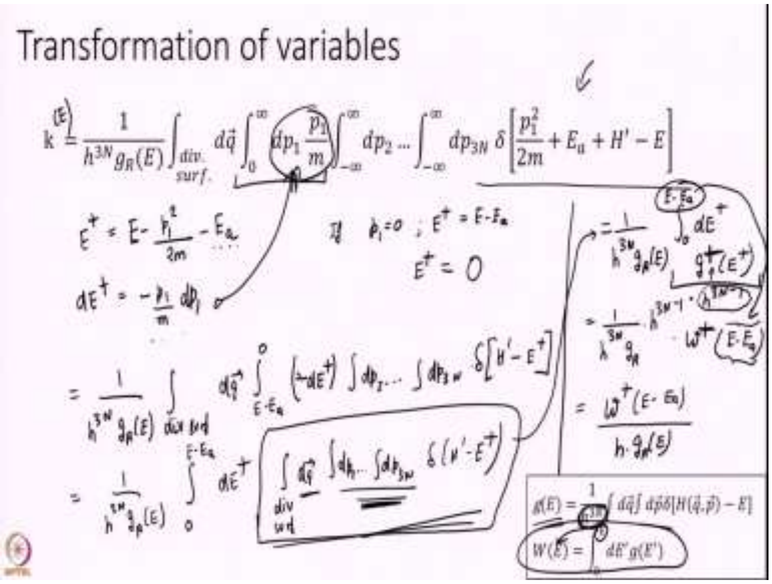

Transformation of variables

$$k(E) = \frac{1}{h^{3N} g_R(E)} \int_{\substack{div.\\surf.}} d\vec{q} \int_0^{\infty} dp_1 \frac{p_1}{m} \int_{-\infty}^{\infty} dp_2 \dots \int_{-\infty}^{\infty} dp_{3N}\, \delta\left[\frac{p_1^2}{2m} + E_a + H' - E\right]$$

$$E^{+} = E - \frac{p_1^2}{2m} - E_a$$

$$dE^{+} = -\frac{p_1}{m} dp_1$$

If $p_1 = 0$; $E^{+} = E - E_a$

$$E^{+} = 0$$

$$= \frac{1}{h^{3N} g_R(E)} \int_{\substack{div\\surf}} d\vec{q} \int_{E-E_a}^{0} (-dE^{+}) \int dp_2 \dots \int dp_{3N}\, \delta\left[H' - E^{+}\right]$$

$$= \frac{1}{h^{3N} g_R(E)} \int_0^{E-E_a} dE^{+} \boxed{\int_{\substack{div\\surf}} d\vec{q} \int dp_2 \dots \int dp_{3N}\, \delta(H' - E^{+})}$$

$$= \frac{1}{h^{3N} g_R(E)} \int_0^{E-E_a} dE^{+}\, g_{+}(E^{+})$$

$$= \frac{1}{h^{3N} g_R} \cdot h^{3N-1} \cdot W^{+}(E - E_a)$$

$$= \frac{W^{+}(E - E_a)}{h \cdot g_R(E)}$$

$$g(E) = \frac{1}{h^{3N}} \int d\vec{q} \int d\vec{p}\, \delta[H(\vec{q}, \vec{p}) - E]$$

$$W(E) = \int_0^{E} dE' g(E')$$

So we get this big expression. Now we will do a little bit more mathematical jugglery. Just a little bit of hocus pocus. We will transform our variables now. I am going to define an E dagger as E minus p1 square over 2m minus Ea, hocus pocus, abracadabra. So dE dagger is equal to, E is a constant, remember I am calculating everything at that energy E, minus p1 over m dp1, Ea is also a constant, so da dagger equal to this.

So this is the one I am looking at. You see p1 over m dp1 here. I get the same thing here. That is why I did that transformation. Now, if p1 is equal to 0, E dagger equal to E minus Ea. I am trying to find my limits. What is the maximum value E dagger can take? Note that I have a delta function sitting here. So I claim the maximum value of E dagger is the, the minimum value of E dagger is only 0. So imagine I have my reaction coordinate.

I have E here. This is Ea. This here is let us say p1 square over 2m. This is then E dagger. So, E dagger is E, total energy E, minus Ea minus p1 square over 2m. So, E dagger cannot be less than 0. Why, because I have this Dirac-delta function sitting here. H prime is positive. So, if E prime is less than 0, this Dirac-delta function will immediately become 0. So, I mean any negative 0. So what I get here is then 1 over h to the power of 3N gR of E dividing surface dq.

So this integral becomes E minus Ea to 0, I notice this thing, is minus dE dagger integral of dp2 to dp3N that I am not touching into delta of H prime minus E dagger. I take this integral, I play around with it a little bit, I take this minus and invert the limits, Integral over dividing surface dq integral from dp2 to dp3N delta of H prime minus E dagger. So let us just look at this expression. What is this equal to? You note that, let me erase a little bit stuff here.

I am out of space. So I am just erasing. So, I noticed that this integral is nothing but g of E. So this is then equal to 1 over h to the power of 3N gR of E integral from 0 to E minus Ea, de dagger g of E dagger. And I have put a little dagger here. Sorry, this is supposed to be g E prime. It was, something is not, I am sorry, I am getting confused myself. Happens with me. I will correct it all of it. Now I am perfect. Now this is right.

And I have a little dagger here to denote that this integral does not involve integral of q1 and p1, this is an integral from q2 to q3N and p2 to p3N. Look at this. It does not involve integral of q1 and p1. That is why I have put a dagger here to remind you of that. And I look at this integral and I see this. So this is nothing but h to the power of 3N. I apologize again, this I should multiply by h to the power of 3N minus 1, because I have this factor here.

So I have this integral and this integral into h to the power of 3N minus 1 will give me g. So I get h to the power of 3N minus 1 into W again dagger of E minus Ea. So that is my integration limit here. So at the end, I get W dagger of E minus Ea divided by h into gR. This E minus Ea, because of this limit. So whatever is the limit here comes here. That is why I put E minus Ea. W dagger again denote that the integration is only from q2 to q3N and p2 to p3N. And this factor of h dN minus 1 emerged, because I had a division by h to the power of 3N here.

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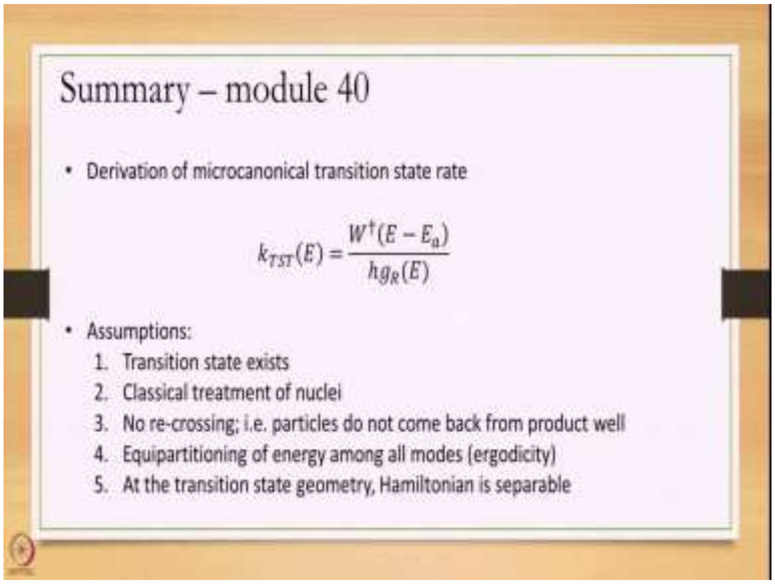

Summary – module 40

- Derivation of microcanonical transition state rate

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

- Assumptions:
  1. Transition state exists
  2. Classical treatment of nuclei
  3. No re-crossing; i.e. particles do not come back from product well
  4. Equipartitioning of energy among all modes (ergodicity)
  5. At the transition state geometry, Hamiltonian is separable

So this is really the final expression. For the microcanonical transition state theory now, this expression looks like W dagger of E minus Ea divided by h into gR of E. And the list of assumptions is very similar to what we had made earlier, transition state exists, nuclei have been treated classically, we are integrating over q and p, there is no re-crossing, so the chi that we choose is the same as before.

What we, when we write this delta function, what it assumes is that all energy states are equally possible. So, I am not discriminating between two points in face space having a same energy. They are equally possible. That is called Ergodicity. It has profound consequences to thermodynamics and statistical mechanics. So I have listed it here. And final assumption is that Hamiltonian is separable at transition state geometry. So following the same set of assumptions, we derive the expression for the transition state theory at constant energy. Thank you.