Chemical Kinetics and Transition State Theory
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Lecture 36
Transmission Coefficient and Molecular Dynamics

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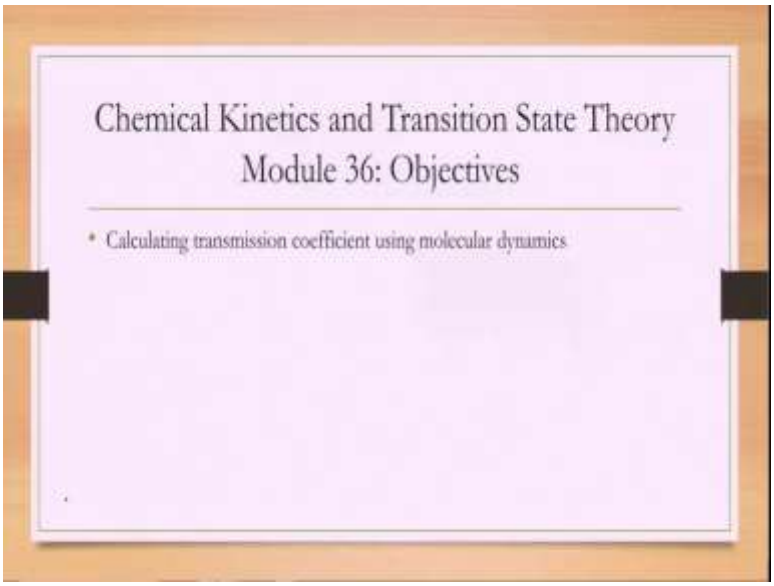

Hello, and welcome to module 36 of Chemical Kinetics and Transition State Theory. This is a continuation of the last module. In the last module what we looked at is a calculation of transition state theory rate constant using molecular dynamics simulation. How we can apply molecular dynamics tricks to do a thermodynamic integration and calculate rate constant. Today, we will extend that a little bit and use the powers of MD to actually improve upon some of the assumptions of transition state theory as well.

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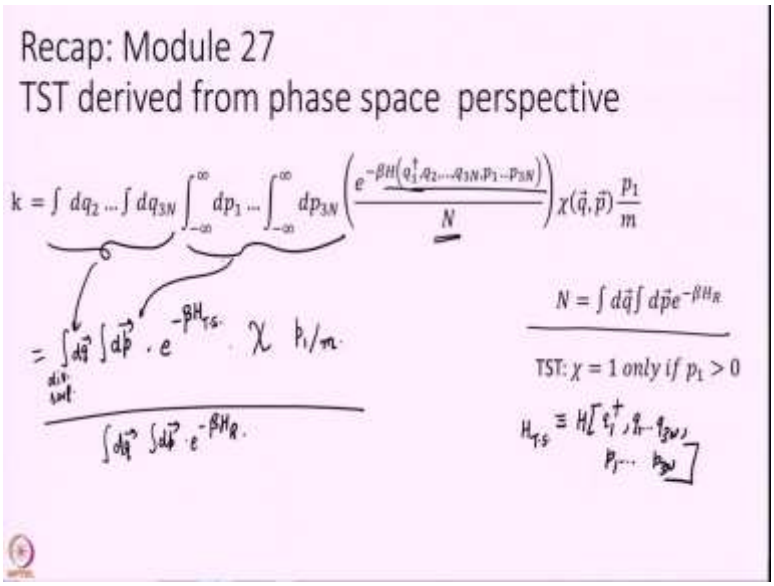

So I will go back to a very old formula we wrote in module number 27. You can go back to that module and have a look. What we had really showed that the rate constant under the assumptions of a classical nuclei and Boltzmann distribution, thermal statistics being true, can be written as this big integral. This integral I will just simplify, just shorthand notation for the purpose of this module, I will write this integral from dq to dq3N as dq over dividing surface.

This notation we have used before as well in the course just to simplify our notation. This integral I will write as dp. And there is no restriction here. It is over all momentum, over all possible values of momentum. This I will write as e to the power of minus beta H transition state. Again, that is a notation we have used before.

H transition state really mean this H q1 dagger comma q2 to q3N comma p1 to p3N. So this H is what I call HTS. Again, the whole purpose is just so that I can write faster. If I write all of this all the time then we would not get anywhere. Multiplied by chi, again, I am dropping function of q comma p but that is always present, just shorthand notation.

And note that I am dividing by N. N is given here. And so this is nothing but QR. Instead of QR, let me write this integral clearly, because this might get confusing since there is no H there. Integral dq integral dp e to the power of minus beta HR, where HR represents the Hamiltonian of only the reactants as we have been using it so far.

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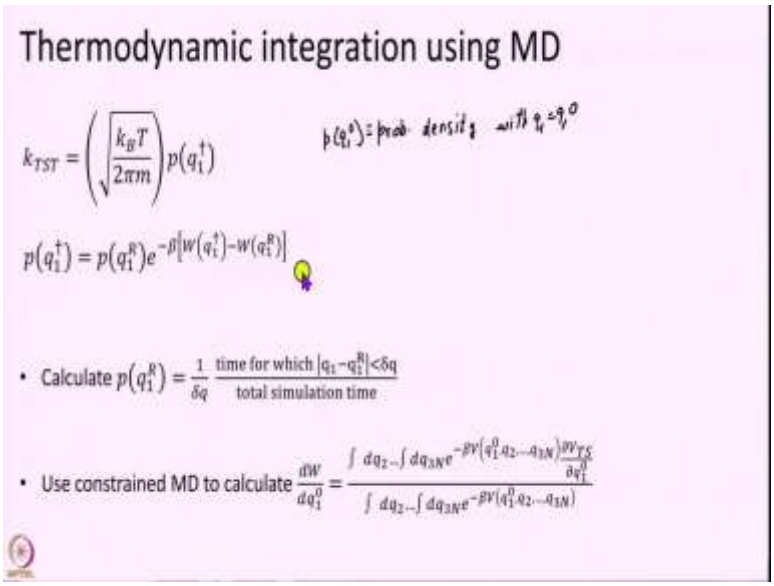

So we used this formula in the last module to derive a slightly different formula for kTST which is amenable to molecular dynamics. So what we had shown is that we can play around with this formula a little bit and right kTST as this formula root kT over 2 pi m, which is a thermal velocity into this function p and p is nothing but the probability distribution of being at q1. So what we had discussed in the last module was that p of q1 naught is the probability density with q1 equal to q1 naught.

So if I set this one coordinate q1 as q1 naught and do a thermal integration over all other variables q2 to q3N, p1 to p3N what will be the probability I will get that is what we defined as p of q1. And so this is p at q1 dagger, where q1 dagger represents the transition state value. And then we had workout scheme to calculate this pq1 dagger. We figured out that p of q1 dagger can be written as p of q1R into this Boltzmann distribution, where W is a kind of a free energy. And then we figured out a scheme to calculate p of q1R and this difference as well from last model.

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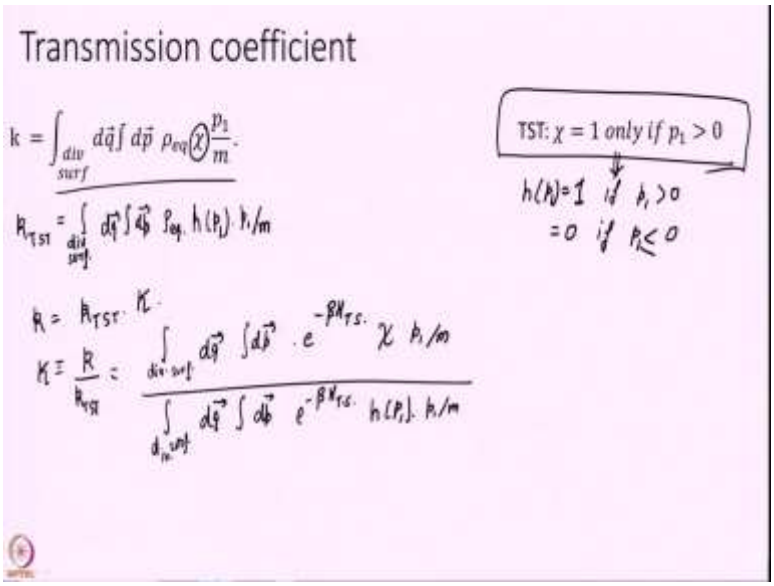

So, today, let us do something more. So this is our actual formula for k, this big integral. Now, kTST is nothing but integral over this dividing surface dq, integral over dp, rho equilibrium into chi is replaced by this. So we write this as a different form which is H of p1. I will define this in just a moment. H of p1 equal to 1, if even greater than 0, this is equal to 0, if p1 less than 0.

So really it is a mathematical way of writing this line. So if I write this H of p1, this integral will automatically be 0 if p1 is less than 0. And my integral over p1 by default will become integral from 0 to infinite, which is what we have been doing. So it is just an easier way of writing it. I am just being a bit lazy, that is all. So instead of writing dp1 separately with a 0 to infinite I have written it in this simple functional form. If you want, you can go ahead and write it in that particular form of 0 to infinity dp1 and dp2 to dpn. What we have done in the last modules, exactly the same thing.

So my point is this kappa, this assumption that we have made, today we are going to lift this assumption and we are going to use molecular dynamics to calculate this kappa more accurately than what transition state theory does. So, let us start. I will simplify my life by defining something like this, where kappa is nothing but it is a definition. So, something stupid. So if I divide these two dq dp rho equilibrium I will just write as e to the power of minus beta transition state chi p1 over m divided by dividing surface dq dp e to the power of minus beta H transition state H of p1 into p1 over m.

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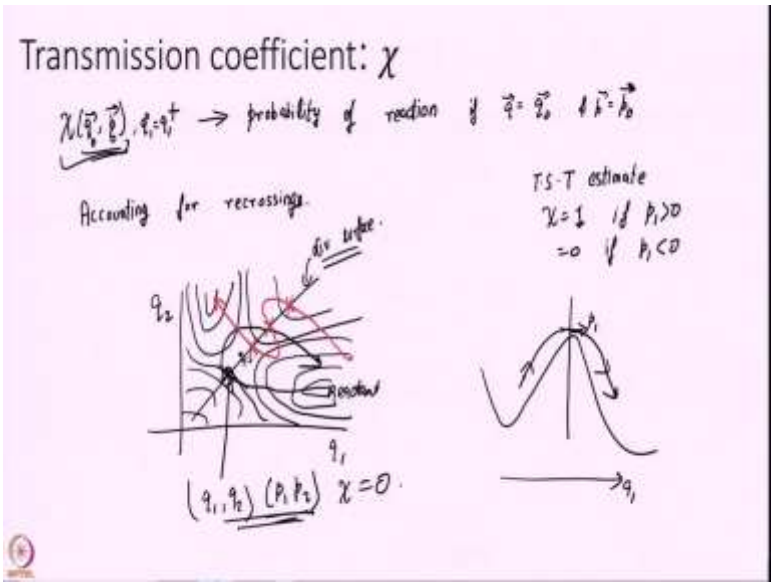

This is fine. But let us think of how we can calculate this expression. Have we made any real improvement? I can keep on defining variables, but what about it. How do I calculate this variable? So, let us give a little bit of moment in thinking what is chi really means. Chi is the probability of reaction if I am at that given q comma p. So let us think about this coefficient a little bit more, this chi with q1 equal to q1 dagger.

This chi tells me probability of reaction if q equal to, let me just say, q naught and p naught equal to q naught and p equal to p naught. So if my p and q are at this value here, I start with this value on the transition state. Remember that transition state is simply specified by q1 equal to q1 dagger, but you have all these other variables with you as well which are q2 to q3, q3N and p2 to p1 to p3N they can be taking all kinds of values.

And depending what their value is, your chi might not be 1. So, chi is a complex dynamical variable which depends on q2 to q3N comma p1 to p3N. It is a function of it. You give me these values and I should be able to figure out what this kappa is for you. So, how do we think about this? This effectively is accounting for re-crossings. So let us think about this statement a little bit. What I mean by that? If p1 is greater than 0 and I say chi is equal to 1 that is my transition state estimate. So let us just come back to it.

So transition state theory makes a very simplifying assumption. It says look only for the value of p1. Forget all about your q2 to q3N and p1 to p3N, p2 to p3N, just look at p1, positive 1,

negative 0. What is the underlying idea behind this assumption? So let us say I have this potential barrier, this is q1, it says that if I am moving in this forward direction, I am reactive.

That is if I would have went back, I would have ended in reactant. If I move forward, I will end in product. So the reality is that we have a multi-dimensional energy surface now. So our energy surface, let us say, let me just draw two of them, the kind of energy surfaces that we drew in the last module. So let us draw something symmetric, something simple. This is let us say my transition state.

Now a trajectory let us say comes from here. This is let us say my reactant. Well, it has a complex energy surface it sees. It might turn around like this and come back. So now when I am looking at, let us say, this point, q1 comma q2 with the momentum that this point, that trajectory reaches this point with. So this is my dividing surface. This is the surface I am integrating over, where I am setting the value of q1 too.

Now, for this particular value of p1 comma p2 comma q2, my chi is basically 0. It is not reactive. I can have another case as well. So let us say I start here. I come here, I come here and I come here. This is a bit more confusing. So I have three points here that I am hitting, two with positive momentum and it is reactive. But the problem is that I am counting this one trajectory three times when I do transition state theory.

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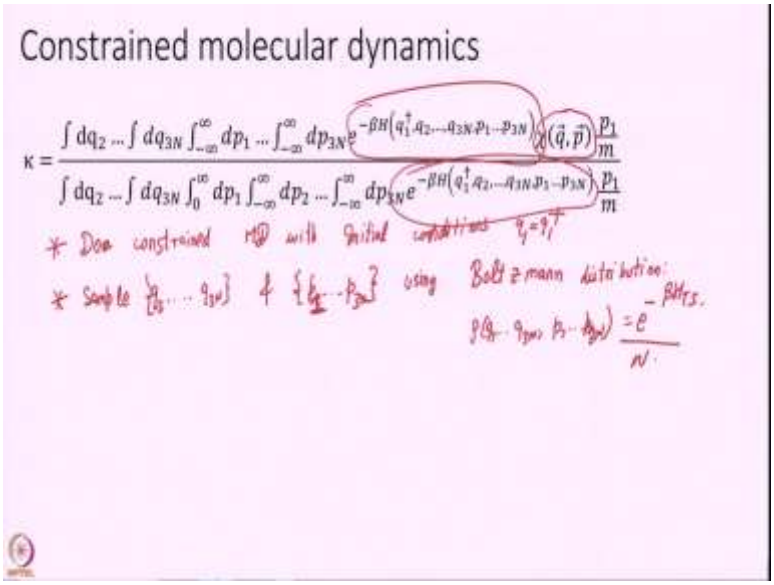

So the main idea that we have is the following. We want to calculate this kappa and I have written the full integral once for you. We want to do this full calculation. We want to solve this big integral, but using MD. So our idea is do constrained MD with initial conditions q1 set at q1 dagger. Sample q2 to q3N and p2 to p3N using Boltzmann distribution to q3N p2 to p3N is equal to e to the power of minus beta H transition state.

So I sample all these q2 to q3N and p2 to p3N, sorry, p1 to p3N. I am so sorry using Boltzmann distribution, because that is what this factor I am getting here. Q1 is set at q1 dagger. And now basically we have to give a recipe of how to calculate this chi. As it turns out calculating chi using statistical mechanics is not easy. There are attempts at it. But molecular dynamics is much more amenable to calculate this chi, because the chi is truly a dynamical quantity. Thermodynamics cannot really describe chi very well.

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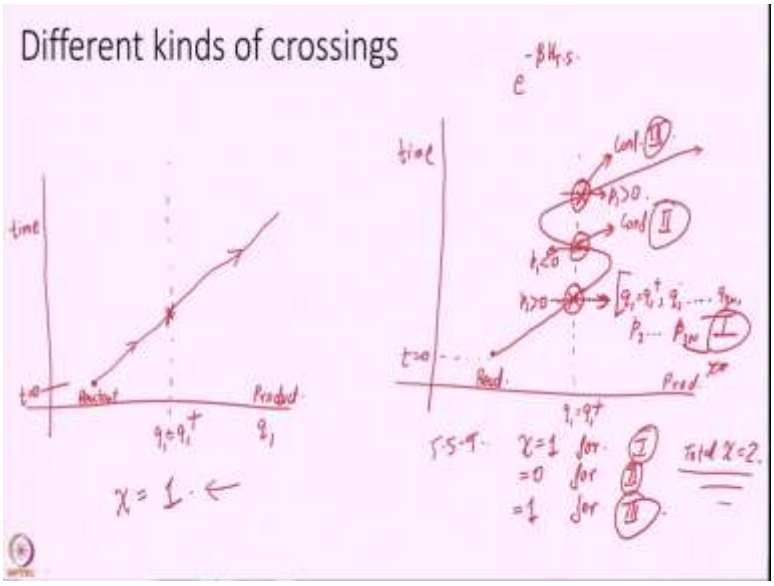

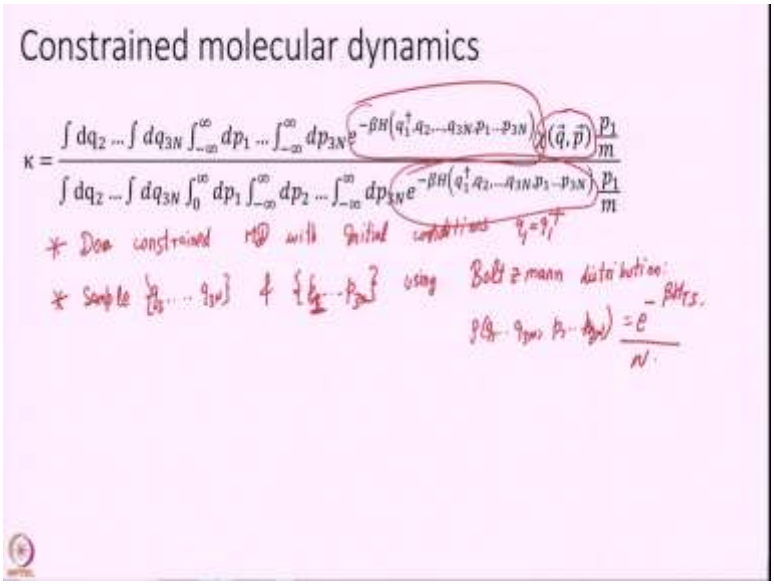

So let us look at a few different kind of trajectories, a few different kind of crossings. So I will making simple figures. Let us say on the x-axis I have q1 and on the y-axis let me draw time. Let us say this is my transition state geometry. Let us say at t equal to 0, my q1 is somewhere here, which is a reactant and this side is product. So q1 is my reaction coordinate. The middle decides a transition state, left of transition state is let us say my reactant, right of transition state is my product.

So as I move in time, let us say, the trajectory does something very simple. So let us start with this one. This is the best case scenario for transition state theory. It crossed the transition state exactly once. So think about your transition state theory. I am really sampling this big integral with q1 set to q1 dagger. So this point here will also be sampled with q1 equal to q1 dagger, and I, although I have not drawn q2 to q3N and p1 to p3N, they are having some value here and they have such values that I get this kind of a trajectory.

If that happens, my life is really, really good. My chi is simply 1 for this trajectory. Let us look at a more confusing trajectory. If this was the whole case, then I do not need this module, then kappa can be, kappa is simply 1. Transition state theory will be perfect. But that is not always the case unfortunately. Life is complex. So there are trajectories, the same let us say I start here, I let us say it hits here the same way, but here my values of p2 to p3N and q2 to q3N are different compared to this one.

So the values of other coordinates other than q1 at this point and this point are different that will lead to different dynamics now. So this one let us say does the following just for example. So, now, when I sample my e to the power of minus beta H transition state, this point will appear, this point will appear and this point will appear. I again emphasize this point corresponds to a certain value, q1 is fixed, but it corresponds to certain values of q2 to q3N comma p2 to p3N.

I will call this configuration, configuration I, I will call this configuration, configuration II and I will call this configuration, configuration III. Now, note, when I sample e to the power of minus beta HTS only constraint is q1 should be q1 dagger, which is true for I, II and III. So, all three points, these three points will emerge in this distribution. I will sample them with some probability, but they will be present.

If that is the case and if I assign chi equal to 1 for this one, let us say I use transition state theory basically. So, if I follow transition state theory, chi equal to 1 for one, equal to 0 for two, equal to 1 for three. So transition state theory will essentially give me a total chi of II. Let us assume that just for a moment that H transition state is, has a potential has a same value at the crossings I, II and III that is not true, but for our discussion let us assume that.

So if I have that, I got a total value of chi of 2, because transition state theory only looked at p1. So p1 is positive here. I am moving in the forward direction here. P1 is negative here and again p1 is positive here. So this one trajectory, I get chi equal to 2, but you see that is the problem. That is precisely the problem. That is the double counting problem of transition state theory or the re-crossing problem of transient state theory.

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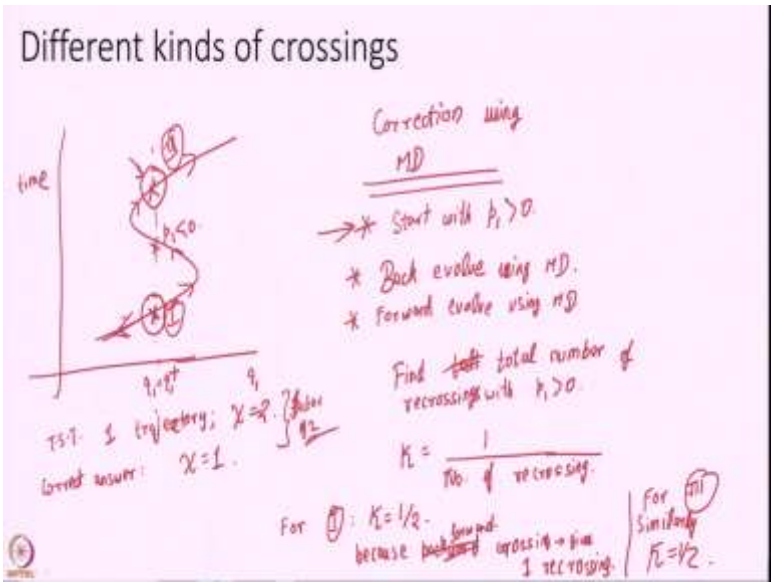

So for this kind of a trajectory, for this one trajectory, I am getting chi equal to 2. But the correct answer is equal to 1. Chi is really counting reactive trajectories that is a true meaning of chi. Chi should include all these three points as one point only, because they are connected through this phase space. They are part of one trajectory only.

So which means that transition state theory overestimates the rate constant by a factor of two in this case. So a simple idea on how will I correct, correction using MD start with p1 greater than 0, back evolve using molecular dynamics. Back evolve really means I am setting t to minus t. Remember that the Newton's laws are perfectly time reversible. So if you give me a value of q comma p, I can also go back in time and tell you what q and p would have been some time ago. So that is very easy to do in molecular dynamics.

Forward evolve using molecular dynamics, find total number of re-crossings, and set kappa equal to 1 over number of re-crossings. So let us just go by it in a moment. So let us see what this will do? Has it solved anything? I just given you an algorithm, but does it, this algorithm solves our problem or not? So, my sampling will only include this point and this point, because I have set p1 is greater than 0. This one p1 is less than 0. So this is not part of my sampling at all.

For these two points, I will go back in time. So I will, let us say, I start with one. I go back in time. I go forward in time, I am sorry, with p1 greater than 0. So if I am sitting at this point, I will go backward in time, I will go forward in time and I will do this trajectory basically and I

will find that I have two points of re-crossings, one is this point itself. But by doing MD, I will also that there was a point three.

So when I evolve forward in time from point one, I will end up with point three which is also a crossing in the, with p1 greater than 0. So for one my kappa will be set at half, because backward crossing, sorry, forward crossing here gave me, gives one re-crossing. So the starting point itself is a crossing plus when I moved forward in time I found another crossing, so the total number of crossings became 2.

For three, similarly, kappa is also half and it is half here because in backward direction now, so if I start with three here, now I will go back in time, then I will find one. So when I propagate backwards in time, I will have another re-crossing. So, I, basically I have two re-crossings. So, now, I have solved my problem. So I get a half from one and half from three and that basically accounts for my factor of two here is accounted for. So that is the main idea.

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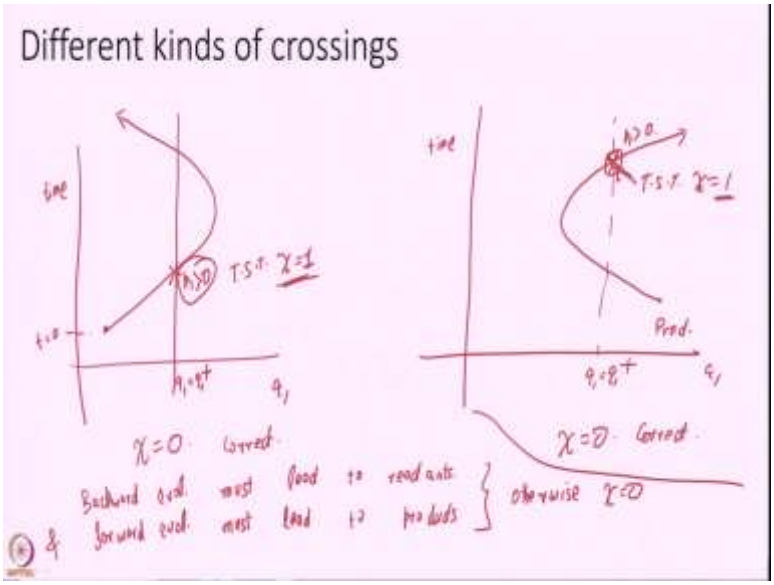

Let me just add one more thing here. Let us imagine another kind of trajectory. This is my time. This is q1. This is q1 equal to q1 dagger. Let us start with a trajectory here. And this trajectory let us say does this. This is not reactive at all. For this trajectory chi must be equal to 0. I can have another trajectory where let us say it does this. For this as well chi should be 0. So this point will come. This has p1 greater than 0.

So I will be sampling this point. I will be sampling this point. So transition state theory would have set chi equal to 1 for this. Similarly, at this point, transition state theory will put chi equal to 1, but this is wrong. This is the correct answer. So we have to account for this. So the simplest idea is backwards evolution must lead to reactants and forward evolution must lead to products. Otherwise, chi equal to 0.

So for this trajectory in my forward evolution, I will end in reactant, hence chi will be set to 0. For this trajectory in the backward evolution I will end in products and hence chi will be 0.

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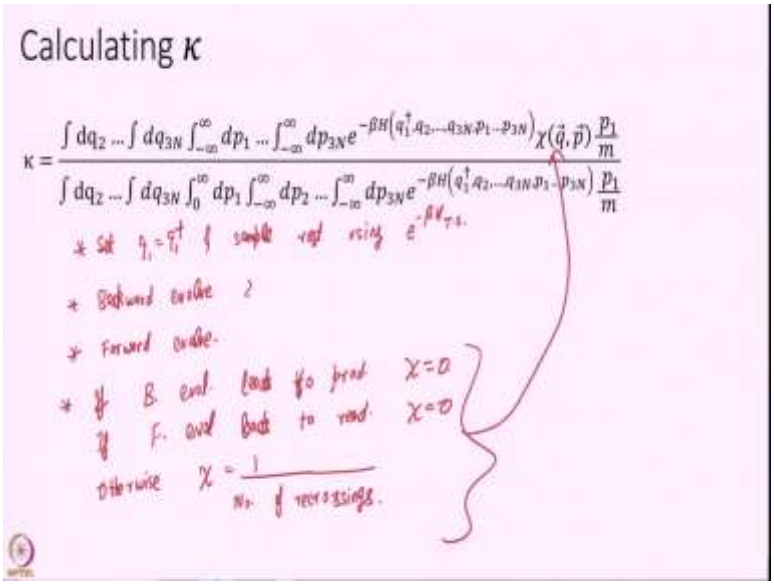

So, in short, to calculate chi what we are doing, set q1 equal to q1 dagger and sample rest using e to the power of minus beta H distribution, backward evolve, forward evolve, if back evolution leads to product chi equal to simply 0, if forward evolution leads to reactants chi is 0, otherwise, chi is equal to 1 over number of re-crossings. So this is the value of chi, I will feed here and calculate these integrals.

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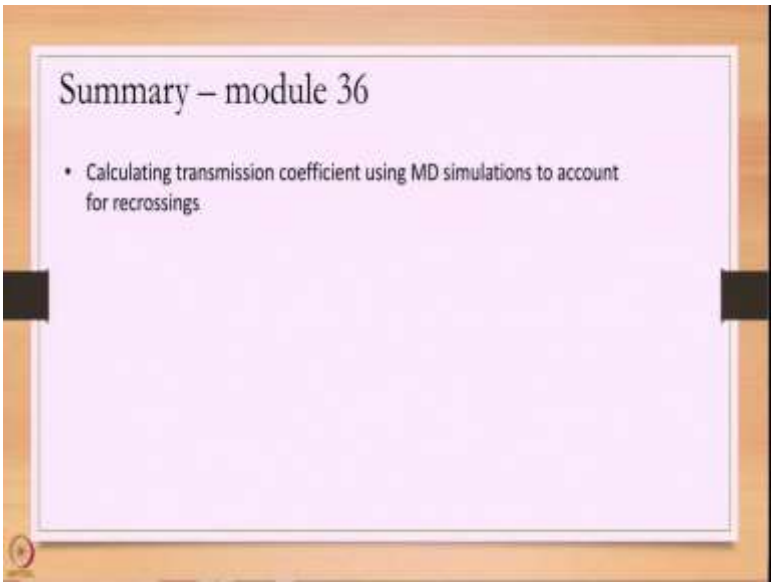

So, in summary, we have today looked at how to calculate this transmission coefficient kappa using molecular dynamics to account for re-crossings, and this kappa will always be between 0 and 1. Thank you very much.