Chemical Kinetics and Transition State Theory
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Lecture 33
Molecular dynamics: Rolling spheres on potential energy surfaces

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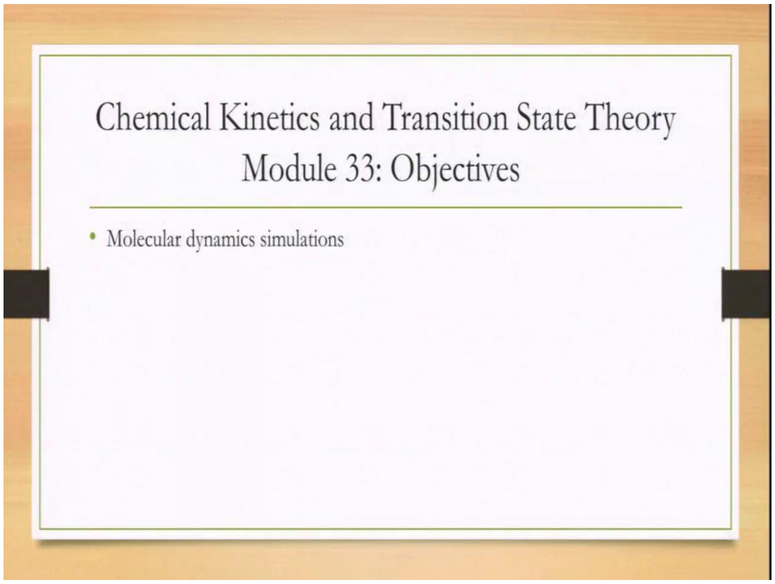

Chemical Kinetics and Transition State Theory
Module 33: Objectives

- Molecular dynamics simulations

Hello and welcome to module 33 of Chemical Kinetics and Transition State Theory. In the last module, we discussed how potential energy surfaces come from. They really come from Schrodinger equation. There is no escape, quantum mechanics is essential. And that potential energy is what we have been using so far in understanding rate theories. When we use this potential as a function of nuclear positions and that we divided into electronic part, rotational part, vibrational part, the origin of that net potential energy really came, was coming from this Schrodinger equation that we discussed in the last module.

Today, I just want to discuss something slightly different. There is a different way to computing rate constants which is via molecular dynamic simulation. So, let us discuss that today. First of all, do we really need this molecular dynamic simulation? We have studied transition state theory, it seems powerful enough, we can calculate rate constants for a wide variety of reactions. Let me give you a couple of examples where transition state theory is very hard to apply. These are called roaming mechanisms. So, I am highlighting here a couple of examples.

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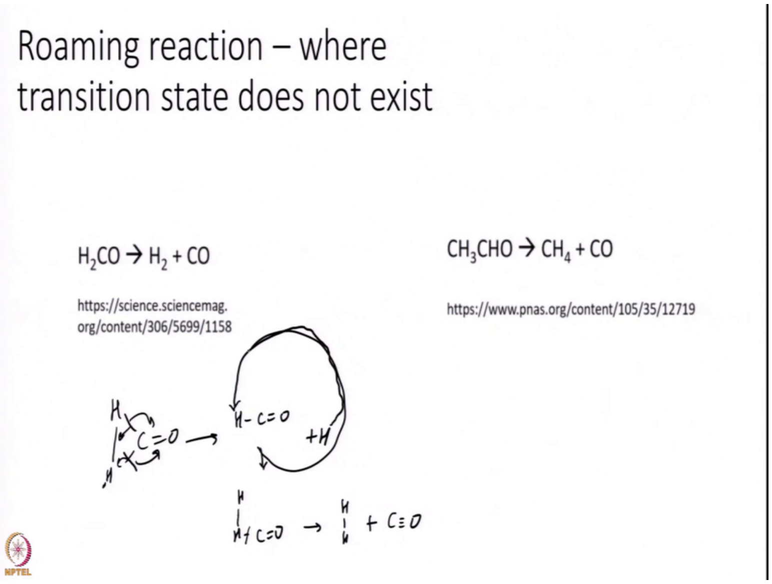

Roaming reaction – where transition state does not exist

$H_2CO \rightarrow H_2 + CO$

https://science.sciencemag.org/content/306/5699/1158

$CH_3CHO \rightarrow CH_4 + CO$

https://www.pnas.org/content/105/35/12719

This is one of the first examples that was first shown H2CO going to H2 plus CO. Now as it turns out, for such a reaction, a transition state does not exist. You can think of this molecule, you have only four atoms here and basically what has to happen here is that you have H2 like this, basically this bond has to break, you have to get a bond here. This bond has to break and this thing has to go into CO. But it is actually not so simple.

What the authors in this paper figure out is that one of the bond breaks first. This hydrogen, this leads to basically something like HCO plus another hydrogen. This then remains like this. This hydrogen then really moves for a very long time, it moves in a big circle, it finds the other hydrogen and you get something like this. And then finally you get H2 plus CO. So, this bond breaks and this bond forms.

So, in all of this, where is exactly the transition state? Remember, transition state is a very well-defined structure. It is the maxima along the reaction coordinate and it is the minima along all other directions. Here we do not have one such concrete structure. You have this hydrogen which is roaming around like this. So, at which configuration I call it the transition state? So, the whole point of transition state theory is extremely hard to apply here. A similar example you can also find in this particular paper I have just provided you and you can look at this reference on your own.

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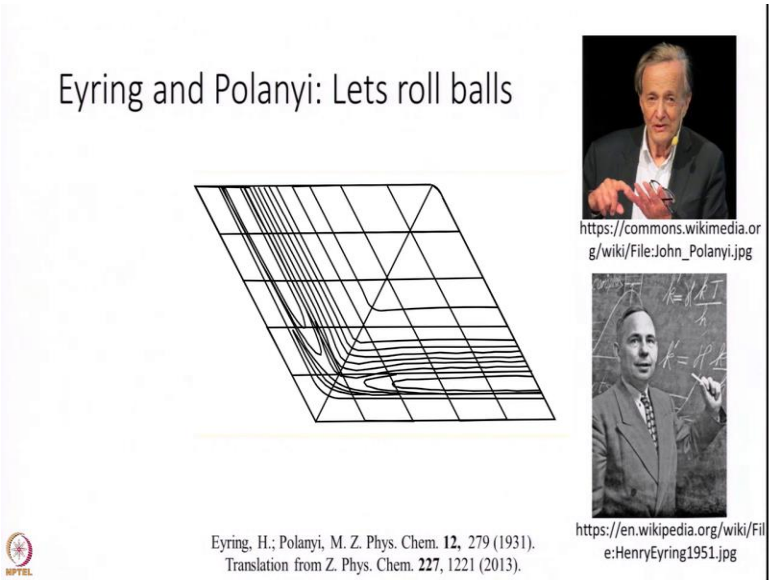
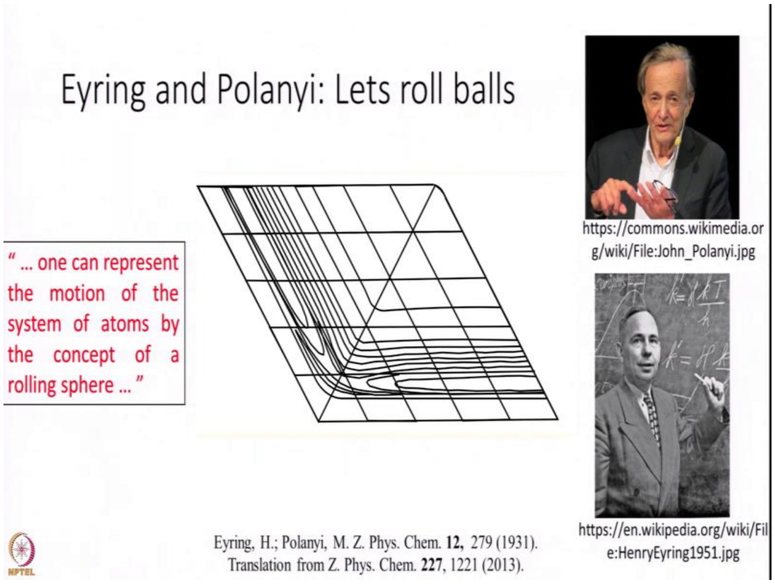


Eyring and Polanyi: Lets roll balls

https://commons.wikimedia.org/wiki/File:John_Polanyi.jpg

https://en.wikipedia.org/wiki/File:HenryEyring1951.jpg

Eyring, H.; Polanyi, M. Z. Phys. Chem. **12**, 279 (1931).
Translation from Z. Phys. Chem. **227**, 1221 (2013).



Eyring and Polanyi: Lets roll balls

" … one can represent the motion of the system of atoms by the concept of a rolling sphere … "

https://commons.wikimedia.org/wiki/File:John_Polanyi.jpg

https://en.wikipedia.org/wiki/File:HenryEyring1951.jpg

Eyring, H.; Polanyi, M. Z. Phys. Chem. **12**, 279 (1931).
Translation from Z. Phys. Chem. **227**, 1221 (2013).

So, what is an alternate? How do we handle such problems? If I cannot apply transition state theory, what do I do? We get back to the idea of Eyring and Polanyi what they had said in 1931. They have said that, if you know these potential energy surfaces, you know this V of XN, let us think of nuclei as classical. They are big enough, we do not have to think of them as quantum mechanical objects, we can just use Newton's laws evolving on this potential energy and calculate dynamics directly rather than going through transition state theory. So let us discuss how that is really done.

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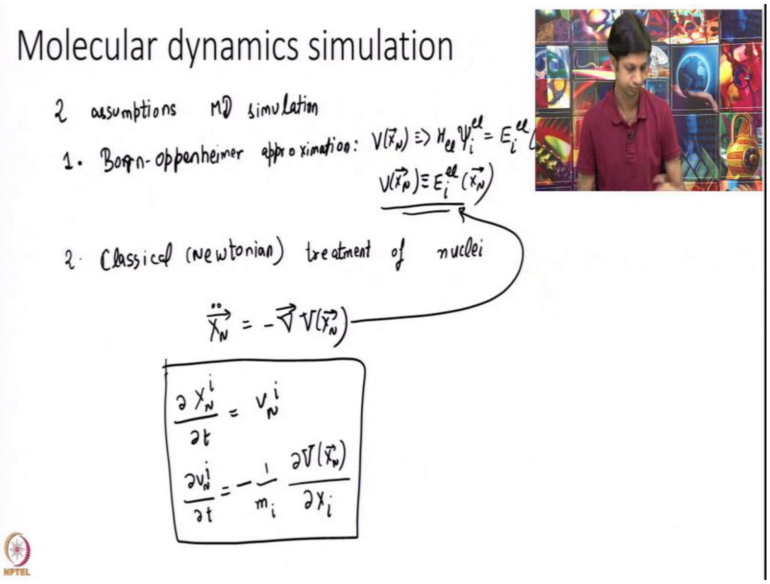

Molecular dynamics simulation

2 assumptions MD simulation

1. Born-oppenheimer approximation: $V(\vec{X}_N) \Rightarrow H_{el}\Psi_i^{el} = E_i^{el}$

$\underline{V(\vec{X}_N) \equiv E_i^{el}(\vec{X}_N)}$

2. Classical (Newtonian) treatment of nuclei

$$\ddot{\vec{X}}_N = -\vec{\nabla} V(\vec{X}_N)$$

$$\boxed{\begin{aligned} \frac{\partial X_N^i}{\partial t} &= v_N^i \\ \frac{\partial v_N^i}{\partial t} &= -\frac{1}{m_i}\frac{\partial V(\vec{X}_N)}{\partial X_i} \end{aligned}}$$

So, this is called a molecular dynamics simulation. That term you might have heard before. And today I will just introduce to you what is molecular dynamics simulation. So, first of all two assumptions go into molecular MD simulation. I will call molecular dynamics as MD. One, I have what is introduced as Born-Oppenheimer approximation in the last module, that is, my potential energy is really given by, and V of XN is nothing but this… So, that is called a Born-Oppenheimer approximation. I will not get into too much more details because that will require too much of quantum mechanics.

The second approximation that we make is classical treatment, classical means nothing but Newtonian, of nuclei. What it means is we are going to use XN double dot equal to minus gradient of V of XN, where V is the same as this V. So, if I write this more clearly as I have been writing over del t is VNi and del VNi over del t is equal to minus 1 over m del V over del Xi.

So, this is what is called Newton's laws that we have seen in this course little bit more. Derivative of position is velocity and derivative of velocity is my acceleration which is nothing but minus derivative of potential with respect to position. So that is Newton's laws F equal to ma, nothing more. So, we want to use these laws with this potential energy to run my dynamics. How do we do it?

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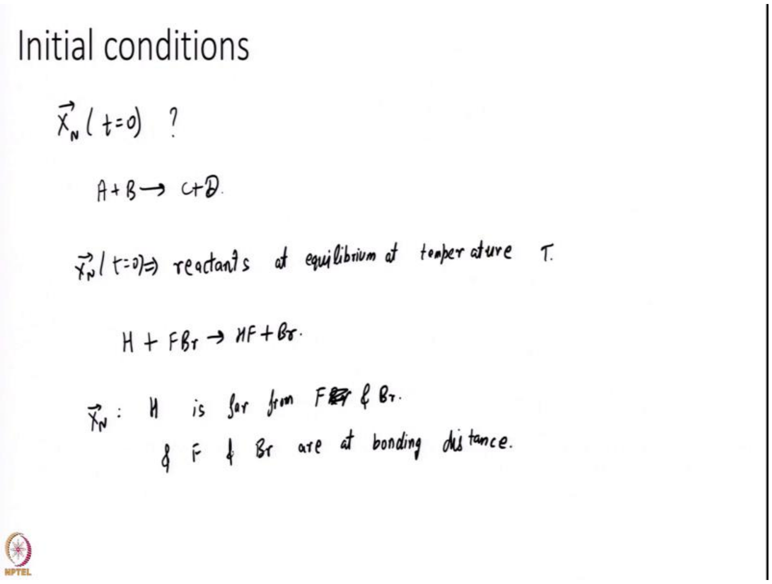

Initial conditions

$\vec{X}_N(t=0)$?

$A + B \rightarrow C + D$.

$\vec{X}_N(t=0) \Rightarrow$ reactants at equilibrium at temperature T.

$H + FBr \rightarrow HF + Br$.

$\vec{X}_N$: H is far from F & Br.

& F & Br are at bonding distance.

In an MD simulation there are a few steps typically and I will just provide you a little bit of a flavor of how these steps come by. So, the first thing is choosing initial conditions. I have to first tell you where does this XN at t equal to 0 looks like and that really depends on what problem you are trying to study. So let us say I am trying to think of some reaction, A plus B going to some C plus D, what should be my initial conditions? My initial conditions then should correspond to reactants at equilibrium at, again, we want this thermodynamics to hold.

So, we have some molecule, you have some collisions happening, you have some notion of temperature there and I am thinking that, well, my, initially I should be reactant, I should look like A plus B. What I really mean by all of this? Let us just imagine some reaction. I am just cooking up some reaction. So initially XN should be in a state where hydrogen is far from FBr, from F and Br and F and Br are at bonding distance. So, I can try to find out what the equilibrium distance of FBr molecule as it is, is whatever number of angstroms and I can think of placing F and Br that distance away and I think of H being very far away.

So that is my initial condition for this particular problem. For every problem therefore the initial condition is going to be different and that is where you have to use your intuition. Modern day programs actually help you. So, if you use something like LAMMPS or GROMACS, by the way these softwares like LAMMPS, you can install on your desktop today itself. They are free software, you can just go to their website, download it and start running. And they will provide you some help on how to choose initial conditions. But at the end of the day, you will have to tell what the initial conditions are.

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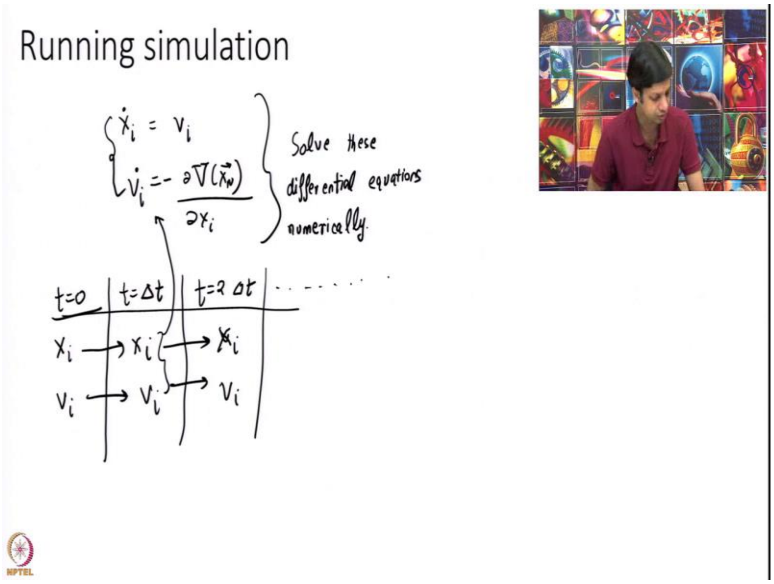

Running simulation

$$\left\{\begin{array}{l}\dot{x}_i = v_i \\ \dot{v}_i = -\dfrac{\partial V(\vec{x}_N)}{\partial x_i}\end{array}\right\}$$ Solve these differential equations numerically.

$$\begin{array}{l|l|l|l}
t=0 & t=\Delta t & t=2\,\Delta t & \cdots\cdots \\
\hline
x_i \rightarrow & x_i \rightarrow & \cancel{x}_i & \\
v_i \rightarrow & v_i \rightarrow & v_i &
\end{array}$$

Now, once I have initial conditions, what I have to really solve is a set of differential equations. My bad, Xi dot equal to Vi and Vi dot equal to minus del potential over del Xi. So, these are nothing but differential equations. Computers are extremely good at solving those differential equations starting from perhaps 60s. People have figured out ways of how to solve these differential equations. There are a number of numerical schemes one uses, something like Velocity Verlet. There are many others, Runge–Kutta methods.

So, we solve these differential equations numerically. And to solve these differential equations numerically, the way is, we cannot solve it for each value of time. We discretize our time as well. So, we know our, at t equal to 0 I know my Xis and my Vis. That is my initial condition that we have chosen somehow using our intuition where I put my hydrogen very far away from FBr or whatever.

Then what I do is, I find using numerical methods, at t equal to some delta t. I choose some finite time step, 1 femtosecond, 5 femtosecond, half femtosecond whatever, some time step. And I use these equations to propagate Xis and Vis here. So, I have a differential equation and I can use a computer to take Xi and Vi at a given time to t plus dt. So, I keep on then doing this. I again feed these Xis and Vis to these differential equations and propagate it here. And I keep on doing it to the time I want it. So how long should I really run it? Again, that comes from intuition. I should run it long enough that my reaction happens. So, it has to depend on rate constants.

So, the idea is you usually run a, you have some intuition where the rough ballpark of the rate constant is. From experiment or a basic let us say you might have a done a collision theory estimate. So, the simulation, the rate constant is of the order of picoseconds. So, I will run the simulation for a few picoseconds. I will see how the dynamics turn out. Maybe it was not enough, so I have to run it longer, I have to run it for 10 picosecond then. So, it is a lot of, in that sense, guess work. You run it, you see how the simulation results come out. And you go back to your simulations and run it again. So that is how these simulations run.

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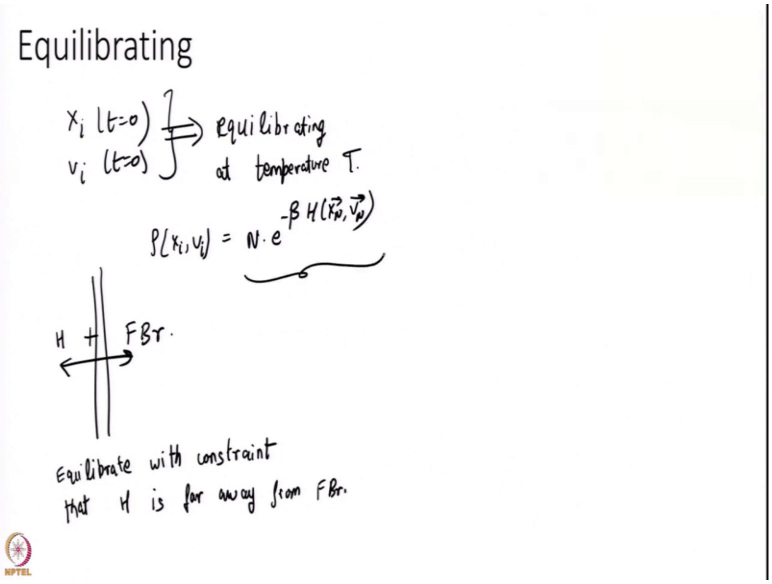

Equilibrating

$$\left.\begin{matrix} x_i\ (t=0) \\ v_i\ (t=0) \end{matrix}\right\} \Rightarrow \text{equilibrating at temperature } T.$$

$$\rho(x_i, v_i) = \underbrace{N \cdot e^{-\beta H(\vec{x}_N, \vec{v}_N)}}$$

Equilibrate with constraint that H is far away from FBr.

One important thing that I just want to bring up is the idea of equilibration. So, once I have my initial conditions, I have chosen these Xis and Vis at t equal to 0, they might not be exactly at temperature t, so our first step really is equilibrating at temperature t. So, I have some temperature in mind. Remember, rate constants are always found at a given temperature. So, I have 300 kelvin, whatever is the temperature of the problem, where the experiment was done let us say. At that temperature I want equilibrium and equilibrium really means that my distribution must be obey Boltzmann distribution.

So, if this distribution is not obeyed then I am not at temperature t. And so, the idea is, at the start of the simulation before I start calculating rate constant or whatever I want to find, I let the system equilibrate at temperate t. What I exactly mean by that? So, again I will come back to my favorite example of H plus FBr. So, what I do is, I let hydrogen equilibrate at their given temperature independently. So, I maintain this distance large.

I do not allow, in my simulation, there are ways of constraining. So, I put some kind of a barrier in between. And I say, you hydrogen you stay there, you can equilibrate separately. You can get your velocities equilibrated far away. FBr, you stay here and you get equilibrated here. So, the bond distance, its rotation and vibrations all this gets equilibrated at temperature t as well.

So, equilibrate with constraint that H is far away from FBr. How to put this constraint is a matter of detail and that actually is really aid for a different course which is on molecular dynamics. But there are ways that I can tell that. So, I have put the hydrogen far away, I have done my, I basically do MD simulation at a given temperature and I make sure that H and FBr are independently obeying this Boltzmann distribution.

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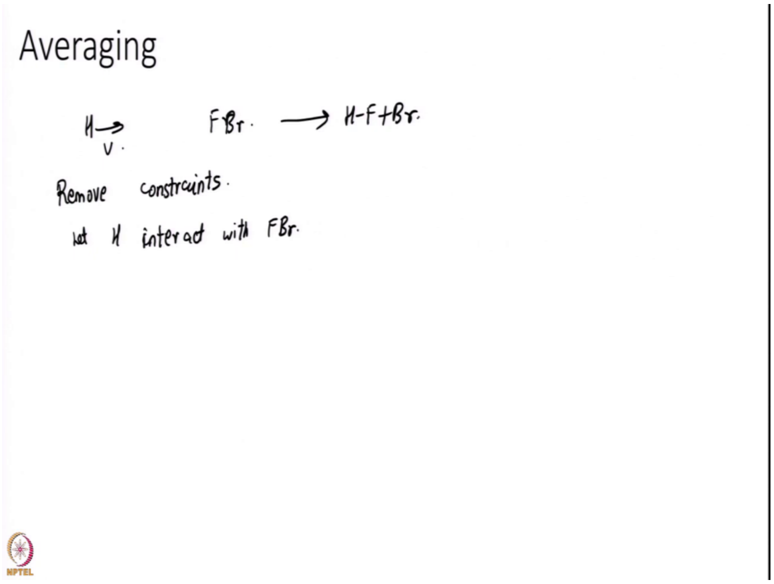

Averaging

$\underset{v.}{H\rightarrow}$ FBr. $\longrightarrow$ H-F+Br.

Remove constraints.

let H interact with FBr.

After that, I remove my constraint. So, I have H FBr far away, then I remove my constraints. So here I am talking of a specific example, but for any given problem whatever it is that identifies the reactants is my constraint. I will make sure that initially I look like a reactant configuration. So, I remove my constraints and I let hydrogen interact with FBr. So, I provide it with some velocity in this direction essentially and I let it hydrogen come close to FBr. And once I go that, I can run my simulation and then this H and FBr will react and I can see this kind of a reaction happen.

So, in MD simulation I literally follow each nuclei individually. I am seeing this hydrogen fluorine and bromine. H is coming close to fluorine and really this reaction is happening atom by atom.

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Molecular dynamics simulation

http://hase-group.ttu.edu/animations.html

So, you can see these simulations, many more examples of these simulations. You can go to this website, hase group, where you can find many animations of these simulations, many movies of these simulations. And you can see how atoms really move, interact with each other and do a reaction.

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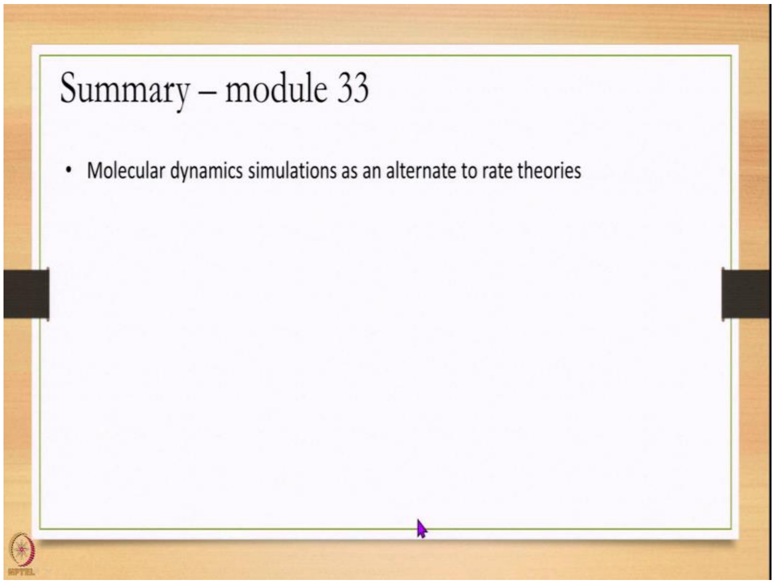

Summary – module 33

- Molecular dynamics simulations as an alternate to rate theories

So, with this we end today. We have just very briefly introduced how molecular dynamics simulations work. We have not went in too many details. The details are too many to be mentioned in one module. And what we can use this MD simulations is really follow all atoms and look at a reaction in detail. And once I have that information of all the atoms, I can also extract rate constant. So, I have the full detail of every possible possibility that is happening. With that we end today. Thank you very much.