Chemical Kinetics and Transition State Theory
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Lecture 32
Hills and Valleys of Potential Energy Surfaces

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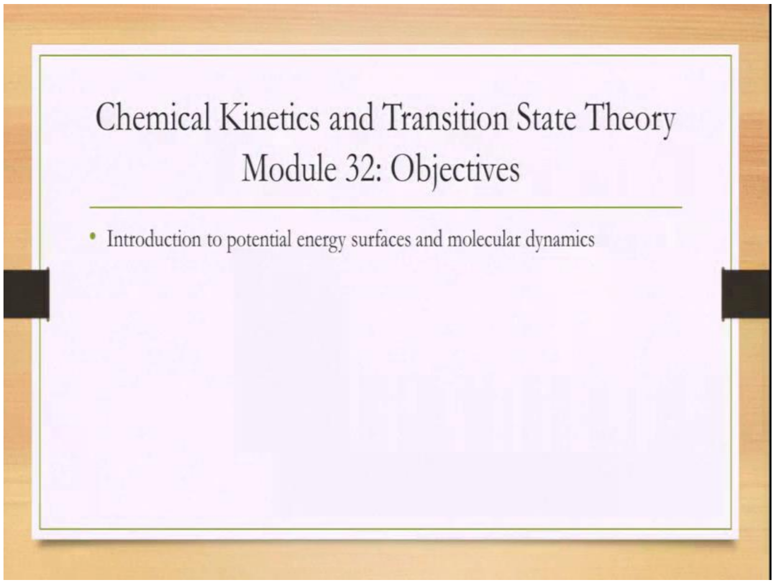

Chemical Kinetics and Transition State Theory
Module 32: Objectives

- Introduction to potential energy surfaces and molecular dynamics

Hello and welcome to module 32 of Chemical Kinetics and Transition State Theory. So now we have finished a basic understanding of transition state theory. Today I want to start another chapter and understanding of few more fundamental things basically leading to molecular dynamics simulations. In today’s module, we will look at one fundamental question, what is this potential energy surface.

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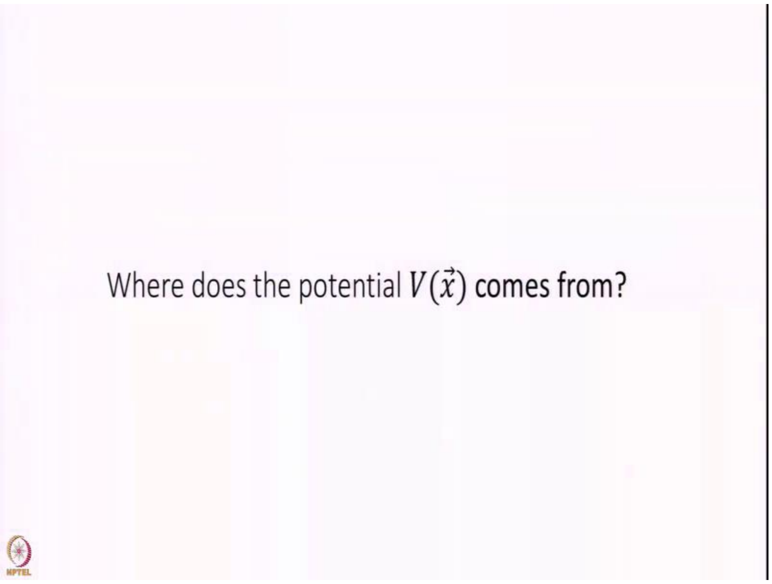

Where does the potential $V(\vec{x})$ comes from?

So, we have been using this potential of x throughout this course. When we write H Hamiltonian as kinetic energy plus potential energy, we use this potential energy. And so today, I just want to give a very brief introduction of what does potential energy truly mean. So, to understand that, it is necessary for us to delve a little bit into quantum mechanics. So let us start with that.

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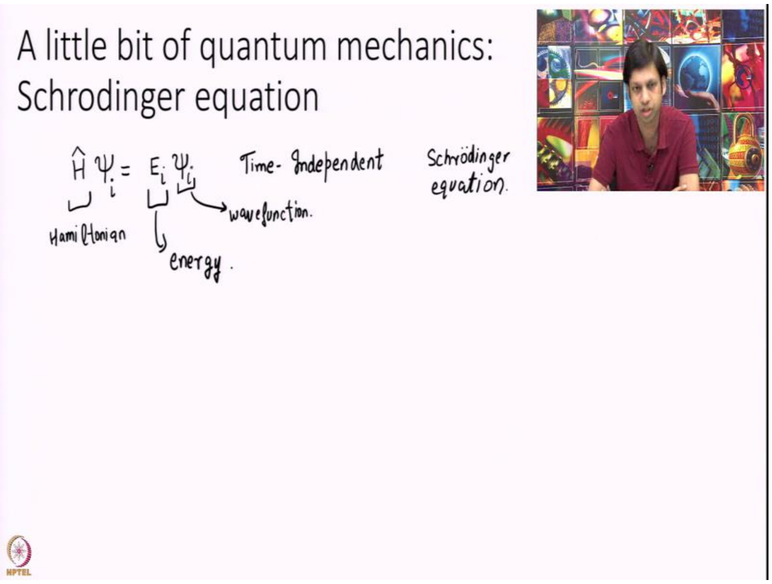

A little bit of quantum mechanics: Schrodinger equation

$$\underbrace{\hat{H}}_{\text{Hamiltonian}}\psi_i = \underbrace{E_i}_{\text{energy}}\underbrace{\psi_i}_{\text{wavefunction.}}$$

Time- Independent Schrödinger equation.

This thing will not really, I mean, I will not have any questions with quantum mechanics in terms of exams and all, but this for knowledge. So, quantum mechanics essentially tells us that energies comes in concrete levels, in discrete levels. They are quantized quantum mechanics. So, the equation that I will be looking at today, I will look at only one quantum mechanical equation which is H psi equal to E psi. This equation is called time independent Schrodinger equation.

H here is a regular Hamiltonian that we have been dealing with. In quantum mechanics these are in the language of operators, do not worry about all that, just a bit of technicality. This psi that is here is what is called wave function. I will not delve into what is a wave function in this course at all. If you know it already, if you have been introduced, good.

In short, wave function tells me the state of the system. So far, we have been looking at what is called position and velocity as the state of the system. In quantum mechanics position and velocity do not exist. What exist is wave function. It is some function that describes my system. That is all I will talk about.

What is important here is this term energy. So, for any given system, if I give you the Hamiltonian, there are ways of solving this time independent Schrodinger equation. And there are actually multiple solutions to this equation. So put in label i. So, this, at the end, turns out to be a differential equation. I am not going to write that differential equation. It is a very brief and overview introduction to quantum mechanics. What is important is that your system exists in these concrete energy states Eis.

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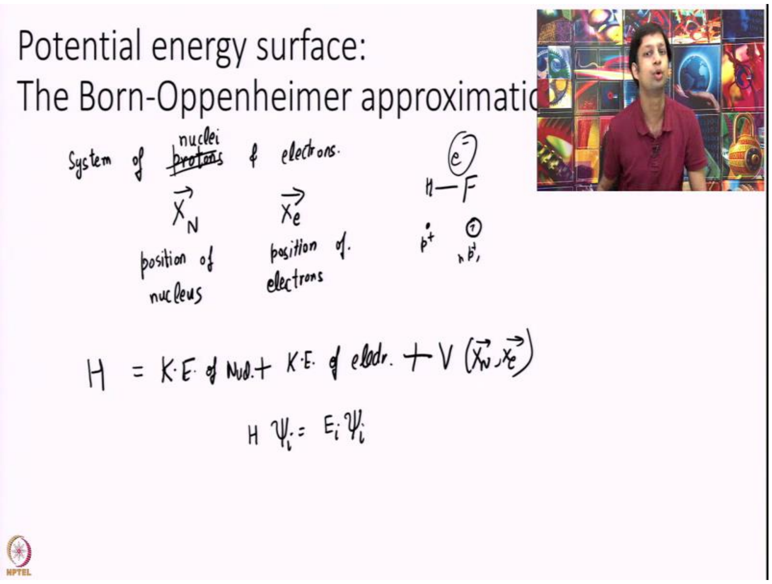

Potential energy surface:

The Born-Oppenheimer approximati

System of ~~protons~~ nuclei & electrons.

$\vec{X}_N$ position of nucleus

$\vec{X}_e$ position of electrons

$$H = K.E. \text{ of Nucl.} + K.E. \text{ of electr.} + V(\vec{X}_N, \vec{X}_e)$$

$$H\psi_i = E_i\psi_i$$

So, where does this potential energy then comes from? What am I doing? Where am I leading to? I am leading to what is called the Born-Oppenheimer approximation. So, let us say you have a system of protons and electrons, that is what molecules really are. They are a system of protons and electrons. You can think of any molecule. H has one proton here, Fluorine is a big molecule with a lot of protons, I cannot remember how many. But you can imagine n number of protons, n number of nucleons and some number of electrons.

Well, let me denote the position of all protons, well, let me, instead of protons, let me just call them nuclei, to be more accurate, because you also have nucleons, as XN and Xe. So, XN is the position of nucleus let us say and this is position of electrons. So, I have multiple electrons and nucleus. So, these are vectors. Position of electrons. So, the thing is I can write the same Hamiltonian as I have been writing so far, which is nothing but kinetic energy of nucleus plus kinetic energy of electrons plus some potential which is nothing but the coulomb potential.

So, Hamiltonian is kinetic energy plus potential energy. I am writing kinetic energy as kinetic energy of nuclei plus kinetic energy of electrons and some net potential energy. I will not even write the form of this. That is a concrete mathematical form that this kinetic energy and potential energy comes in. Let us not worry about that.

Now this equation, equation that I want to solve now is H psi i equal to Ei psi i. It turns out this is near impossible to solve. Mathematicians have tried it for a long time, but one just cannot do it. Even with using computers this equation is close to impossible to solve.

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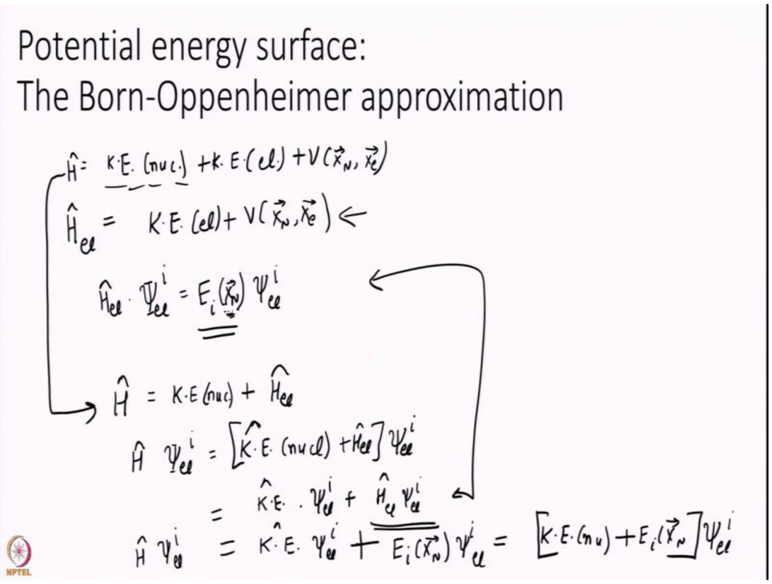

Potential energy surface:
The Born-Oppenheimer approximation

$$\hat{H} = \underline{K.E.(nuc.)} + K.E.(el.) + V(\vec{x}_N, \vec{x}_e)$$

$$\hat{H}_{el} = K.E.(el) + V(\vec{x}_N, \vec{x}_e) \leftarrow$$

$$\hat{H}_{el} \cdot \Psi_{el}^{i} = \underline{\underline{E_i(\vec{x}_N)}}\, \Psi_{el}^{i}$$

$$\hat{H} = K.E(nuc) + \hat{H}_{el}$$

$$\hat{H}\, \Psi_{el}^{i} = [\hat{K.E.}(nucl) + \hat{H}_{el}]\, \Psi_{el}^{i}$$

$$= \hat{K.E.} \cdot \Psi_{el}^{i} + \underline{\underline{\hat{H}_{el} \Psi_{el}^{i}}}$$

$$\hat{H}\, \Psi_{el}^{i} = \hat{K.E.}\, \Psi_{el}^{i} + E_i(\vec{x}_N)\, \Psi_{el}^{i} = [K.E.(nu) + E_i(\underline{\vec{x}_N})]\, \Psi_{el}^{i}$$

So, what we do is what is called the Born-Oppenheimer approximation introduced in 1927 or 28. So, I have written this Hamiltonian as kinetic energy of nucleus plus kinetic energy of electrons plus some potential energy. So, to make progress what we do is define another Hamiltonian as just the kinetic energy of electrons plus potential, the full potential. I have just not written kinetic energy of nucleus here.

And what I am going to do is H electronic, I am going to solve for us the electronic Hamiltonians eigenfunctions and eigenvalues. And I solve this equation for a fixed value of nuclear positions. This is a tricky concept to understand and it takes time to grasp this point. So let me repeat this. What I have done, I fix all the nuclear positions. I have HF molecule let us say, I clamp the hydrogen nuclei, I clamp the fluorine nuclei, fix them.

I am only looking at kinetic energy of electrons that is energy is, electrons are mobile, we have some kinetic energy and I am looking at the net potential that the electron is filling with respect to these clamped hydrogen and fluorine and I solve H psi equal to E psi for this Hamiltonian. There are ways of doing it. Let us not get into how to solve that. But this actually can be solved using a computer. This is by the way called electronic structure theory solving this equation.

So, the energy that I get is depends on the, this HF distance, on the H and F positions. If I change this position, my potential energy will change. How the electron is interacting with H and F will be different depending on where this H and F are exactly located. So, this energy that I had depends on X and N now as an artifact of the point that I have clamped H and F or the nuclei. So, if you had water, I would have clamed oxygen and the two hydrogens, whatever is the molecule. I have looked at all the nuclei, fixed their positions and solved H psi equal to E psi.

I get some energy. Now for a different nuclear configuration, I will get a different energy. So, this Ei depends on XN. But this is only H electronic part, my real Hamiltonian was this full thing with kinetic energy of nuclei. So, H is really kinetic energy of nuclei plus H electronic, where H electronic was defined here. Now if I apply this H on the psi electronic of I, something interesting will happen.

So, I will have kinetic energy of nuclei plus H electronic on psi electronic, this is equal to then kinetic energy of electrons on psi electronic. I am just opening the bracket. I have to put these little hats to be accurate. Do not worry if you do not understand why those hats are present there on these Hs. Now this is equal to kinetic energy. And H electronic on psi electronic I take from here, so this is equal to nothing but kinetic energy of nucleus plus Ei of nuclear positions on... So, I have just applied H into psi electronic of I, I have not made any actually approximation so far.

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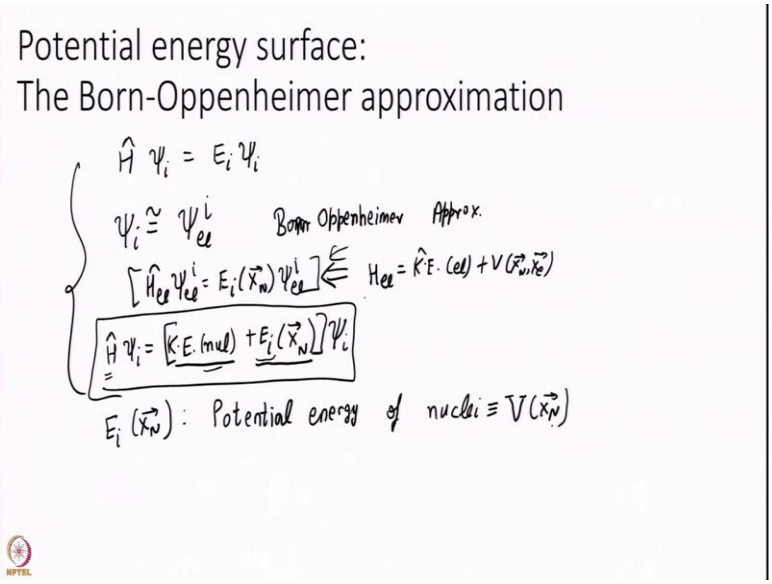

Potential energy surface:
The Born-Oppenheimer approximation

$$\hat{H}\,\psi_i = E_i\,\psi_i$$

$$\psi_i \cong \psi_{el}^{i}$$ Born Oppenheimer Approx.

$$\left[\hat{H}_{el}\psi_{el}^{i} = E_i(\vec{X}_N)\,\psi_{el}^{i}\right] \Leftarrow H_{el} = \hat{K}\cdot E\cdot(el) + V(\vec{X}_N, \vec{X}_e)$$

$$\boxed{\underline{\underline{\hat{H}}}\,\psi_i = \left[\underline{K\cdot E\cdot(nucl)} + \underline{E_{\underline{i}}(\vec{X}_N)}\right]\psi_i}$$

$$E_i(\vec{X}_N)$$: Potential energy of nuclei $\equiv V(\vec{X}_N)$

The approximation comes in assuming, remember, we want to solve H psi i equal to Ei psi i. Approximation is psi i is equal to psi electronic i. This is called the Born-Oppenheimer approximation. So, psi electronic again is H electronic applied on psi electronic i equal to Ei.

Now, what we have noted is H acting on psi i looks nothing but kinetic energy of nucleus plus some energy which is also a function only of nuclear positions acting on psi i.

So, we basically, what is Hamiltonian now? Hamiltonian is kinetic energy plus potential energy. So, now this looks really like kinetic energy of nuclei plus some energy of position. So, we call Ei of XN to be potential energy of nuclei. So, this might be a slightly confusing term. This potential energy of nuclei actually includes kinetic energy of electron in it. Remember that we have got this Ei by solving this equation and H electronic was kinetic energy of electrons plus potential. So Ei actually contains kinetic energy of electrons in it. It is simply the net potential that the nuclei are feeling with each other after I have removed away the electronic positions.

So, this whole trick is really a way to get rid of electronic positions. We are able to get an equation finally which looks completely like a nuclear kinetic energy plus nuclear potential energy. And I have somehow hidden the electronic part into this Ei into, while I have solving this equation here. So, this is the trick. And therefore, I think of Ei of XN as potential energy of nuclei and so I will start writing this as V of XN.

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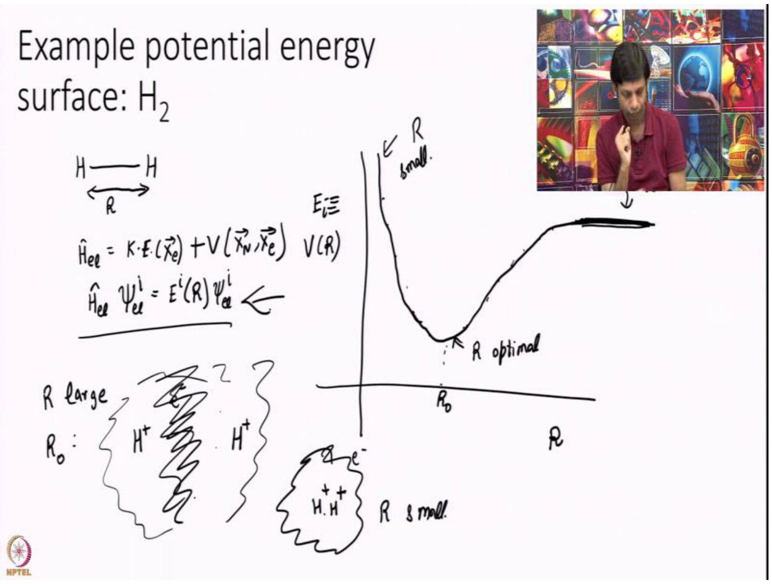

Example potential energy surface: H_2

$$\hat{H}_{el} = K\cdot E\cdot(\vec{x}_e) + V(\vec{x}_N, \vec{x}_e)$$

$$\hat{H}_{el}\,\Psi^i_{el} = E^i(R)\,\Psi^i_{el}$$

So, just to give you an example, let us just think of H2 molecule, just making things more concrete. So, remember H2 has only one vibrational distance here. Let me call that distance as capital R. So, what I am going to do is the following. I calculate the electronic Hamiltonian as kinetic energy of two electrons. H2 has two electrons in it, one from the H1 second from the second hydrogen plus the potential energy of the two hydrogens and the two electrons. I solve H electronic into psi electronic i equal to Ei as a function of R psi electronic i.

So, I fix this R, I calculate, I solve for this equation, never mind how, those detail I am not getting into. There are many ways now that you can solve this electric Schrodinger equation. Those is like a package like Gaussian or BALPRO or ORCA, any of these softwares can solve this differential equation. But this differential equation was solved for a given value of R. So, at the end of the day what I get is, I plot R here and Ei which is the same thing as V. So, for a given value of R, I solve for Ei and I will get different values at different plots.

Now, let us just imagine how this plot will look like. I have already shown it to you. But let us just qualitatively discuss this plot. When R is large, the two hydrogens are very far separated from each other. You see then the, it does not matter if I change it a little bit, they are so far separated that the potential energy will be a constant like this or almost constant if not exactly constant when R is closing to infinity. The two hydrogens do not know each other at all.

Now at some distance of R which I will call R naught, what you have is when the hydrogen, the H2 molecule is forming a good bond. You know H2 molecule forms a very stable bond. And so that is depicted by a minima on this energy surface. So that is the location, when you have this hydrogen here which is nothing but a proton, another hydrogen nuclei here, and you have this electron cloud smear throughout. And this location R naught just happens to be the point which is optimal. So, your two protons are actually repelling each other. They have both positive charges. And positive charges repel each other.

And at this particular distance it just so happens that the electrons can distribute themselves in a fashion which can stabilize these two charges the most. So, you will have a lot of electron distribution actually coming in the center. And once R becomes really small, so if the two hydrogen atoms comes really close to each other, well, what happens then is that the electrons cannot squeeze in between here. So, your electrons are like this here. And the two protons is repel each other very hard. So, you get a very large energy.

The two protons are very close and they are repelling each other and the electrons are not able to help that much, because they are just too close to each other. When they become a little bit far away, the electrons can come in between and shield this repulsion from each other. And once they become too far, then it is irrelevant. The two protons not even see each other. They are so far away. Let us say they are 1 kilometer far away. The two protons do not see each other. So, if I make even small differences I will still get a flat energy surface here. So, this is R large, this is R optimal and this is R small.

So, this is just an example of how an energy surface looks like for a specific molecule. Now you can choose any other molecule you want. You can choose methane, water, proteins, however be the molecule, the concept remains the same. I have all these nuclei for a given nuclear position I am solving for this equation and I am calculating Ei. Now as these nuclei configurations are changing, I will re-find this Ei and that will be my new energy.

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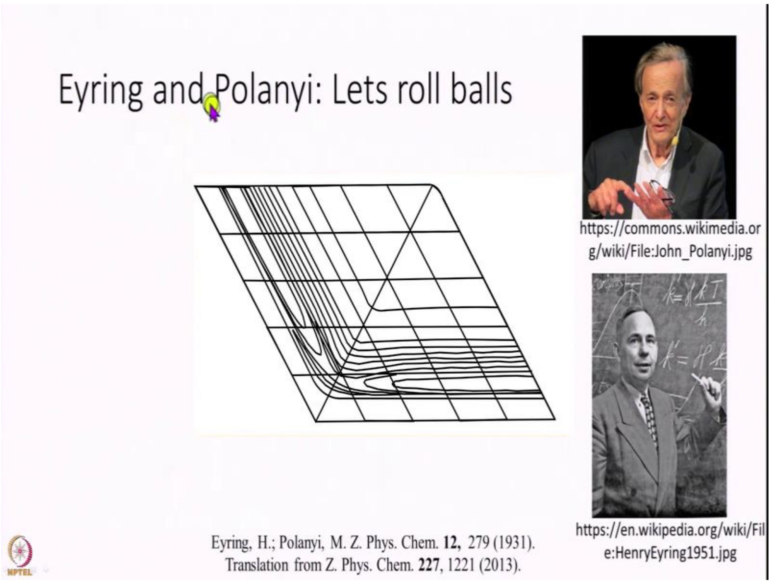
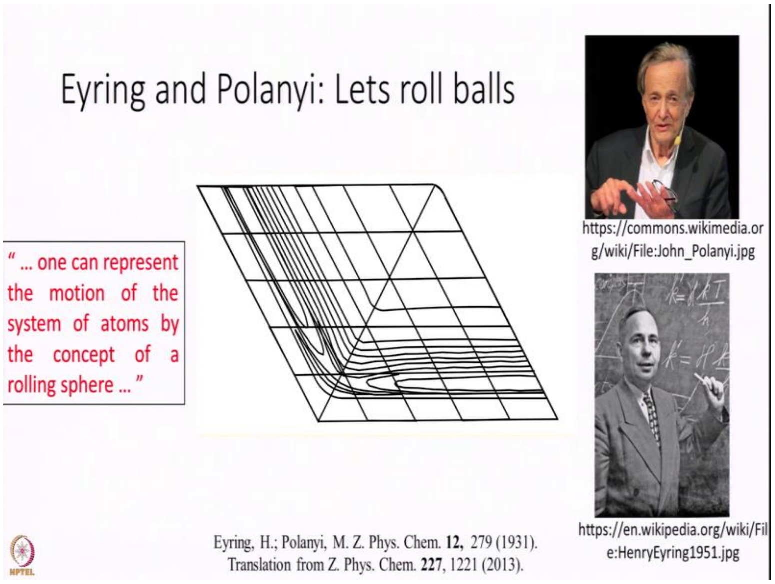


Eyring and Polanyi: Lets roll balls

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).
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So, I was want to tell you about work from a far of era in 1931 here introduced by two famous people Eyring and Polanyi. So, these gentlemen were both have been overall huge amount of span of time, instrumental in understanding rate theories in many, many different ways. They 1931 in this paper, so a translation of this paper you can also see here. You can open this paper and read this if you want. It is a English translation. The original paper is in German, if I believe.

They were the first people to do something very interesting. Born and Oppenheimer introduces idea of potential energy surfaces in late 1920s, either ’27 or ’28, I forgetting the year. Eyring and Polanyi said, one can represent the motion of the system of atoms by the concept of rolling sphere. So, they said, I have these energy surfaces, however complex they look. This figure is directly from their paper.

So, they said, let us think of these nuclear nuclei as classical particles. They are big and heavy. Electrons are so small, their mass is so small that I cannot read them classically at all. That is going to be a disaster. But nucleus protons or higher entities, I can start thinking classically. So, Eyring and Polanyi said, I have this potential energy with me, why not start reusing Newton’s laws to start thinking of dynamics on this potential energy surface.

So, they literally was thinking that I have this rough energy surfaces with minimas and valleys and some transition state sitting in between like this here, so let us roll, so let us say this is my reactant here, this is my product here, let us start with my reactants as some, think of this as spheres rolling on these complex energy surfaces. And you think of these as having some energy rolled a ball on this energy surface and this comes here and it moves into some complex fashion dictated by the valleys, the ridges of this energy surface and you react and come out here. So, these are literally, you can really think of this as marbles rolling on some energy surface, on some surface. So, this was first introduced by Eyring and Polanyi. So, we will discuss their ideas in the next module which is basically called molecular dynamics simulation.

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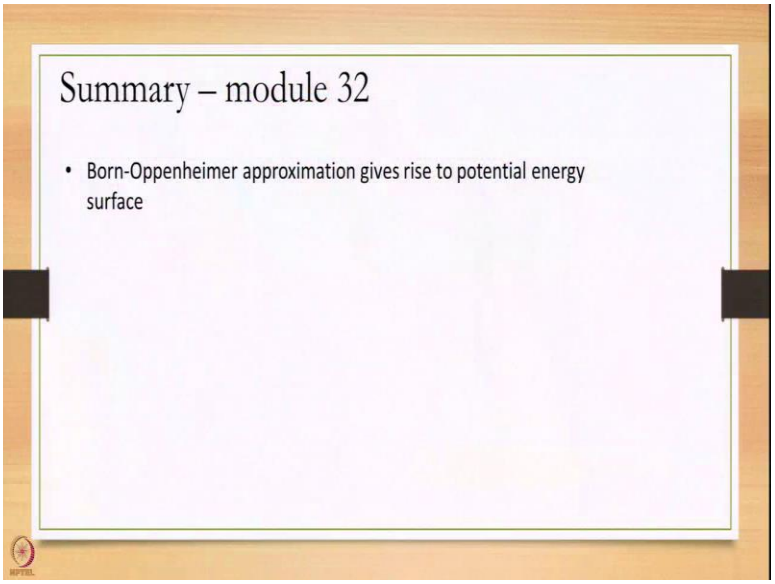

Summary – module 32

- Born-Oppenheimer approximation gives rise to potential energy surface

In today's module, we have just discussed the basic idea of where potential energy itself comes from. It comes from the Born-Oppenheimer approximation. So, you can get a potential energy as a function of nuclear position. In the next module let us see how we can use this potential energies to run molecular dynamics. Thank you.