Concepts of Chemistry for Engineering
Professor Chidambar Kulkarni
Indian Institute of Technology, Bombay
Center of Distance Engineering Education Programme
Lecture 66
Potential energy surfaces of H3 system

Hello, everyone, welcome to the module on intermolecular forces and potential energy surfaces. We are currently discussing about potential energy surfaces and the potential energy surfaces of different kinds of molecules, either triatomic or even other kinds of systems. Before we get into looking at potential energy surfaces in a little more detail in this lecture, let us just recap our memories on what we discussed in the previous lecture.

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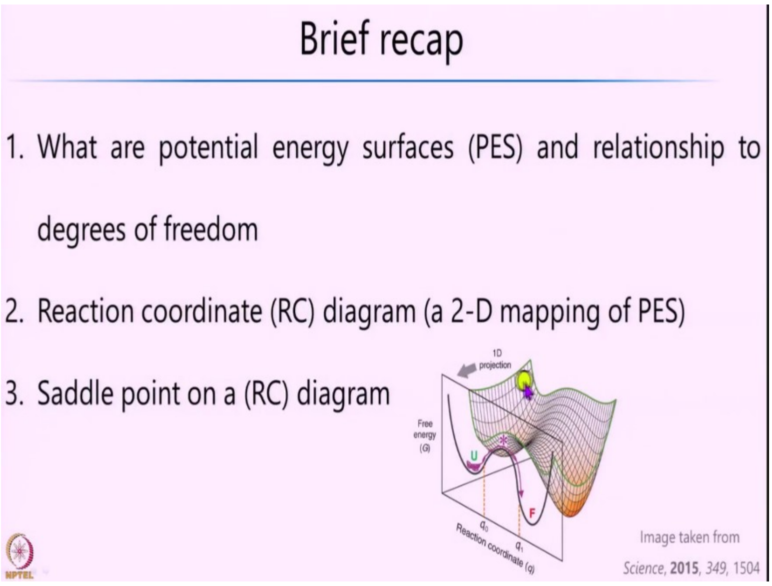

Brief recap

1. What are potential energy surfaces (PES) and relationship to degrees of freedom
2. Reaction coordinate (RC) diagram (a 2-D mapping of PES)
3. Saddle point on a (RC) diagram

Image taken from *Science*, **2015**, *349*, 1504

In the previous lecture, we had started out by looking at what are called as potential energy surfaces, and we had said that these are nothing but a three-dimensional or n-dimensional hypersurface in which by playing around with the coordinates or different modes or different degrees of freedom of a given molecule or atoms, ions, one can actually look at the potential energy of the system and such a diagram of potential energy versus the coordinates is what one would call a potential energy surface. And in case of where we are looking at chemical reactions, these coordinates are typically the vibrational degrees of freedom, such as the bond lengths, bond angles, and various other degrees of freedom.

So, we had seen that based on the kinds of molecule one could have either a hypersurface of 3N minus 5 or 3N minus 6, where N is the number of atoms or ions in the given system. Further, we had also said that these three-dimensional surfaces can also be mapped on to two-dimensional picture, which is called as a reaction coordinate diagram. And here what one does is, to look at along a particular coordinate of interest that is either a particular bond length or a bond angle or even a combination of them and then draw them on a two-dimensional representation.

This is typically what one would use in looking at the transition states of a given reaction or even the transition state theory of a particular species. So, having said this we had also learnt or discussed, what is called as a saddle point, which is a very important aspect when we talk about potential energy surfaces and reaction coordinate diagrams.

So, if we take a diagram such as shown here, the one which you had looked at in the previous class as well, what we said is that this point where going from the one valley to the other, the hill one crosses is what is called as a saddle point, and we are seen that it is called saddle because of the way it looks like, that is, on the two sides the energy is actually going down and on orthogonal sides the energy actually increases.

So, an important point to note is that a saddle point is invariably a highest energy point on a two-dimensional reaction coordinate diagram. However, when it comes to a potential energy surface of three or n-dimensions, it is not the highest energy points, it is always somewhere in between, because there are points of highest energy such as you could see here on the green parts of the surface are the ones which are actually having higher range compared to the saddle point.

So, a key distinction is on the two-dimensional picture, that is the reaction coordinate diagram, saddle point represents the point of highest energy. Whereas, on a n-dimensional or a n-dimensional hypersurface which is called as a potential energy surface, saddle point does not represent the point of highest energy. This is a very important distinction to keep in mind.

So having sort of refresh the memories on what are called his reaction coordinate diagrams, and potential energy surfaces, now let us start looking at a very simple case of a H3 system. So, for that, I am going to try and write down the reaction which we are interested in first.

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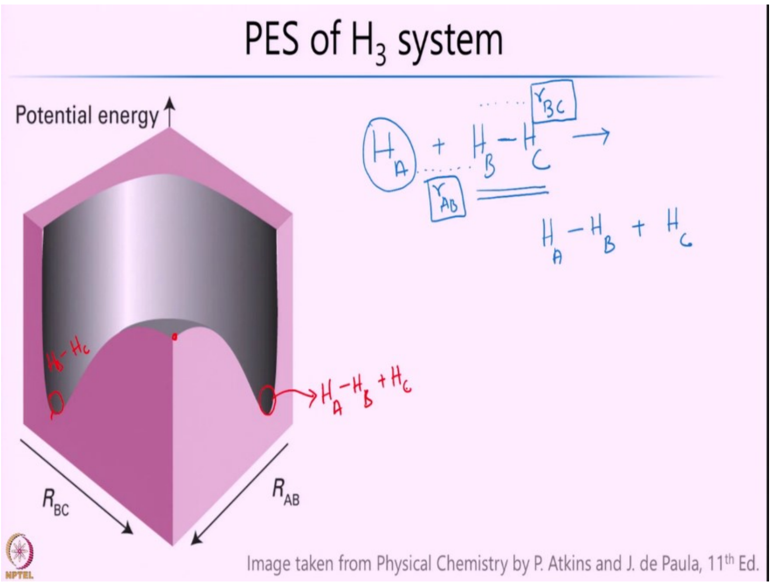

PES of H_3 system

$H_A + H_B - H_C \rightarrow$

$= H_A - H_B + H_C$

Image taken from Physical Chemistry by P. Atkins and J. de Paula, 11th Ed.

So, let us say, I have an hydrogen atom HA which is interacting with the hydrogen molecule. Just to distinguish the hydrogens I am writing them as H, A, B, and C, and this would give me HA, HB, plus HC. So, if I am interested in this particular kind of a system where a hydrogen atom is reacting with the hydrogen molecule to give rise to a similar product, but it is a slightly different connectivity.

In this particular scenario, what can happen is, the two entities that is the HA and HB, HC can actually approach in two different ways. One is, they can approach in colinear fashion that is HA is approaching the BC bond or it can also approach in a non-collinear fashion that is at a different angle or at a particular angle. For the sake of the convenience and it also turns out that that is the most reasonable way, we shall look at only the collinear case that is the HA and HB, HC are actually interacting in a more of a head-on fashion.

So, if we now restrict ourselves to the collinear way of interaction then, in order to represent this, we can actually choose two coordinates or two degrees of freedom. One is, the bonding between the HA, HB that is we are going to form a new bond between HA and HB so we can look at the how does the potential energy varies as a function of this that is our rAB and we can also look at how does the potential energy varies as this bond actually gets rupture that is rB and C.

So, these are the two parameters which we can vary and look at how does the total energy or the potential energy of the system varies. So, if you now agree that these two parameters are good enough to describe the particular system, we are interested in that is H3 in this particular case, then one can come up with a potential energy surface which is shown on the left-hand side.

And invariably, such potential energy surfaces are constructed by what are called as electronic structure calculations, which are typically based on quantum mechanical, quantum mechanics-based competitions, where both his parameters, that is, the distance between the HA, HB and the distance between the HB, HC are varied and at each of the coordinates that is each of these points, the total energy of the system is or the production area the system is calculated and that is plotted as a function of these two coordinates.

And if, one does it, we would for the H3 system we would end up in a diagram which would look like this. So, we will try and dissect this a bit more and try to understand this. So, let us start by looking at this diagram in a bit more detail. Here I am trying to look at HB plus HC, so I have HB, HC which is bonded and I do not yet have HA, which is still interacting with it.

So, if I just take the reactant that is HB and HC then I would see that the one which is one we can see on the left-hand side is the one you can look at it as a one-dimensional potential energy surface of HB, HC. That is, you have an equilibrium bond distance where the HB and HC are bonded, and now, in this particular case, the HA is somewhere here. This at an infinite distance.

And only once the HA starts approaching the HB, HC the energy of the system varies and then they interact and ultimately lead to the product where HA and HB are bonded and HC is left out free. And that is what one would find if you look at this particular part of the potential energy surface, here you have HA, HB which are bonded and HC is now free.

So, I hope, you see or you can imagine this where I am going from, one, two-dimensional kind of a potential energy surface of one hydrogen molecule to another that is the product and what is interesting is, how or what path does it take, that is something which is very important and we shall look at it in a bit more detail.

But to look at it in a more of a bird's eye view, what we have is, we have two degrees of freedom in the H3 system, that is, the two bond lengths which can be varied that is rAB and rBC and if we take these two as the variables, one can construct a three-dimensional potential energy service, where two axis are these two coordinates and third axis is the potential energy and that would look like what is shown here in the on the slide. I hope, this is clear or at least understandable. And if that is the case now let us go ahead and look at how does one actually take this and map it onto a two-dimensional picture so that it is easier to understand these potential energy surfaces to for further analysis.

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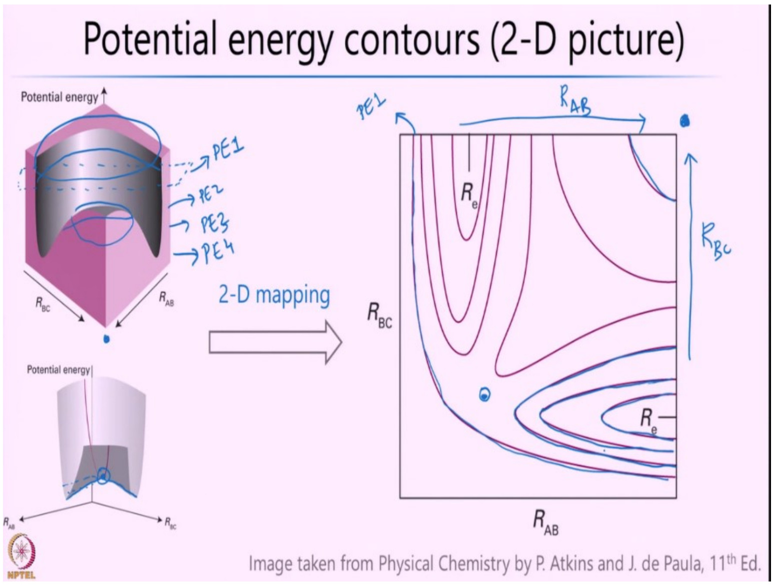

Potential energy contours (2-D picture)

Image taken from Physical Chemistry by P. Atkins and J. de Paula, 11th Ed.

So, again, we start with to map this potential energy surfaces from a three-dimensional to two-dimensional picture, let us just start by looking at this 3D picture which we have a H3 system, which is what we just looked at in the previous slide. And a just another way of looking at it is that you can now forget about the pink parts and only look at the gray area. If you just concentrate on the gray area, all I have done is, I have just scooped out the pink portions and I have just left with the gray area. And if you just now look at the gray area what you would see is something like this.

And the most the important point to note in this is that here you have the reactant which is this particular part, and then you go to the product which is this on this side that is this coordinate but what is important is, while going from the reactant to the product you go through a slightly higher energy position, which is actually hidden, if you look at this three-dimensional picture.

You do not see this higher energy point when you look at it, when you look at a three-dimensional picture. So, that is the reason why we have scooped out the pink portions and then hopefully it is a bit more clear, that while going from the reactant of the product, you have a barrier which you cross and then fall into the product regime. So, now the question is, how do I map this into two-dimensional picture.

So, to do this, what people typically do is what are called as slicing or counter maps, and that is what you see here on the right-hand side. This is what is called as a 2D contour map of a H3 system. And the way to obtain this is, first, what we need to realize is that if you actually look at this picture the three-dimensional picture, here, you have the rBC and the rAB actually both pointing at one particular direction and, whereas, if you look at the now the 2D picture, they are actually not in the exactly same orientation.

That is, this two-dimensional picture is obtained or at least it is shown by just tilting it at a particular angle. So, please realize that this diagram is actually not in exactly the same way as this three-dimensional potential energy surface, but it is just slightly tilted, so that the 2D map becomes a bit more clearer.

So, just to make that clear that point. So, if you now take this. So if you now, look at this picture, what you see is that rAB and rBC are pointing towards the top right-hand corner that is this, whereas, if you now look at the three dimensional potential energy surface, you have these two pointing at the down.

So, you will have to actually take this three-dimensional object or three-dimensional potential energy surface and rotate in such a way that this the bottom corner actually turns to the top right corner. So, then you would be able to translate or at least you will be able to imagine the how one can go from a three-dimensional surface to a two-dimensional contour maps. So, this is point number one.

And the second point is, what typically people do is, once I have done that rotation that just in plain rotation, then what people typically do is, you take a slice or in other words, you choose a particular potential energy. For example, I will let us say choose this. I am just drawing a plane here. So, I have chosen a particular potential energy let us say, I call it PE1. So, then, at this point, I will look at the and for both the coordinates how does the potential surface energy look like. And I see that, that would typically correspond to this, something like this.

Because you have the this, this shape which is going here, this particular line or this particular curve is what one would get as this, when you cut through it, you would get this particular line. So, that is what I am trying to show here. And to some extent, you would also cut this that is here somewhere you would cut, if I pass a plane through it, and these are the two lines you would get for a given particular potential energy.

Now, I will come down a bit, and I will again put, again slice it or I will again go to a different potential energy, let us say I call it PE2. So, then, I can actually keep doing like this. I can just keep slicing this or taking a slice at different potential energy surfaces, and look at how does the 2D map look like.

So, as I keep doing this, till you come to this point or till you come to this point you only cut these two sides, that is, this side and on the other side is this. Once you hit this particular point somewhere, as you keep going down the potential energy you will hit this point. At that point, you are mostly at this juncture. And now, if you actually go down further, then what you see is that you actually see this can be imagined like a small hill here.

So, if you have a small hill then if you are cutting through this, then you would get you would get these kind of let us say curved lines, this is what one would get, as you go below the top of this hill. This is the top, this is the hill top, if you go below that, then you would start getting curvatures like this. And you can actually, as you go even down, further down you would this will become actually the radius of this or the radius will become lower and you would end up at the minimum of the particular bond, that is either the reactant or the product. So, this is what typically is done to obtain our two-dimensional contour from a three or n-dimensional potential surface.

So, I will again repeat a few of the salient features which are used to attain a two-dimensional contour, that is first, you take the three-dimensional surface and you slice or you take a cut at different energies at different points and then look at how does the 2D plot look like, and that is all that you are trying to plot here on the right-hand side. And I hope this is you can visualize this to at least some extent that the way we are able to construct.

And the most important point is that if you take a look at this the bottom left picture then you will realize that there is a small hill with a barrier which is actually hidden in this three-dimensional, complete three-dimensional potential energy surface. And only below the barrier you start seeing the corresponding counter maps which correspond to either the reactants or the product. So, I hope, this gives you a feel of what are these 2D contour maps. So, having had some feel for this now let us go ahead and try to see the H3 system in a little more detail.

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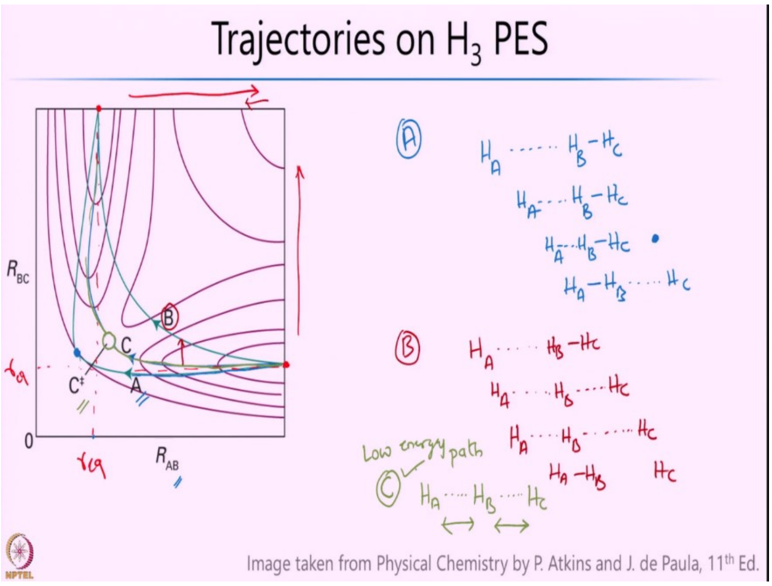

Trajectories on H_3 PES

Ⓐ $H_A \cdots\cdots H_B - H_C$
$H_A \cdots\cdots H_B - H_C$
$H_A \cdots H_B - H_C$
$H_A - H_B \cdots\cdots H_C$

Ⓑ $H_A \cdots\cdots H_B - H_C$
$H_A \cdots\cdots H_B \cdots\cdots H_C$
$H_A \cdots\cdots H_B \cdots\cdots\cdots H_C$
$H_A - H_B \qquad H_C$

Low energy path
Ⓒ ✓ $H_A \cdots\cdots H_B \cdots\cdots H_C$
$\longleftrightarrow \quad \longleftrightarrow$

Image taken from Physical Chemistry by P. Atkins and J. de Paula, 11th Ed.

So, here again, what is drawn is the same picture, which I showed you on the previous slide, that is, the rBC and the rAB. And what I would want you to realize or appreciate is the following. That if you now look at the I am just going to draw a dotted line here. So, this is the equilibrium distance for AB which is the product, and similarly, I can draw something along this line and this is the r equilibrium bond length for the reactant that is B and C.

And if I were to, this is where the they would all the energies would go towards infinity or towards the isolated atoms. So, if I have this particular picture, so then, if let us say, I have an hydrogen A which is coming towards HB, so how should it come on the potential energy surface? So, there are three possibilities, and we shall look at all of them in detail.

So, the possibility number 1 is, or let us call it A because that is the notation we are using here. So, I have HA and HB, HC so this is coming approaching this so, what I have tried to show is that the HA is approaching the HB, HC progressively and at that moment the HB, HC is kept constant or the equilibrium bond length of HB, HC is kept constant, it does not move.

And at beyond a certain point, now, after this what happens is, that, HA and HB bond and then you have HC which is left out. So, this is one particular scenario where I have the HA which is approaching the HA is approaching the HBC progressively and in all this time the HB and the HC bond length or the equilibrium moment is kept constant, it does not changed. This is one particular scenario you can think of.

If that is the case let us see, how does the potential energies or the trajectory would look like on a 2D counter. So, we said that rBC is the equilibrium distance for the BC. So, that is what we have kept constant here. If you now look at the trajectory which is marked with A that is this particular line, if you start taking a look at this particular line the r equilibrium is more or less constant, it does not change pretty much till you hit this line, till you hit this curve. And through all of this what is changing is, the hydrogen atom, which was far away is actually slowly coming in, slowly coming in and trying to go towards HB, HC bond that is what we have shown here on the right-hand side.

Once it is at almost this particular juncture, let us call this dotted point, at this point, what happens is then, suddenly the HB, HC bond would break apart and then the HA, HB would bond would form and you have a significant lowering of energy and that would lead to formation of the r equilibrium AB which is the product here, which is what you would see. So, this is one particular trajectory the reaction can take place.

But if you already notice, what you see is that this is along a slightly higher energy path because you are looking at it from this path almost coincides with an outermost line, which means, the reaction is taking place along a higher energy surface. So, now, the other option or the other possibility is what is called as B let us take a look at the B.

So, the HA is here and let us say HB, HC is to begin with. So, in this particular case, what is happening is, HA is approaching the HB, HC. But in this case, the HB, HC bond is actually getting loosened up far more quickly, it is actually going from the equilibrium bond length the HB, HC is slowly opening up or its HB, HC are dissociating much more rapidly than the approach of the HA. This is another scenario.

So, you can think of these two are the most classical ends of the spectrum. So, if this is what is happening, then you would go along this path which is shown here B that is at even a small approach of HA, which is along this direction, you see that there is a significant lowering of the r equilibrium that is this angle, this distance is actually now going is increasing. And by the time it comes to equilibrium, it has increased so much and then suddenly it will then it will the HB, HC will break and will form a HA, HB.

Then one can write HA, HB and HC is lost. So, this is another example where the dissociation is much more pronounced compared to the approach of the incoming hydrogen atom. However, the another possibility is that both these processes, that is, approach of the hydrogen atom and the weakening of the HB, HC bond can occur to the same extent or to a similar extent. So, that is what we will call it as a case C.

So, in this case, the approach and the breaking, these two processes are occurring at the same distance or are occurring to the, occurring to a same extent. So, in that case what would happen is, you will take this particular path which is the C you go along the path C, and then, you ultimately end up in the product here.

So, this path, where you get the, where you go through this particular pathway is when you actually cross that small hill which I told you in the previous slide, where we had scooped out the pink part and only looked at the gray part. I hope, you remember that there is a small hill and along the path C actually you have crossed the top of that hill which is the C. And it turns out that C point C is the or the C dagger which is shown here is the least energy path among the A, B, C.

So, the reaction would invariably would like to go along C rather than A and B because A and B are higher energy or this is the low energy path, the C. So, this point or the C dagger is what is also called as a saddle point or a transition state and the geometries in and around that are what are called as activated complexes.

So, if a reaction is taking place along this particular trajectory or path then there is more likelihood of the reaction falling into the products rather than when it goes along A and B. So, I hope, this has given you at least some idea on how to look at the trajectories on a potential energy surfaces, taking H3 as an example. With this, we shall stop now. In the subsequent classes we shall look at a bit more of the finer details. Thank you.