Introductory Quantum Chemistry

Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 16
Tunnelling-Part II

We were actually discussing the phenomenon of Quantum Mechanical Tunnelling. This happens with particles which obey quantum mechanics that essentially, makes that light particles very light. Atomic and nuclear particles will exhibit this phenomenon of tunnelling. And the problem that you were thinking of is drawn on the board there is a barrier of width a.

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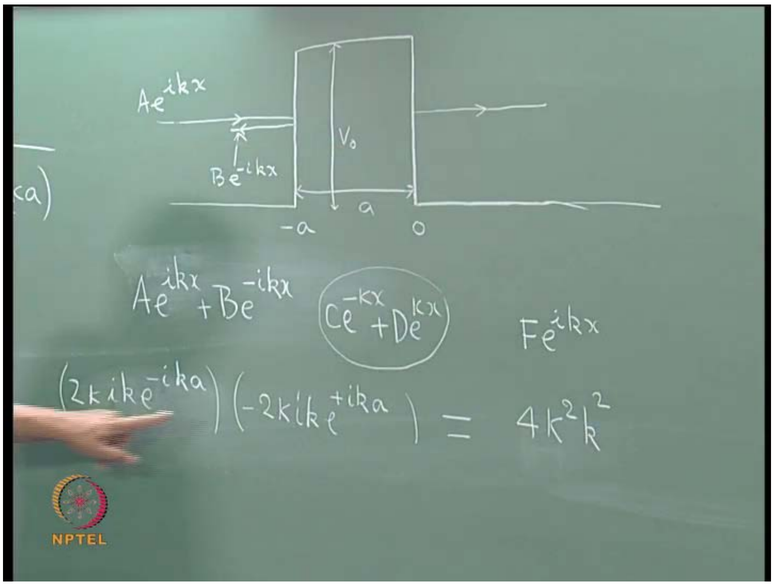

And, it has a height of V 0. And a particle of mass m is incident from the left hand side that is; actually represented by this wave function. And the possibility is that the particle may get reflected which is represented by that part of the wave function or the particle may go to the other side which is represented by this part of the wave function. And in the barrier in the region of the barrier.

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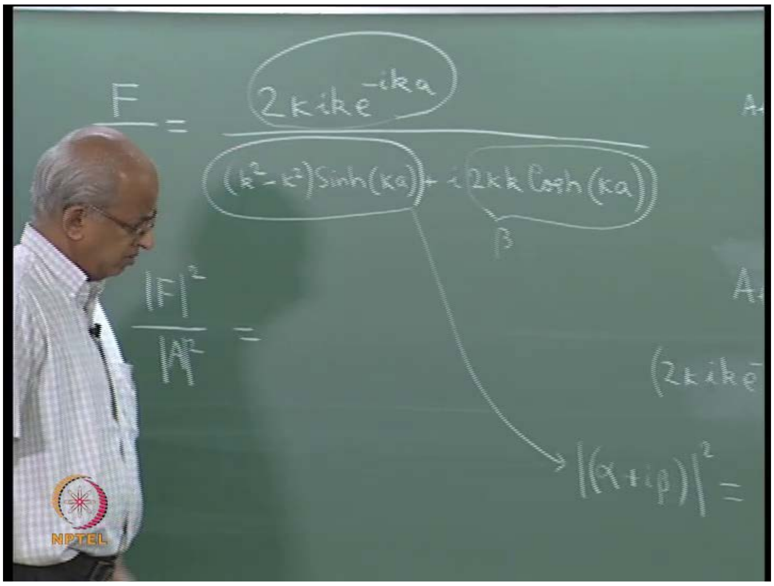

You see the wave function is given by that expression. And did I load the algebra? We eventually arrived at an expression for F divided by A which is to reproduce on the board. And the quantity that we want to calculate is actually; the square of the magnitude of F by A; why is it? So, when you see the number of particles that are incident from the left hand side is essentially determined by A. In fact, it is proportional to magnitude of A square. And the number of particles that come out on the other side if you had done this experiment with a beam of particles, the number of particles that will come out on the other side will be determined by magnitude of F square. So, therefore; the transmission coefficient or the tunnelling probability for the particle will be given by magnitude of F square divided by A square magnitude of A square.

And, so, therefore; I mean, I want to calculate this. How will I calculate this? When you see I shall calculate the magnitude squared of that quantity and divided by the magnitude squared of that quantity, that is; all that I need to do. So, let me first calculate the magnitude square of this quantity. So, you see you have 2 kappa i k e to the power of minus i k a. So, this is the complex number. And if you had any complex number how will you calculate its magnitude square? All that you need to do is you take the number multiplied by its own complex conjugates. So, when you take the complex conjugate of this you are going to get minus 2 kappa i k e to the power of plus i k a. Notice what has happened there was an i here and therefore; I have put an minus i and there was an minus i here that therefore, converted to plus i. And if it calculated this the result is the following this term and that term will cancel each other. You are going to get 4 kappa square k square and this i and that minus i will give you minus i square, but remember i square is minus 1.

So, therefore; the net answer is just 4 kappa square k square. In a similar fashion I am going to calculate the magnitude square of this, notice that you say this is the actually of the form some constants which I may refer to as alpha. And another constant which is this one I shall denote it as beta. Where this part I am denoting as alpha and that part I am denoting it as beta. So, therefore; it is of the form alpha plus i beta.

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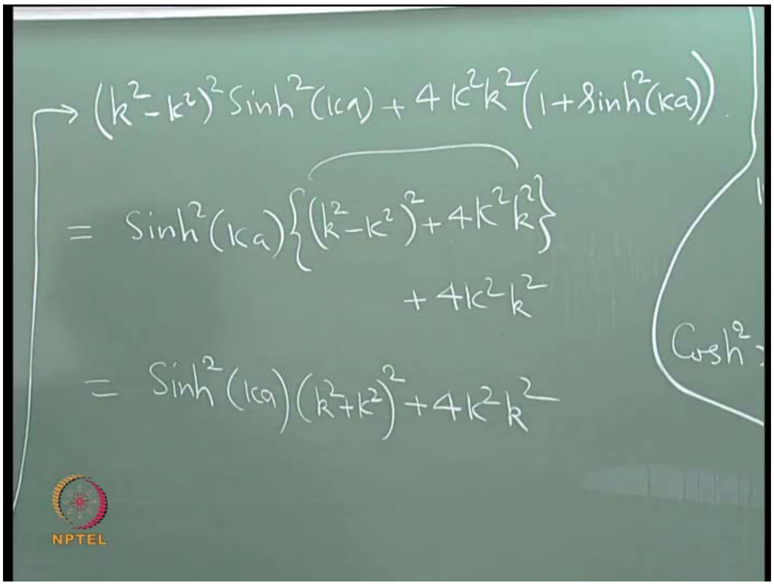

And, I want to calculate magnitude of this square. And if you know a little bit of about complex numbers, you would realize that this noting, but alpha square plus beta square and. So, what I have to do is I have to take the square of this, add to it the square of that. So, what would be the result? It is going to be k square minus kappa square sin h kappa a. You take the square of this and square of that add to it the square of that term which will be 4 kappa square k square cosh square kappa a. And let me continue this up here, k square minus kappa square, 4 square sin h square, kappa a plus 4 kappa square k square, you have cosh square of kappa a. But there is a trigonometric eternity which is use full it says that cosh square x, can be written as 1 plus sin h square x for any x. So, I am going to use that and hence; I am going to get here 1 plus sin h square kappa a. And that actually; is equal to you can see that there are terms common in right there are terms that contains sin h square.

So, I will write this as sin h square kappa a into k square minus kappa square the whole square plus 4 kappa square k square plus 4 kappa square k square. And this is nice, why it is nice? Because I can maidenly simplify this part. Let me just write the answer because it is symbol. So, that is the answer. So, where you have it evaluated the magnitude square of the numerator, we have also evaluated the magnitude square of the denominator

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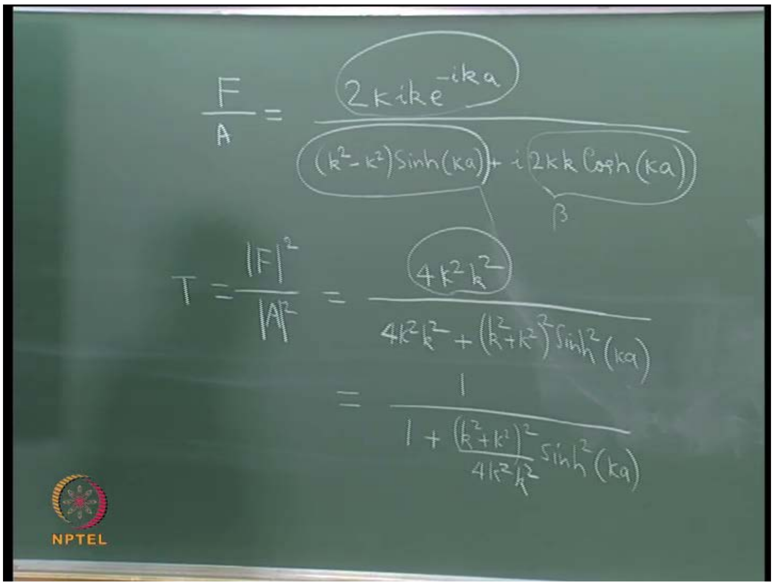

And, you can use this result is to get an expression for F square divided by A square, which we will preferred as the tunnelling probability or the transmission coefficient. And denote by the symbol capital T. So, what is the answer if you collected all this results? The result is 4 kappa square k square, that is; this fact, this term divided by 4 kappa square k square that is; actually, this term that I am writing or this term that I am writing. So, this is the answer for T. And we can write it in an even simpler form by saying that, I will divide numerator and denominator by this term.

So, therefore; you would have a 1. And if you divided the denominator by that term you will have 1 here also. So, therefore; you will have 1 divided by 1 plus k square plus kappa square, the whole square divided by 4 kappa square k square sin h square kappa a. So, this is our final expression for the transmission coefficient or in the case where energy of particle is less than the barrier height. We referred used to refer as the tunnelling probability. And now; if you like we can actually, substitute the expression for k square and kappa square.

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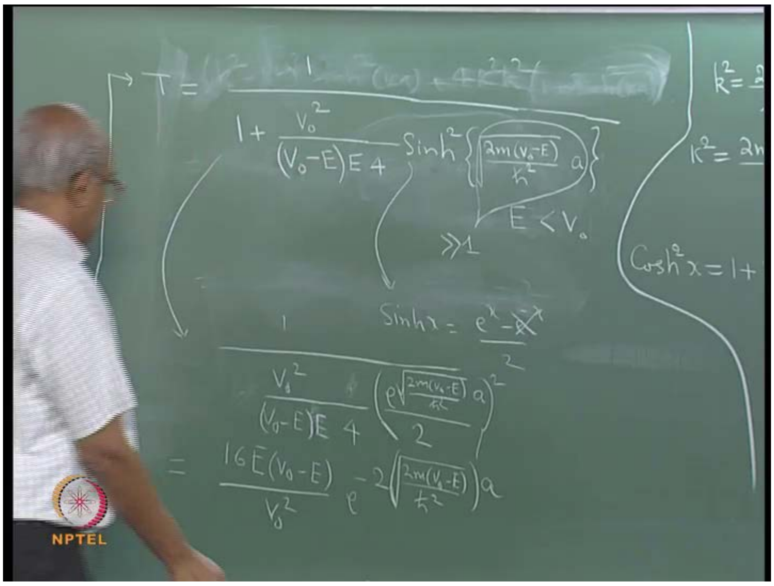

Let us do that I have the expression for k square I also have the expression for kappa square. So, if you substituted those things. Let me do it here, well this is fairly straight forward substitution I shall just write the answer. I will write this kappa a in more detail and I am going to get. So, this is; the answer written in a little more detail. And this expression is nice because it tells you how the tunnelling probability or the transmission coefficient actually, depends upon the height of the barrier which is contained in here, it is contained in there also. It also tells you how it depends upon the energy of the incident particle? And as well as on the width of the barrier. Now, also remember that I have derived this assuming that energy of the particle is less than the height of the barrier.

So, let us imagine a situation where the particle is rather heavy. May be, something like a carbon atom or something like that well struggles raging of what I should say is this or that is much larger than unit is suppose, that is; the limit that I would like to think of. In order for that to happen, you see either mass has to be large or the barrier height has to be large or the width of the barrier has to be large if one of these things is satisfied. So, that the net term this net term is much much larger than 1. Then you can see what is going to happen? See sin h square or sin h x actually, is e to the power of x minus e to the power of minus x divided by 2. And if x is very large which is what we are thinking of this e to the power of minus x can be neglected. And therefore; under that limit this will become 1 divided by1 plus V 0 square divided by V 0 minus E into E divided by 4 sin h square where actually, sin h x may be approximately e to the power of x divided by 2.

So, therefore; I shall have e to the power of square root of 2 m V 0 minus E divided by h cross square. This square root covers that h cross that also e to the power of a. I have to take the square of that, this is the answer. And further you see if this term is very large I am safe in neglecting these 1 in comparison with that m. So, let me forget that m this 1.And, hence what is the answer that I get? Well I seem to have forgotten half which should have been here, because is sin h x is given by e to the power of x divided by 2. So, now, again I can simplify this expression in this particular limit the answer that I get will be 16 E V 0 minus E divided by V 0 square e to the power of minus 2.

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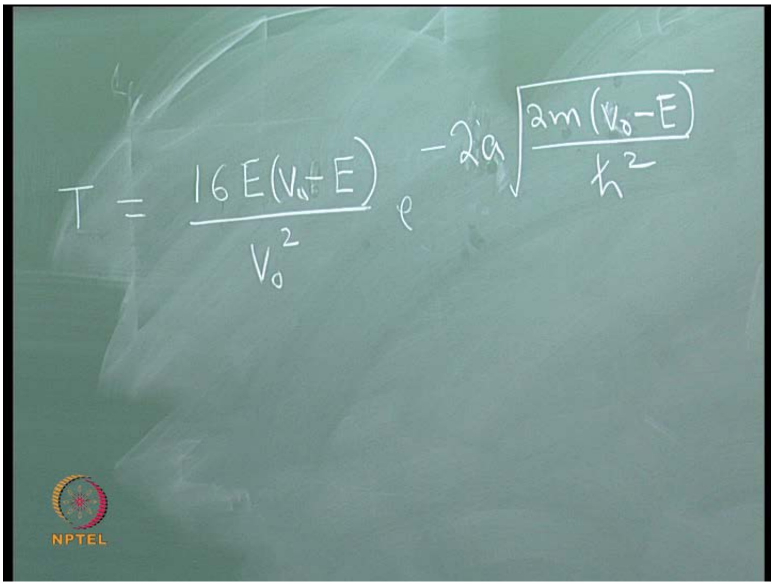

So, this is the result that I get. Now, this is an interesting expression why is it interesting? The reason is this. So, remember V 0 is the height of the barrier. And a is the width of the barrier.

So, suppose, I make the height of the barrier larger; that means, I am increasing the volume V 0 what will happen to the tunnelling probability? The answer is physically obvious if I made the barrier more difficult to go through then; obviously, the tunnelling probability will decrease. And that is actually reflected in the equation you see you have V 0 in the exponential though if you increase V 0 what will happen? This time it is going to get smaller. Because V 0 is in the exponent with a square root it will get smaller of course; and further if you made the barrier width larger; that means, you are going to increase the volume a. Again, as expected you will find that the tunnelling probability decreases. Again, you should remember, that is; it is decreasing in an exponential fashion. And therefore; the decrease is rather rapid as you make the barrier wider and wider the probability that the particle will pass through decreases very rapidly.

And, again you can ask how does it depend upon the mass of the particle while if the particle is very heavy? Then you would expect that it obeys classical mechanics rather than quantum mechanics. And in classical mechanics the particle will never go to the other side. And you look at this expression you have m sitting again in the exponent. So, if you increase the mass of the particle the probability that the particle will tunnel through decrease again very rapidly.

And, so In fact; actually it is found that electrons of course; can tunnelled very easily. But in comparison with that a proton, which is much heavier will tunnel with a much lesser chance. And if you think of an atom like carbon it is much much heavier than the hydrogen. And therefore; there are almost no cases except may be one that I know where a carbon atom actually, tunnels through a barrier. Now, to get an idea of how the quantity depends T upon V 0 E and a I shall make plots I shall show you the plots. And in order to make the plots.

You see I shall make use of some variables which do not have dimensions. So, what I shall do is I shall measure the incident energy of the particle incident energy of the particle is E. So, I shall think of having the variable E divided by V 0. And you can see E is energy V 0 also is energy. So, E by V 0 is dimension less. Similarly, from here; I can introduce another dimension less object which I shall define as delta. And delta will be defined to be equal to h cross square divided by 2 m a square.

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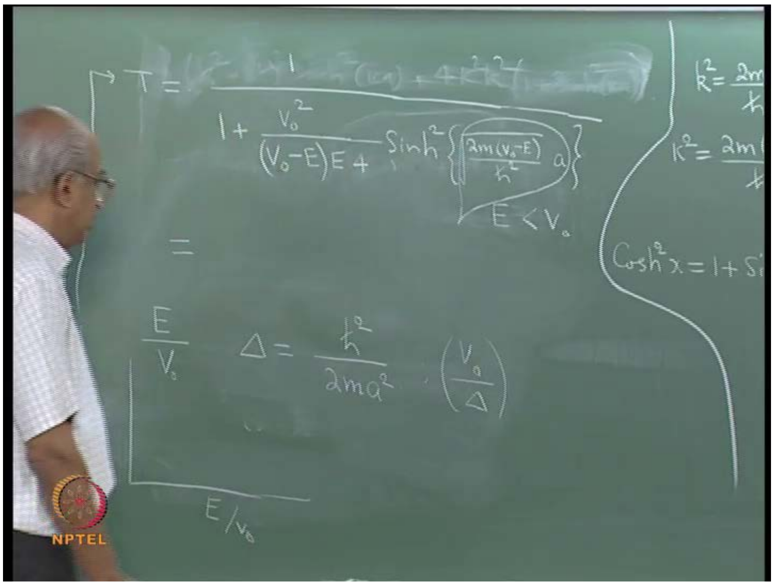

Let me just check this definition. So, this is delta if you look at this you see delta depends upon the mass of the particle and their width of the barrier. And if you calculated the dimensions of this quantity you will find that the dimensions are that of energy. And therefore; I can have another dimension less quantity which is V 0 divided by delta.

So, what I will do is I will make plots in which I shall show the tunnelling probability or the transmission coefficient as a function of E by V 0 right. E by V0 will be taken along the horizontal axis. T will be along taken along the vertical axis. And I shall make the plot for different values of this ratio of V 0 by delta ok.

Let us look at such a plot. See for example; this plot is for V 0 by delta equal to 25 remembers that, V 0 by delta is dimension less. And for such a situation if you plotted T as a function of E by V0.You will see that the result is this blue curve. And just to compare what I have done is that I have also plotted the transmission coefficient for a classical particle another. For a classical particle if the energy is less than V 0. You see you are in this range where the horizontal axis varies from 0 to 1.

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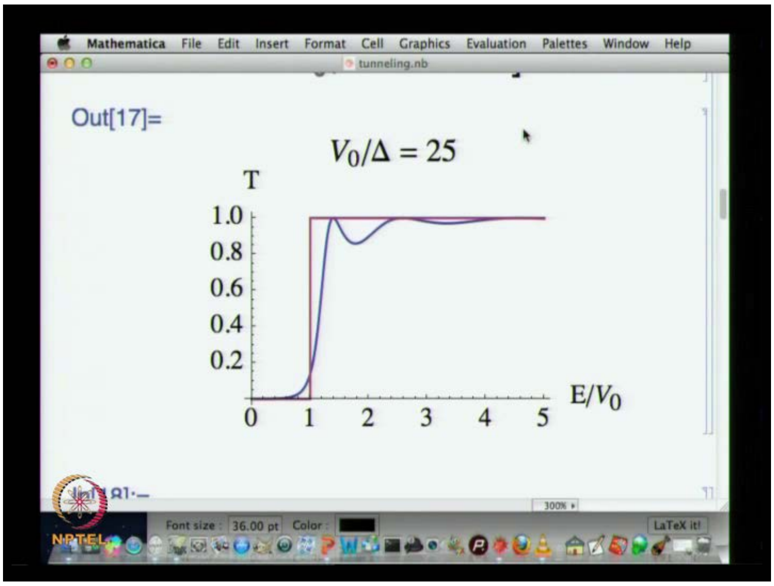

So, in that range for a classical particle T will be equal to 0. And if E greater than V 0 you are in this range and for a classical particle that they value of T will be equal to 1. So, therefore; in this range you have classical E you have T equal to 0. And in this range you have classically T equal to 1. And therefore; you have a step function like appearance. So, that would be the rate case.

If the particle behave classically, but quantum mechanically if you say that V 0 by delta is equal to 25 the curve is this blue curve. And you can see that even in the case where the energy of the particle is less than the height of the barrier. The particle can actually go through this part shows that there is a finite probability of tunnelling for the particle. And the other thing that you should notice is that even if the energy of the particle is greater than the height of the barrier for example, here; the probability that the particle will go through is not unity that it in classically, it would have been unity, but it is not.

So, in the case of a quantum mechanical particle, for example; at this value V their transmission coefficient is only 0.4 which means; that if I had 100 particles incident one edge on the barrier only 40 of them will go through, the remaining 60 will be reflected. So, it is actually possible to derive an expression for the reflection coefficient also. What would be that R? Would be given 1 minus T is the transmission probability or transmission coefficient. And therefore; the reflection coefficient will be given by 1 minus T you can calculate that also.

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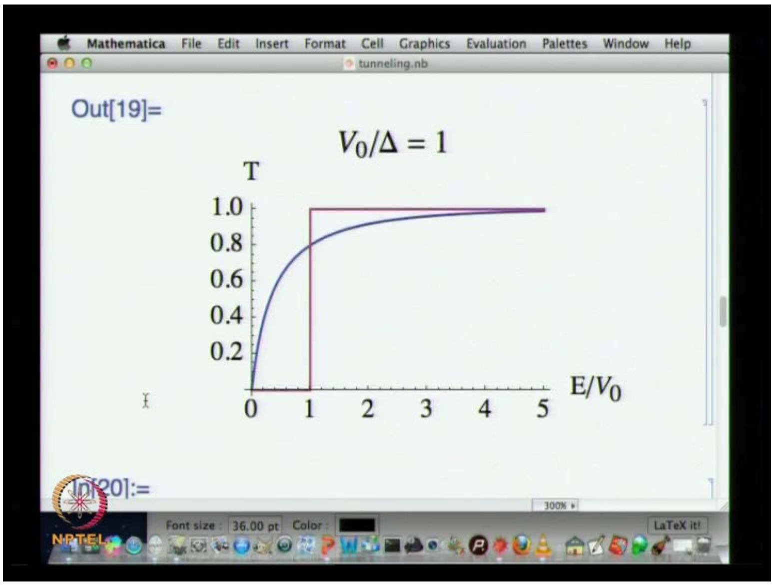

Now, suppose you had a different value for V 0 by delta. What would happen? Well this is what V0 by delta is equal to 16. And I also have a plot for the case where, V 0 by delta is 1 this means; that the V 0 by delta is 1. What does it mean? This actually means that you see the either the mass of the particle is very small or may be width of the particle is very small. And in such a situation what happens?

You can see the plot if you plotted T against E by V 0 you get this curve which shows that there is considerable probability that the particle will tunnel through, which is not surprising because you see the it is a light particles. So, it would go through the barrier as a wave and go to the other side. Now, coming to its importance in chemistry, when this expression which I just rubbed off I actually needed with it is the16 E into V 0 minus E divided by V 0 square e to the power of minus 2 into square root of a.

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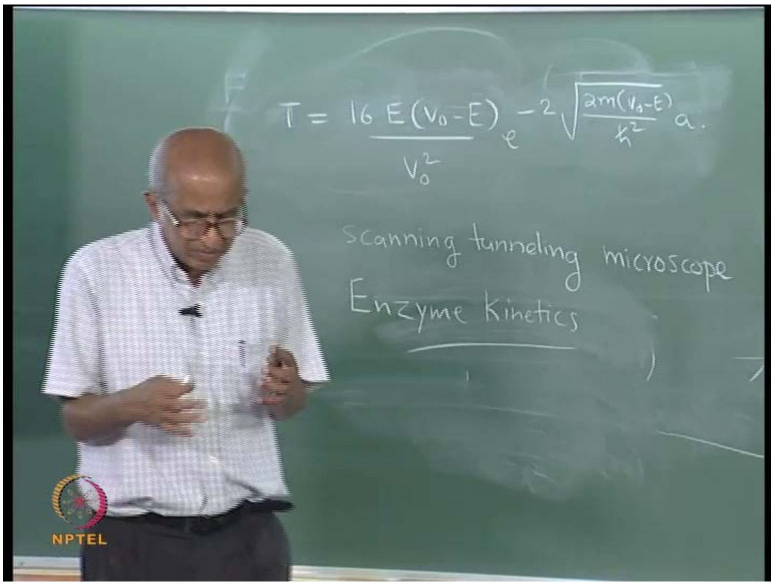

Now, let me tell you the different phenomenon in which tunnelling sorry, different experiments in which tunnelling can be observed. The most important one is actually, this technique which is referred to as the scanning tunnelling microscope. So, this the technique now, which is very widely used.

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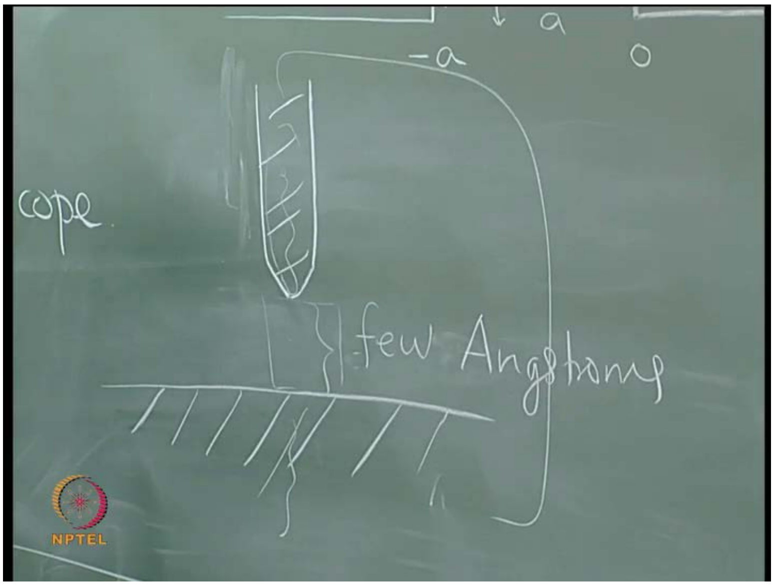

It has the normal as application in chemistry. What she is done is, you have a very sharp metallic tip something like that. And it is believed that the tip is actually perhaps, only 1 atom at the end. And it is a metal and what you do is you bring it near the designative of another metal. And you bring it may be within about 2 Armstrong's or 3 Armstrong's or 6 Armstrong's. I mean a few Armstrong. Now, you know that there are free electrons in this metal tip. There are also free electrons which are free to move in anywhere in the metal. There are free electrons here, there are free electrons there. But this portion is just vacuum. So, therefore you see if you think of an electron in the in the tip it can move freely anywhere within the tape. And that electron of course; can move freely anywhere in this region, but you see in this region there is no metal. And therefore; that region would act as a barrier. So, the situation is analogous to this, but of course; this is a three dimension where, what we have considered is a one dimensional example. So, what you can do is you can actually bring the metal close.

So, that is; the tip closes to the metal surface. And then I apply a potential difference between these 2. And that potential difference will actually, cause the electron to tunnel through the barrier to the other side if you apply potential difference. You can actually, observe a current because of this tunnelling process. And this is a technique, that is; immensely useful in surface tanks. So, this is one application and the other application that I would like to mention is in Enzyme Kinetics. Now, there are hydrogen over proton transfer reactions occurring in biological systems. And these usually are cartelised by enzymes. And hydrogen or proton they you know that they are rather light in comparison with other nuclei. So, if you think of a proton it is 12 times lighter than the carbon atom. If you think of a hydrogen atom or a proton it is roughly 12 times later than a carbon atom. And therefore; it is mass regency is small ok.

And, in such a situation it is actually, possible for a reaction to proceed by proton tunnelling. I suppose you know little bit about chemical reactions see whenever you have a chemical reaction there is a barrier that the system has to cross the barrier is usually represented by something like this. And so you imagine you have a proton on this side it can actually in general what it will do is the proton has to climb over the barrier to other side that we normally says thermal activation. But on the other hand the closed proton is a quantum mechanical object it is forcible for the proton to tunnel over the barrier. And go to the other side.

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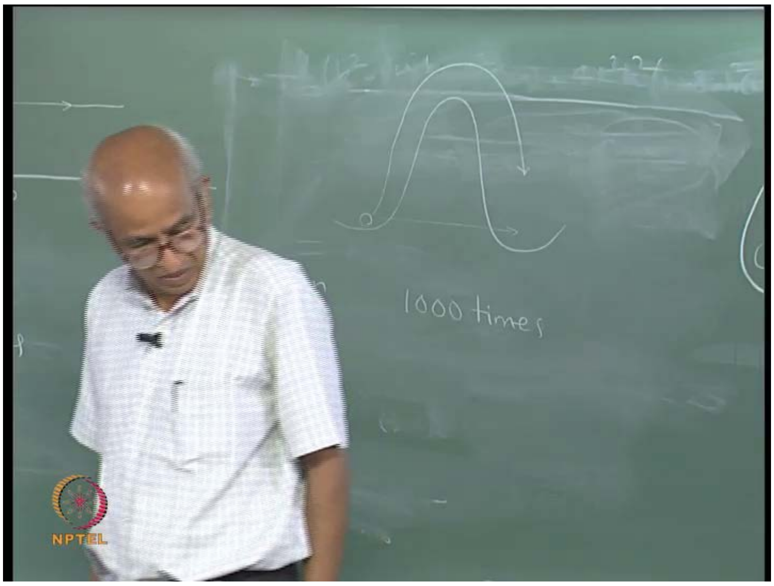

And it has been suggested that, it occurs in a same kinetics and it has been suggested that tunnelling actually, speeds up the process, speeds up the reaction up to perhaps, about 1000 times. So that is another very interesting application or another very interesting system were tunnelling occurs. Then if you remember your organic chemistry you see there is this molecules cyclobated dyne. This is cyclobated dyne; this is an unstable molecule because it does not satisfy the chuckles foreign plus 2 rule.

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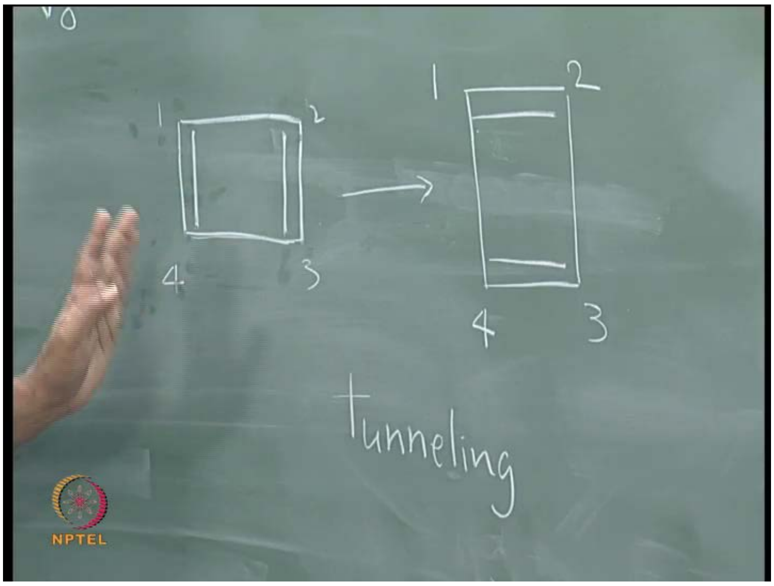

It has only 4 electrons in this conjugated system. And as a result of that it is unstable. But I mean; if you look at the ground state of the molecule the geometry actually would be like this. You have 2 enthral like bonds and a 2 single bonds here. So that, this is term actually, is like a rectangle. And at very low temperatures we can keep the system at very low temperatures. And if you keep it isolated from other cyclobated dyne molecules. So that, there is no reaction between the 2 perhaps, you can put it in organ metrics. And keep it at very low temperature then you can actually, isolate the system. But then if you think of this molecule you see it can also let me just number the carbon atoms. So, 1, 2, 3, 4 you can have this molecule.

You can have an arrangement where that the build bonds are not between 1 and 4 and 2 and 3, but they may be like this. So, the double bonds are between 1 and 2 and 3 and 4 it is same molecule. But the way the bonds are distributed in their distributed among the carbon atoms is different, but this and that would have the same energy. And hence; you see if you melt the molecule with this arrangement it is actually possible for the molecule to change over to that arrangement.

But of course; to undergo that change what should happen is that this 2 bonds should elongate and those 2 bonds should contract and that requires energy. And therefore; to go from here to there is a barrier. But it has been suggested that this process occurs through tunnelling. And this is very interesting, this is; why it is interesting because you see in here, the atoms that are moving actually involved carbon atoms also. And therefore; this is not a hydrogen atom tunnelling, but the tunnelling process involves carbon atoms also.

And, so this would be an example, where a much heavier atom tunnels. Then another interesting process where tunnelling is very important is nuclear fusion. You know that the sun gives out it light because fusion reaction happens in the sun. So, what is fusion reaction? While you see imagine you have 2 nuclei let us say 1 nuclei is here, may be a proton or some nucleus it does not matter. What it is the nucleus will be positively charged here, is another nucleus I mean minable simple positive charge, but let us say it has for the sake of simplicity? Let me just put 1plus ion on each one of them. So, these 2 nuclei have to come together and react to give a heavier nuclei they have to fuse together to give a heavier nuclei there to give a heavier nucleus.

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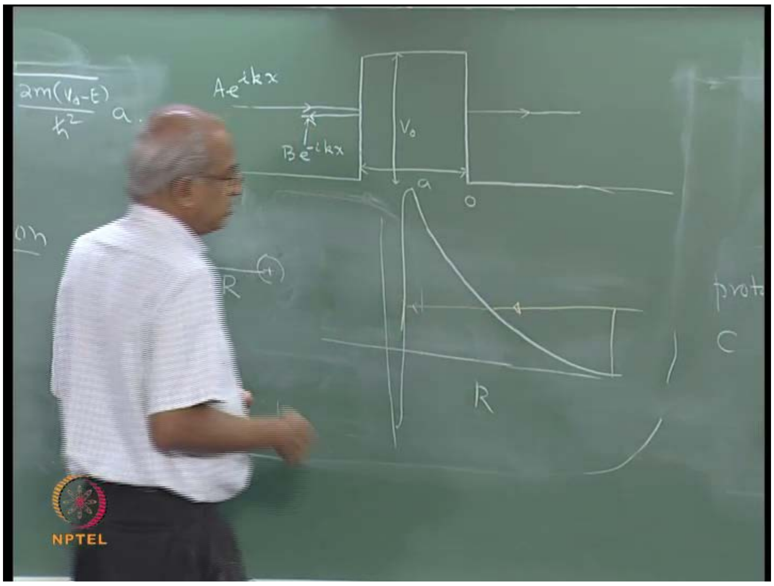

So, because these are positively charged there is repulsion between the 2 as the 2 are approaching each other what will happen? If you plotted the total energy of the system as a function of the distance between the 2. Let me say the distance between the 2 is denoted by R. And it has plotted the energy of the system as a function of the internal of the distance between the 2 nuclei.

So, there is colon berg repulsion between the 2 nuclei is. So, what will happen? The energy will actually, go on increasing to a large value. But then when they are sufficiently close to each other right. The particles within the nucleus will feel the attractive interaction with the particles of the other nucleus. Nuclear force is essentially, as a result of which the energy of the system will turn around and come down. And that is why the fusion reaction can actually take place which will turn around and come down. And therefore; suppose you see you are bringing the 2 nuclear together with an energy with a kinetic energy of let us say that much ok.

Now; obviously, you see this is not enough to go over the barrier. And In fact; if you think of the sun you see the average kinetic energy with which the 2 nuclei come together is not enough for the system to go over the barrier and fuse together. And therefore; in the sun when a nuclear fusion reaction takes place it is always through tunnelling. So, what happens is that the system tunnels through here and then with the 2 fuses together. And finally; one more interesting example, you know that in your mobile phones you have if touch screens which are sensitive to touch. And something like 3years ago people have made a film.

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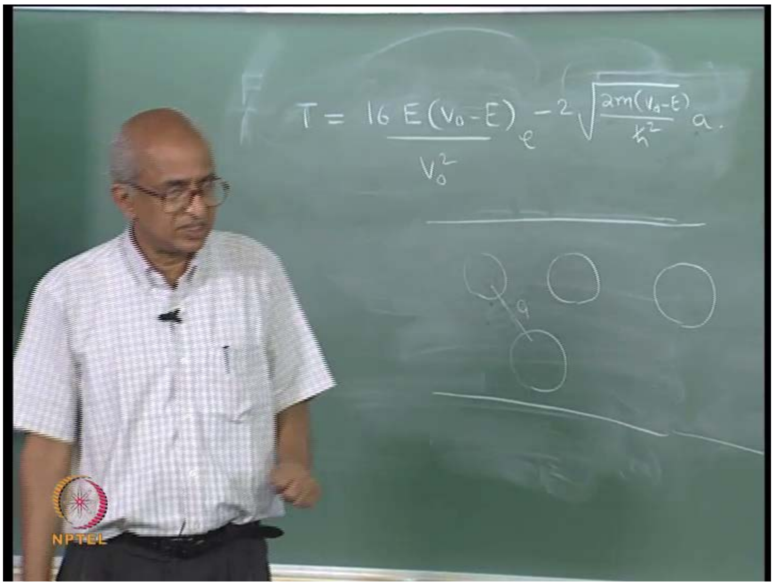

Now, this is film which is actually touch sensitive. And which walks based up on quantum mechanical tunnelling. So, imagine you have a polymer film. And you have metallic, Nano particles embedded maybe; I should draw a bigger figure. This is a film and you have metallic particles, Nano particles embedded in the film. And it is actually possible for electrons to tunnel from this Nano metallic, Nano particle to that metallic, Nano particle of course; it is a distances should not be very large it may be something like because these are electrons are tunnelling and they are lighter than protons. And therefore; they can tunnel over larger distances. But may be something like 16 Armstrong's or 20 Armstrong's or may be less which the distance that they can tunnel right.

But notice that you see that the tunnelling probability is very sensitively depended up on the distance between the 2 particles or the height of the barrier. You see here you have a metallic, nano particle there you have a metallic, nano particle. And you probably have polymer metrics in between these 2. So, if you change this distance this is our essentially over a if you change that distance the tunnelling probability will increase their huge amount. And now; what you can imagine is that, imagine you touch the film from the top then that you are applying pressure on the film, as a result of which this distance will change.

And, hence the tunnelling probability will change. And therefore; the current that can flow through the system, the conductivity of the system actually will increase very rapidly if you just touched it. And this has been used to make touch sensitive screens. In fact, very interesting videos of many of these thing are available in you tube. I suggest that you should have a look at you tube you just search for quantum tunnelling. And you will find many of these videos. I think I will stop here.

Thank you.