Quantum Chemistry of Atoms and Molecules
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Lecture-11
Quantum Mechanical Tunneling

We have discussed particle in a box where the particle was confined in a box with infinitely high walls as far as in terms of potential energy. And then we completed the discussion in the last module saying that experimentally it was seen that alpha particles come out of radioactive nuclei even though their kinetic energy is lower than the potential barrier offered by the nucleus from which they come.

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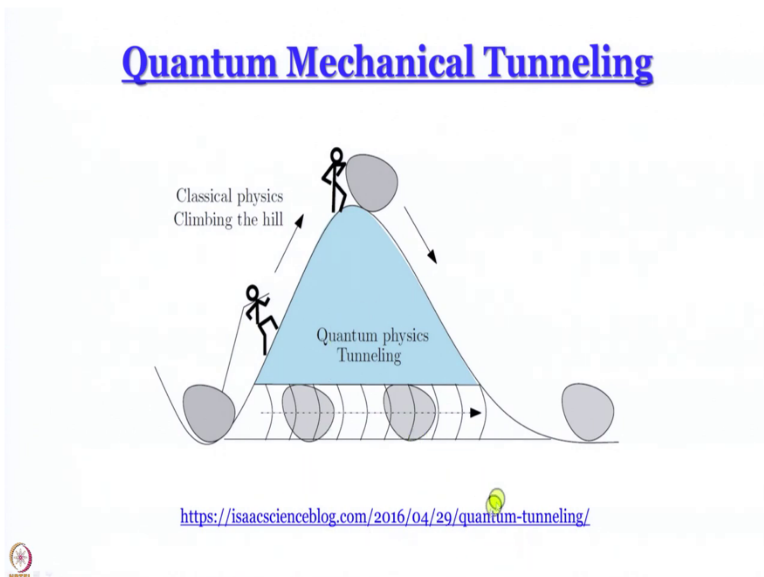

So, the situation was pretty much like this cartoon where well this is available on the Internet where you are supposed to push this stone above a small hill in classical world we push it up and then we have to come to the other side which means you have to surmount the energy barrier. In quantum world as we will see and as is suggested by this alpha particle experiment it appears that a quantum particles can tunnel through it is as if there is a tunnel so you cannot do not have to go up the hill you just go from here to here through the tunnel.

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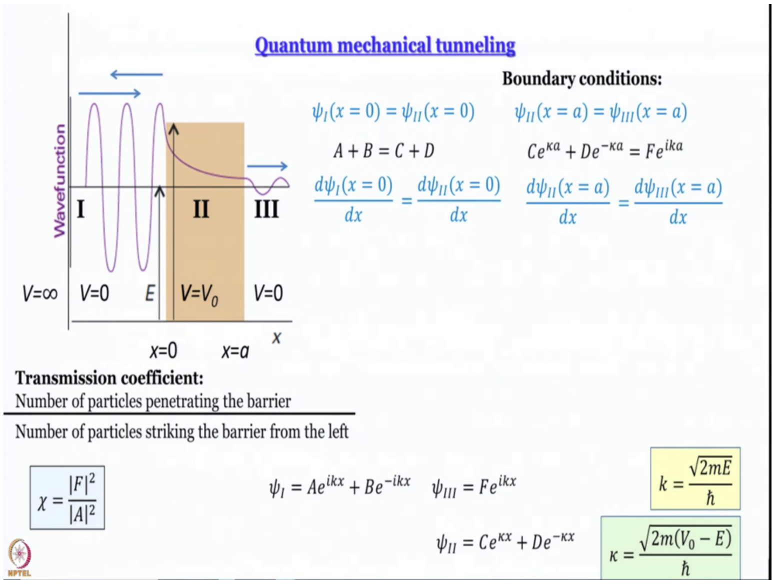

This phenomenon is called quantum mechanical tunneling and that is what happens when we have a potential barrier which is finite and not infinite. So, let us understand the system that we are going to discuss. So, what we have is that we have the same particle in a box if we start from the left-hand side we have an infinite potential in the model that we are discussing in the next step we are not going to discuss it here but I encourage you to do it by yourself self-study.

One can also see what happens when this potential is also not infinite but to make things keep things simple let us say the first potential barrier is infinite. So, if you go to the left you have V equal to infinity then you have region 1, analogous to the box we had earlier where V equal to 0, so as long as the particle is in region one this its potential energy is equal to 0 and then there is a an energy barrier of finite height and finite width.

Now we have written x equal to 0 here where the second barrier starts because that makes the mathematics easier one could write this is x equal to 0 this is x equal to L the expressions will be a little more complicated that is all. So, here are what we say is that let us say that we have a barrier whose width is a small a. So, starting point is x equal to 0 endpoint is x equal to a so beyond x equal to a once again V equal to 0.

But between x equal to 0 and x equal to a, V is some finite value of V0 ok this is the height of the barrier and what is the energy of the particle? Let us say the energy is E you will notice here that E is the arrow denoting E is smaller than the arrow denoting V why because do not forget the entire question arose out of that radioactivity problem where kinetic energy of the alpha particle was less than the potential barrier offered by the nucleus ok.

And remember this E here is as long as it is in this region it is essentially kinetic energy when it goes here it will have contributions from potential energy also, so three regions. First region very similar to the box except for the water on the right hand Psi region one will be equal to 0 region 2 will be equal to V 0 region three where V equal to 0 once again the difference between 1 and 3 is that this is unbound it can go up to x equal to infinity.

Let us slide Schrodinger equation for these three equations three regions and while I speak I encourage those of you who are seeing this video taking this course please grab a pen and a notebook and start writing yourself that way we understand better. So, Schrodinger equation for regions 1 and 3 are the same, why? Because V equal to 0, so that is going to be minus h cross square by 2 m d 2 Psi dx 2 is equal to E Psi very simple ionic only kinetic energy is there no question of potential energy potential energy is equal to 0 no problem.

What about region 2 that also is simple minus h cross square by 2 m there is a typo here I am sorry minus is missing oh no there is no typo I have actually rearrange the equation h cross square by 2 m multiplied by d - Psi dx 2 is equal to V 0 - E x Psi Schrodinger equation for region 2 where V equal to V 0 is after rearrangement h cross by 2 m d 2 Psi d x 2 equal to V 0 - E x Psi please write Schrodinger equation yourself as minus h cross square by 2 m d 2 dx 2 + V 0 operating on Psi and giving Psi and convince yourselves that upon rearrangement you are going to get this equation h cross square by 2 m d2 Psi dx 2 equal to V 0 - E Psi.

So we have written Schrodinger equation no problem. What will the wave functions be for region 1 it is like free particle or well particle in a box and this time instead of writing that sine function let us write A e to the power ikx plus B to the power minus ikx you might remember from our earlier discussion that one can use either this or that because when you have exponential imaginary terms there are linear combinations lead to cosine or sine terms.

Whether that function is imaginary or not depends on the coefficients A and B in case of particle and coefficients are such that coefficient of cos term is 0 coefficient of sine term is a real number. So, we can still write A e to the power ikx plus B to the power minus ikx we do that because we have this idea that e to the power ikx, e to the power minus ikx are eigen functions of the linear momentum operator.

What about Psi 3 same thing but let us just write different expression for the different coefficients let us write F e to the power ikx plus G to the power minus ikx, k remember is root over 2m E by h cross. What about Psi 2 again we can write a similar form of wave function C e to the power this time we write Kappa x we write it a little differently because here the situation is different for region 2 than for regions 1 and 3 V 0 is nonzero. So, we write Kappa incidentally if you see Atkins book Atkins has used Kappa for this region if you read pillars quantum chemistry book K and Kappa interchanged.

So what I have essentially done is that I have adopted Atkins nomenclature, Atkins convention but I have performed the treatment as discussed in pillars book as you understand for complicated expressions one can rearrange to get another complicated expression. Expression will get is the one that is there in pillars book but end of the day no matter which book it is provided her correct they all mean the same all right.

So Psi 2, Psi in region 2 here in the barrier is C e to the power Kappa x plus d to the power minus Kappa x we will come back to what kind of wave function that would be and here it is important to understand that that imaginary function is not there because we will draw it in the real. Also Kappa is root over 2m not E but will V 0 minus E divided by h cross that is important because you have rearranged it in this way it is a differential equation this is what the solution is going to be.

Now let us apply some boundary conditions. What are the boundary conditions? Psi must be continuous upon going from region one to region 2 and going from region to region 3 Psi at x equal to 0 Psi 1 at x equal to 0 must be equal to Psi 2 at x equal to 0 and Psi 2 at x equal to a here must be equal to Psi 3 at x equal to a ok and since the size here are real we have a real wave function in this region as well.

One more boundary condition that will apply here and did not apply in particle in a box really is the continuity of the first derivatives d Psi 1 at x equal to 0 dx psi 2 dx at x equal to 0 they must be equal to each other same holds for the first derivative of Psi 2 and Psi 3 at x equal to a. Knowing this we can try to draw the wave function of this system and this is what it is going to look like inside this well sort of a box we have a sine function kind of thing.

And since both sigh and d Psi dx has to be continuous here it will go like this same thing will happen here. Now let us talk about the shape of the wave function of Psi 2 C e to the power Kappa x plus d e to the power minus Kappa x what is it? One can easily see that this e to the power minus Kappa x is a decay in x, e to the power plus Kappa x is a rise in x. So, depending on what kind of coefficient C and D are what you expect is you expect it to go down and come up. What we actually work with we will see that later.

Second thing is why do we call this quantum mechanical tunneling because now we see that because of this continuity we have some wave function outside. We have written and a wave function outside here as well right, so some wave function is there outside but understandably the maximum amplitude in region 3 is much less than the maximum amplitude in region 1 because our model is that the particle is by and large in this confinement.

Looks like a little bit of it comes out so probability of finding the particle in region 3 is going to be nonzero definitely but it would better be less than what it is inside the box itself all right. And we are going to make use of this later on as well. Let us look at this first term for Psi 1 in region 1 the first term in the expression for the wave function is amplitude multiplied by e to the power ikx and from our previous discussion we know very well that this wave function is an eigen function of the linear momentum operator and the eigen value is kh cross plus kh cross.

So if you draw an arrow for it this is the arrow we should draw. What about the second 1 e to the power minus ikx that is an eigen function of linear momentum operator once again with eigen value of minus kh cross and as we have discussed earlier it means that the magnitude is same what direction is opposite. So, what we see inside is that we have the particle moving in either direction. What about region 3 we can think so if we are talking about the particle leaking out then a net leaked out would mean that the only direction that we need to consider is this we need not consider particles coming back.

Because in the steady state situation no particle will actually go in so you can get away by drawing only one arrow and then we can actually remove the second term because if you have to consider this G equal e to the power minus ikx then we have to also consider reverse barrier crossing well it might be required in a more complicated treatment. But in the simplistic treatment we can just neglect it so the second term goes.

And what we have been able to achieve so far is that we have been able to simplify the expression of at least one of the wave function and go down for two terms 2, 1 Psi in region 3 turns out to be F e to the power ikx. Now what we need; what we want to know is what is the probability of the particle; getting through this barrier? This is given by this quantity called transmission coefficient which is the ratio of number of particles penetrating the barrier divided by number of particles striking the barrier from the left.

Number of particles penetrating the barrier would be given by the square of the amplitude will be mod square of the amplitude F right because square of amplitude is intensity. Number of particles striking the barrier from the left would be given by mod square of A. V stands for particles going away we do not worry about that we only worry about particles impinging on the barrier from the left. So, ratio of mod square of F and mod square of A gives us transmission coefficient which is written as Chi and that tells us how efficiently the tunneling is taking place.

So, the next task is to find an expression of the transmission coefficient let us go ahead. So, from this first boundary condition that Psi has to be continuous at x equal to 0 what we get is for Psi 1 put x equal to 0 you get A + B for Psi 2 again we put x equal to 0 we get C + D. So, we get A + B is equal to C + D that is the first boundary condition. The second boundary condition that we use is Psi is continuous at x equal to A if we put so what are the regions involved region 2 and region 3 in Psi 2 if you put x equal to A what do we get C e to the power Kappa a plus D e to the power minus Kappa a.

And in the expression for Psi 3 if you put x equal to A we get F multiplied by e to the power ika so this is what we end up getting from the boundary conditions that wave function is continuous we get A + B equal to C + D and we get C e to the power kappa a plus D e to the power minus Kappa a equal to F e to the power ika. Now let us move on to the second set of boundary conditions where the first derivatives are said to be 0 at the boundaries.

So d Psi dx is equal to 0 for Psi 1 what does that mean? If that is equal to 0 then what we get essentially is ik multiplied by A - B is equal to Kappa multiplied by C – D what is the first derivative of Psi for region 1 at x equal to 0. Let us differentiate this we get ika e to the power ikx + ikb e to the power –ikx. Now put x equal to 0 you get aik multiplied by a - i k multiplied by B that is what gives left hand side of this expression.

Now let us go to d Psi two d x, d Psi two dx at x equal to 0 what do we get what is this; what is Psi to C e to the power e to the power kappa - C multiplied by e to the power Kappa x + D multiplied by e to the power minus Kappa x let us differentiate we get Kappa multiplied by C e to the power Kappa x plus well minus Kappa multiplied by D e to the power minus Kappa x, so take kappa out you get C e to the power kappa x minus D e to the power minus Kappa x, x is equal to 0 hence we get kappa multiplied by C – D.

Similarly I leave it to you to work out that from the fourth boundary condition we get kappa multiplied by C e to the power Kappa a see here there was an advantage x equal to 0 so that explanation term vanished we do not have any such luck here. So, we have to write kappa multiplied by C e to the power Kappa a - D e to the power minus Kappa a is equal to ik multiplied by F into e to the power i ka.

So, we have got four equations and from these four equations what is our job? Our job is to find the ratio of mod square of F plus mod square of A.

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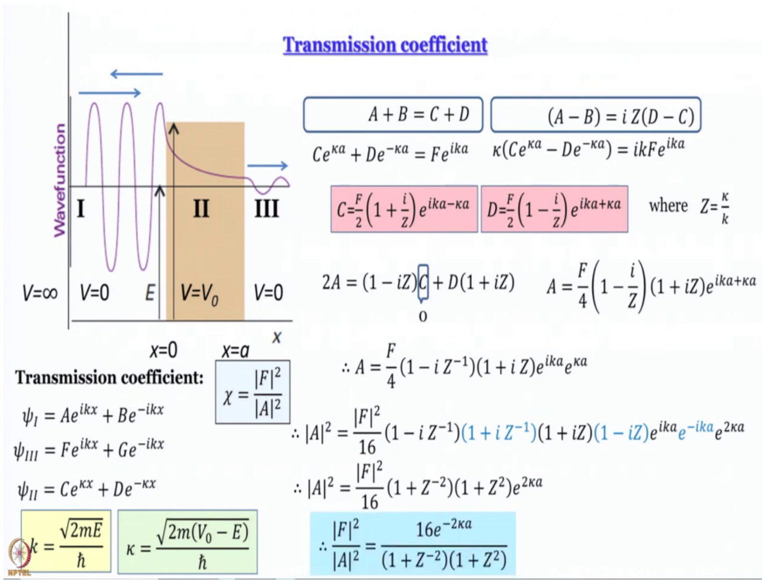

To do that let us well first of all simplify this a little bit only keep things that are important, not keep things that are not, here on the left hand side we have definition of transmission coefficient we have the wave functions with one exception this G e to the power minus ikx term is not even there so it might as well remove it. So, this G e to the power minus ikx we do not really need to worry about anymore Psi 2 is equal to C e to the power Kappa x + D e to the power minus Kappa x and Kappa are defined.

And here what we have done is on the right hand Psi we have removed the boundary conditions we have simply retained the relationships that came out of that. Now let us use them what you get is D e to the power kappa a multiplied by F e to the power i Kappa a minus C e to the power Kappa a this is when you make be the subject of formula. So, we get an expression for D okay. I go a little fast in this portion because this is just algebra knowing the steps one can work out easily.

So we get an expression for D and from this expression this equation we can work out another expression for D and we can eliminate these we get something like this. So, going further we can get expressions for C as well. Remember the substitution we have made is Z equal to Kappa divided by K. So, this is what we have got we have got two expressions 1 in C, 1 in D both contain F in the right hand side and we have defined Z as Kappa divided by K.

Now let us take these and plug them into the first simpler equations that we had. If you look at the second one just division by ik yields A - B is equal to iZ multiplied by D – C. so, 2A turns out to be 1 - iZ multiplied by C + D multiplied by 1 + iZ, C for the sake of simplicity one can set to be equal to 0, why so? Why will be set C to be equal to 0 because if you look at the expression C is something that corresponds to exponential rise.

D corresponds to exponential decay with respect to x and of course this decay is going to predominate over the rise because the amplifier amplitude of the wave function here in region 3 has to be much less than that in inside the box. So, C is not exactly equal to 0 but D much larger than C and we can set it to equal to 0 hence we get an expression for A in terms of F. Now this is what we have got you can work out mod A square this is the expression that we get and now we have got what we needed.

For the benefit of those who are going to work this out by themselves all the complex conjugates are written in blue. While working out mod A square or mod F square what we essentially do is that we multiply every imaginary quantity by its complex conjugate so just following this one can work it out themselves. So, here we have this expression and our job is done because we have obtained the expression for the ratio of mod square of F and mod square of A that essentially is the transmission coefficient.

And the expression we get is 16 e to the power minus 2 Kappa a divided by 1 + Z to the power -2 multiplied by 1 + Z square. I have skipped working the steps of the algebra here please work them out yourselves and in case there is any doubt I will be happy to clarify them in the live session that we are going to have some time in the first half of the course itself.

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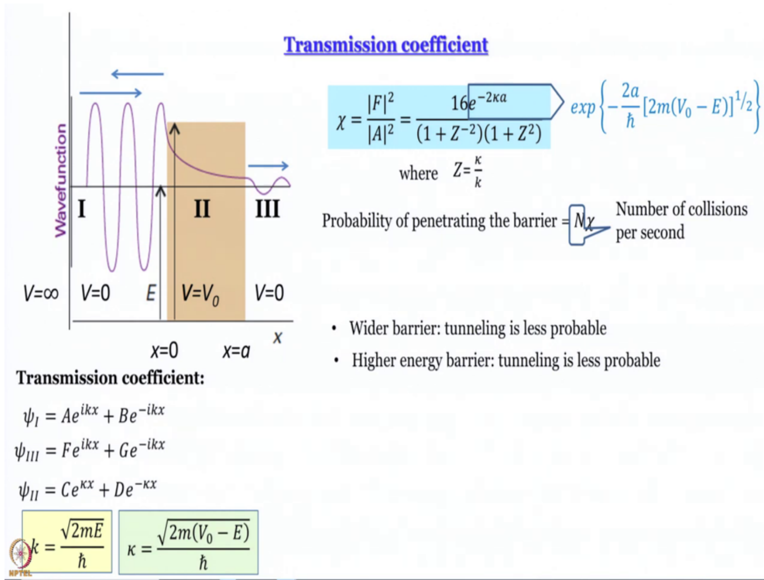

So here we are we have got an expression of the transmission coefficient that we had seeked. We have got the expression to be 16 e to the power minus 2 Kappa a divided by 1 + Z to the power -2 multiplied by 1 + Z square remember Z is Kappa divided by K. What does this expression tell us what is transmission coefficient what does it mean? That is a larger value of transmission coefficient would mean a larger probability of the particle tunneling through the finite energy barrier.

So, let us see on which factors it depends upon probability of course would be N multiplied by Chi where N is the number of collisions or number of times the particle impinges on the barrier per second. So, now C e to the power -2 Kappa a that is the really interesting part because Z is essentially a constant for a system it is just a ratio of Kappa by k. So, this denominator would be a different constant for a different for different systems.

But for a given system it will be constant nevertheless. So, let us expand the e to exponential term a little bit and we get this to be e to the power 2 a by h cross multiplied by 2 m multiplied by square root of V0 - E this is the expression that teaches us two important things about the tunneling process. First of all it is not very difficult for us to see that for a wider barrier tunneling is less probable. Well we can see it from the diagram itself.

See it is what we have here as we said is that it is sort of a decay right actually it is a curve that would go through a minimum but if we can have a thinner barrier then this here due to continuity this would be the amplitude of the wave function emanating into region 3. If you go further then this amplitude becomes smaller and smaller and smaller. So, from this diagram itself we can understand what you are talking about.

And if you look at this expression it is an exponential decay in terms of A which is the potential barrier. So, for a wider barrier tunneling is less efficient we can say lesser amount of tunneling takes place. And for a higher energy barrier also tunneling is less probable because we have V 0 - E to the power half here so what would happen if V 0 is very high once again this Chi would become smaller I forgot to write the third point.

So let me just say it the other quantity that finds its place in this expression is N. So, for a lighter particle it is easier to tunnel for a heavier particle it is not so easy. So, these are the 3 things that we learn sorry for not having written the third one wider barrier less tunneling higher energy barrier less tunneling higher mass less tunneling and that sort of explains why we do not see it in the real world because they are all massive objects you see tunneling very nicely for electrons. How you do see it for protons not so easy to see it for into a tritirium okay we will come to that when we discuss the examples in the next few minutes.

Now all these things that we have done this might sound as something that is well good algebra and good calculus nice theory but it also has tremendous applications and manifestations in real life around us.

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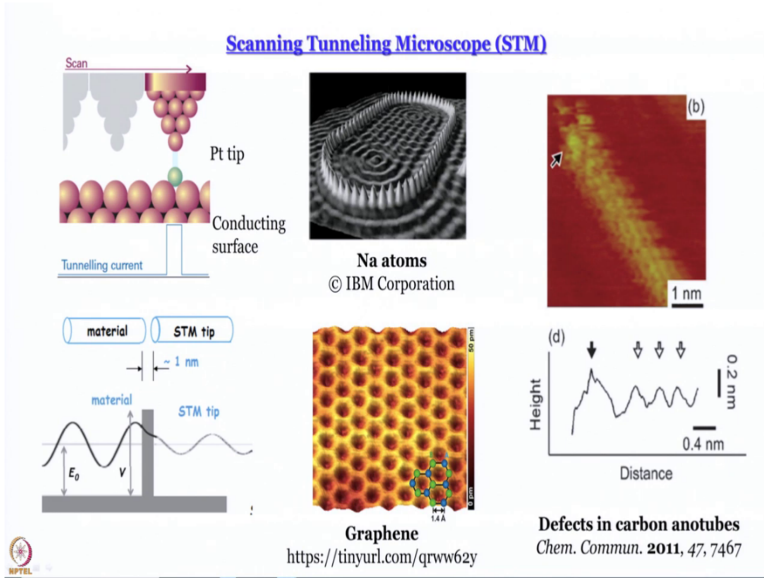

One very important application that has been worked out using tunneling is called scanning tunneling microscopy so this is the this is is taken from Atkins physical chemistry book what you have there is that you have a tip of a platinum or some size very highly conducting metal. And if you interrogate a conducting surface with it what happens is electrons from the tip can go through can overcome the energy barrier and go there.

So if you complete the current in the circuit then you get this tunneling current that shows up and higher tunneling current of course means greater tunneling. So, what you do is you can maintain a constant tunneling current by moving the tip up and down and by how much the tip is moving gives an idea of what kind of surface you have. So, by using this one can get a nice image of the surface of a conducting material this is called scanning tunneling microscopy.

There are other variants atomic force microscopy that are performed that are used using modifications of this technique. So, the idea is this here we have a same tip here is the material and in between them there is a barrier. Okay so the electron can tunnel through this barrier that is the basis of the measurement and by using scanning tunneling microscopy one can get nice images at with atomic resolution.

Here you see an image of sodium atoms here you see an image of graphene very often we chemists are accused of pretending that we can see molecules. Now we can say with confidence that we do not pretend we do see molecules and that is thanks to this strange phenomenon called tunneling. Here I show you another image just to manifest just to reiterate how precise this technique is what you see here is a carbon nanotube.

And you can see the length scales that we are interrogating here this carbon nanotube has a defect somewhere here and if you look at the plot of height versus distance to maintain the constant tunneling current you see that this height suddenly takes a jump. So, this is the kind of measurement that you can make you have one nanotubes single nanotube in which there is one defect you can see it. Thanks to this strange phenomenon of tunneling of electrons through finite potential energy barrier.

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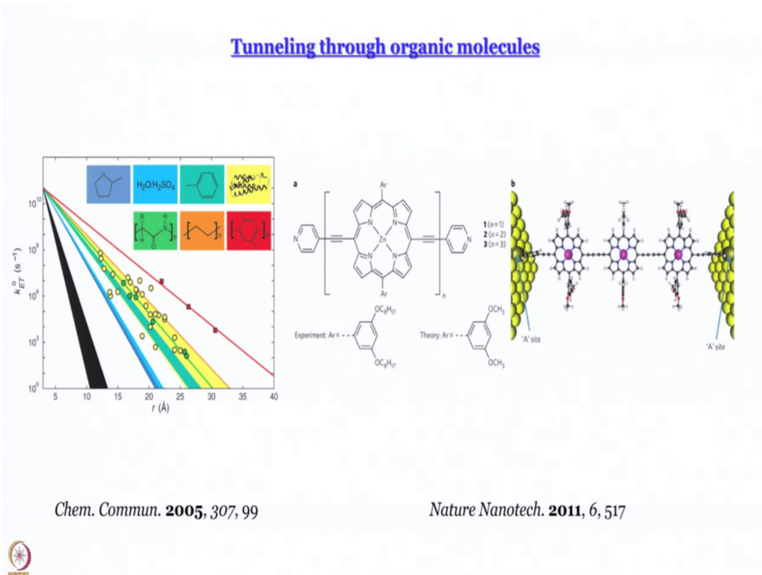

These are more examples from published papers in the last 10-12 years. The first one shows how tunneling takes place through different organic molecules. Second one takes this kind of a molecule here porphyrin joint with each other kept between two gold plates and they have shown how the dependence of tunneling current is on the length of the for firing chains. And these give us very important understanding of the molecular systems themselves.

For those of you who are researchers I strongly encourage you to read these papers at least once then you will appreciate this technique a little better.

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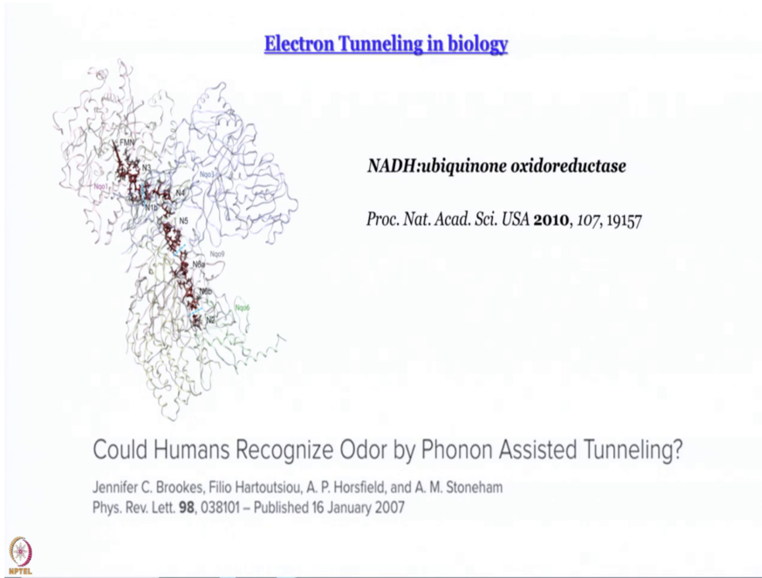

So, what we have discussed so far is tunneling that we have that human beings have forced to happen to observe certain things or demonstrate certain things nature itself has plenty of systems in which tunneling takes place. What you see here once again from a published paper of about 10 years ago is a protein which plays an important role in the process of respiration. It is a respiratory protein named does not really matter for the time being whoever is interested may read this paper.

But what you see here in this colored what you see in color here is the electron tunneling pathway that takes place in this protein naturally and which plays a very important role in this function of the protein in the respiratory system. So, electron tunneling in barrier end is something that is there in nature as well. It is not necessary that we have to intervene and make electrons tunnel. In fact one question that some student had asked me some time ago and I could not answer is how we do is smell.

We understand how we see, how do we smell why is it that certain molecules stimulate our olfactory glands. Nowadays it is believed by a section of scientists that phonon assisted tunneling has an important role to play in smell as well and it is not as if electrons only tunnel protons are 2000 times heavier than electrons but still protons do tunnel.

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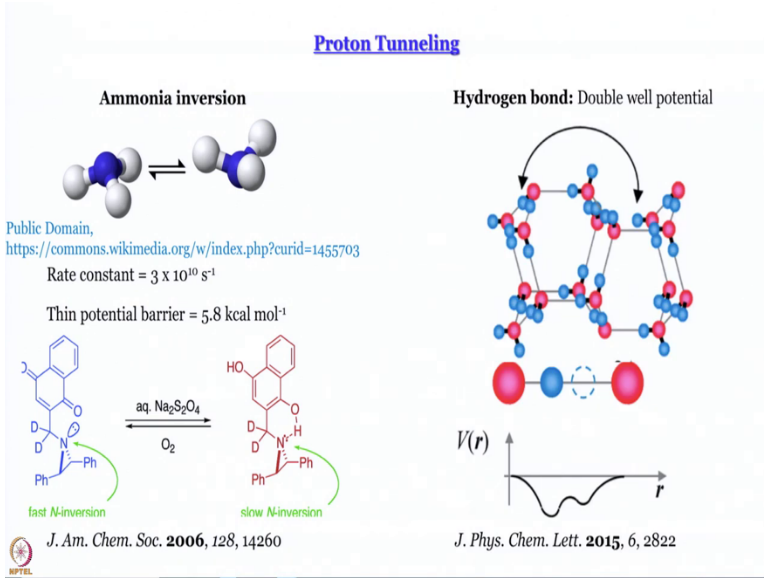

And something like an example of proton tunneling is very well-known in chemistry in the form of ammonia inversion ammonia can keep on inverting very efficiently an extension of this is Walden universe. In organic molecules the rate constant is unusually high 3 to 10 to the power 10 per second that is because the potential barrier is 5.8 kilo calorie per mole and the electron the proton can tunnel through.

If you take NV 3 instead of NH3 this rate is slowed down significantly why because of that mass term in that exponential decay in the tunneling coefficient expression for tunneling coefficient. Here is another example of a paper where this kind of inversion has been arrested by replacing by just by reduction of this quinone to hydroquinone so hydrogen bonding with the OH group engages this electron pair and does not allow the inversion to take place.

In fact in our group we have done some work on aminoquinolines using the same principle. In fact even in hydrogen bond in hydrogen bonded systems so a proton transfer takes place tunneling has an important role to play. If you see what you see here is ice at low temperature nice ordered structure of ice. Now if you consider a hydrogen atom it is covalently bonded to a an oxygen atom and hydrogen bonded to the next oxygen atom.

Now if it hops from this side, what did they say oxygen yeah so if you if it hops on this oxygen atom to this oxygen it will move very little bit so now what we see is that when it is covalently bonded to this oxygen atom that corresponds to an energy minimum. When the same proton is hydrogen bonded to another oxygen atom it corresponds to a second energy minimum depending on the relative energies we get symmetric or asymmetric double well potential.

And a double well potential associated with the barrier. This barrier once again is more or less of 5.8 kilo calories per mole.

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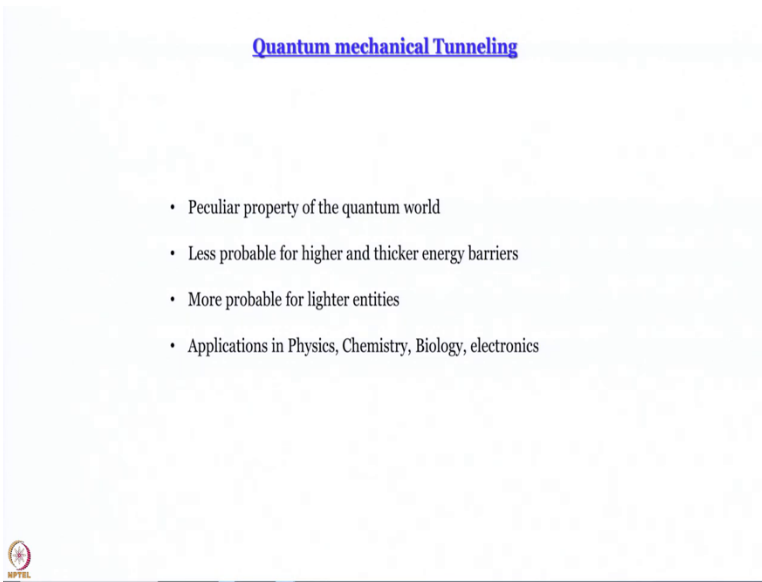

So the proton can tunnel so we have seen several examples of tunneling that takes place in chemistry and beyond chemistry tunneling that we make we force to happen tunneling that is already there in nature. And what we have learned in this slightly long leash module about quantum tunneling is that first of all this is a peculiar property of the quantum world that is not manifested in the macro world essentially because of the mass effect.

Secondly it is less probable for higher and thicker energy barriers and here I have said it more probable for lighter entities. There are many applications in physics chemistry biology and one thing I have not touched upon for the sake of time is electronics. So, even for engineers it is important to understand the phenomenon of tunneling. So, that brings us to an end of the discussion that we wanted to perform for particle in a box and its variants.

Next we move on to other systems but some of us might be wondering where are the molecules where the atoms where are the orbital's we will get there. But before that let us talk a little bit about some other quantum mechanical systems a rigid rotor and a harmonic oscillator because they are good models for molecules in rotation and molecules in vibration and also rigid rotor model prepares us for the discussion that we are going to have on hydrogen atom that is what we will do in the next few modules.